

A Stable Porphyrin-Based Porous mog Metal–Organic Framework as an Efficient Solvent-Free Catalyst for C–C Bond Formation

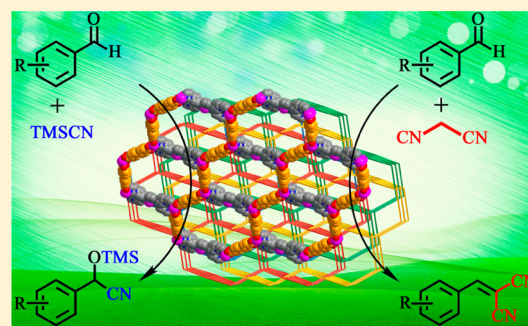
Wei Jiang,[†] Jin Yang,^{*,†} Ying-Ying Liu,[†] Shu-Yan Song,^{*,‡} and Jian-Fang Ma^{*,†}

[†]Key Lab for Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

[‡]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Supporting Information

ABSTRACT: We herein report the porous 4-fold interpenetrated **mog** (moganite) metal–organic framework (MOF) $[\text{Cd}_3(\text{tipp})(\text{bpdc})_2] \cdot \text{DMA} \cdot 9\text{H}_2\text{O}$ (**1**·Cd; H_2tipp = 5,10,15,20-tetrakis(4-(imidazol-1-yl)phenyl)porphyrin, H_2bpdc = biphenyl-4,4'-dicarboxylic acid, DMA = *N,N'*-dimethylacetamide). The incorporation of Cd and carboxylate oxygen affords **1**·Cd rich Lewis acid and basic sites. This MOF **1**·Cd was then applied as an efficient heterogeneous catalyst for the important cyanosilylation of aldehydes and Knoevenagel condensation reactions. **1**·Cd features excellent catalytic performance and recyclability for the cyanosilylation of various aldehydes with trimethylsilyl cyanide (TMSCN). Moreover, **1**·Cd shows highly efficient catalysis and substrate selectivity for Knoevenagel condensation reactions of various aldehydes with malonitrile. The high catalytic activity and stability toward C–C bond formation make **1**·Cd a promising heterogeneous catalyst.



INTRODUCTION

Cyanohydrins, as an important family of compounds, have been extensively employed as significant organic intermediates for α -hydroxy carboxylic acids, α -hydroxy aldehydes, β -hydroxy amino alcohols, etc.^{1–4} For the syntheses of cyanohydrins, trimethylsilyl cyanide (TMSCN) is one of the most popular cyanating reagents for nucleophilic addition to carbonyls to produce cyanohydrin trimethylsilyl ethers. Thus, the search for efficient catalysts for cyanosilylation of aldehydes or ketones with TMSCN has become a greatly significant topic.^{5–7} In this regard, Lewis acids can serve as electrophilic catalysts to activate carbonyl compounds.^{8,9} Over the past decades, a variety of efficient homogeneous and heterogeneous catalysts have been widely studied for cyanosilylation reactions.^{10–15} Currently, heterogeneous solvent-free catalysis has attracted extensive research interest.^{16,17}

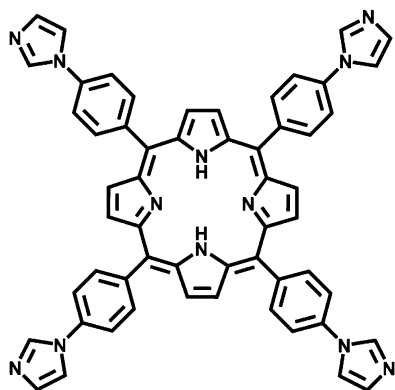
As an emerging class of crystalline materials, porous metal–organic frameworks (MOFs) have gained tremendous attention owing to their great structural diversities and potential applications.^{18–21} One of the especially interesting applications for porous MOFs is that connected with their heterogeneous catalysis. Toward this direction, some functional MOFs have been developed as efficient heterogeneous catalysts capable of catalyzing various organic reactions.²² It is noted that the greatest advantage of MOFs in comparison to some more traditional porous materials is their chemical versatility and tailorability.^{23,24} The combination of appropriate unsaturated metal sites and active organic linkers makes porous MOFs highly promising heterogeneous catalysts.^{25–27} In this regard, crystalline

porphyrin-based porous MOF catalysts have attracted great interest because of their enhancing stability after the inclusion of porphyrin, which also affords active environments for various catalytic reactions.^{28–30} Multicarboxylate porphyrins have always been used as the linkers for constructing porous MOFs with superior stability and excellent catalytic performance.^{31–33} In contrast, both N-donor-based porphyrin and rigid dicarboxylate acids as mixed ligands to fabricate catalytically active MOFs remain largely unexplored.^{34,35}

Motivated by the prospects mentioned above, we assembled a new N-donating 5,10,15,20-tetrakis(4-(imidazol-1-yl)phenyl)porphyrin (H_2tipp ; Scheme 1) and a rigid biphenyl-4,4'-dicarboxylic acid (H_2bpdc) to afford a rare 4-fold interpenetrated **mog** (moganite) MOF, $[\text{Cd}_3(\text{tipp})(\text{bpdc})_2] \cdot \text{DMA} \cdot 9\text{H}_2\text{O}$ (**1**·Cd; DMA = *N,N'*-dimethylacetamide). Thanks to the Lewis acidity provided by Cd(II) ions and Lewis basicity supported by the coordinated bpdc^{2-} anions, **1**·Cd exhibits excellent catalytic performance toward both cyanosilylation of aldehyde and Knoevenagel condensation reactions under solvent-free conditions. More importantly, the catalyst **1**·Cd can be easily recovered and recycled during the catalytic process. To our knowledge, this work represents the first example that a porphyrin-based crystalline MOF has been employed as an efficient heterogeneous catalyst for C–C bond formation under solvent-free conditions.

Received: December 28, 2016

Scheme 1. Structure of Porphyrin-Based H_2tipp Used in This Work



RESULTS AND DISCUSSION

Crystal Structure. Crystals of $1 \cdot Cd$ were synthesized with H_2tipp , H_2bpdC , and $Cd(NO_3)_2 \cdot 4H_2O$ under solvothermal conditions. Single-crystal X-ray analysis reveals that $1 \cdot Cd$ belongs to the triclinic system with space group $P\bar{1}$. During the

refinement of $1 \cdot Cd$, the disordered solvents were removed by applying the SQUEEZE routine in PLATON.³⁶ As illustrated in Figure 1a, the asymmetric unit of $1 \cdot Cd$ contains one Cd^{II} -tipp, two $bpdC^{2-}$ anions, and two Cd^{II} atoms. $Cd1$ is four-coordinated by four pyrrolyl nitrogen atoms from one porphyrin core to give a Cd^{II} -tipp linker. Either $Cd2$ or $Cd3$ is octahedrally coordinated by two bidentate carboxylates from two $bpdC^{2-}$ anions and two imidazolyl groups from two different $tipp^{2-}$ ligands. Each Cd^{II} -tipp linker bridges four Cd^{II} atoms, and every $bpdC^{2-}$ anion links two Cd^{II} atoms. In this way, a striking 3D framework with a large nanosized channel was achieved along the b axis, as shown in Figure 1b. The large cavities in the framework are further partially occupied via mutual interpenetration of three identical frameworks, leading to formation of a rare 4-fold interpenetrated porous **mog** framework (Figure 1c,d). In spite of the 4-fold interpenetration, there is still enough void space in the framework filled with solvent molecules. After removal of the guest molecules, the total accessible volume of 2056.6 \AA^3 per unit cell was determined by using PLATON, which accommodates approximately 40.3% of the unit cell volume (5104.2 \AA^3).³⁶

Chemical Stability. The porphyrin-based MOFs usually exhibit excellent stability after treatment with solvents.^{37,38}

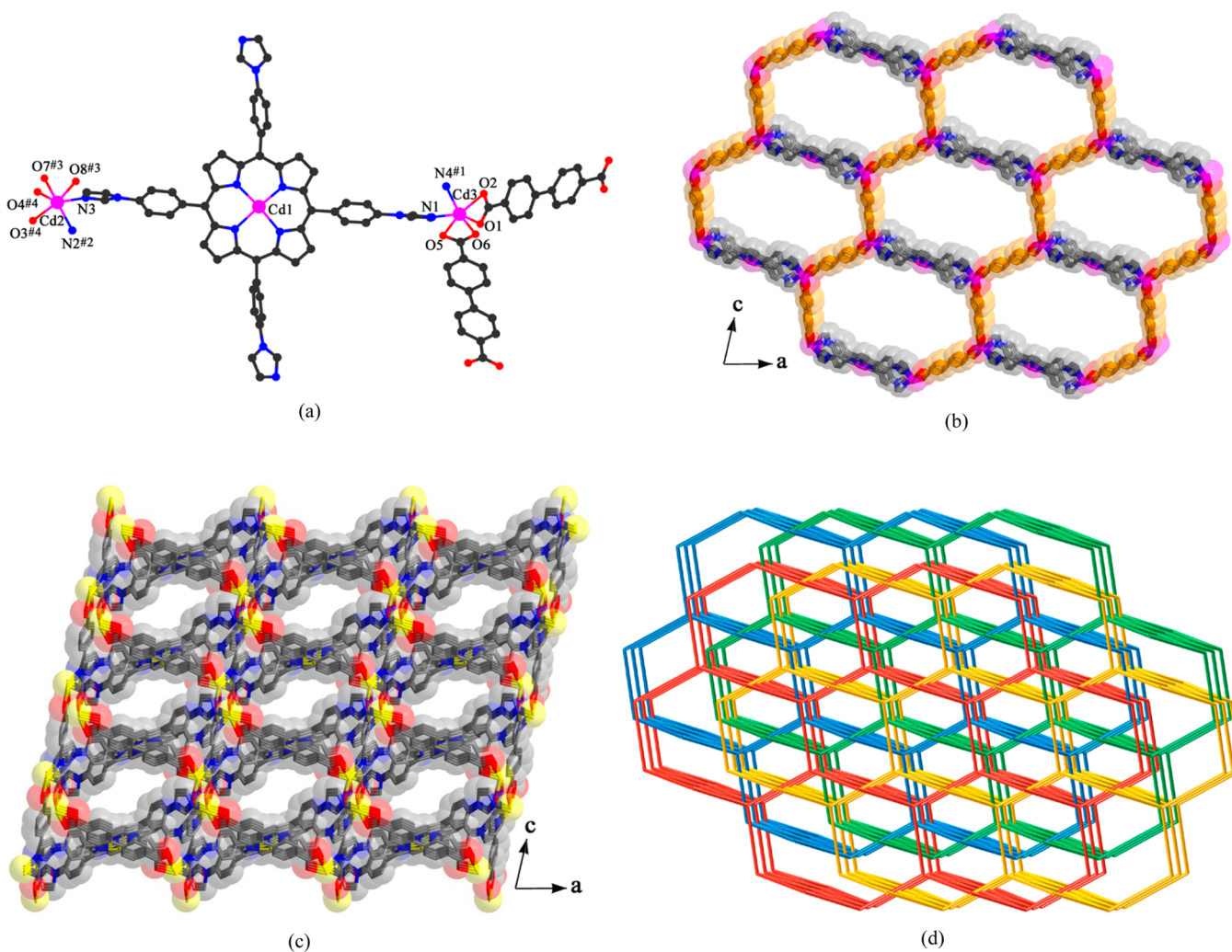


Figure 1. (a) View of the coordination environments of Cd^{II} atoms. Symmetry codes: (#1) $x, y - 1, z$; (#2) $x, y + 1, z$; (#3) $x - 2, y + 1, z$; (#4) $x - 1, y + 2, z - 1$. (b) View of the 3D framework of $1 \cdot Cd$ along the b axis. (c) View of the 4-fold interpenetrated framework of $1 \cdot Cd$ along the b axis. (d) Schematic representation of the 4-fold interpenetrated (4,4)-connected **mog** net.

We herein tested the stability of **1**·Cd by immersing the samples in various organic solvents, including DMF, CH₃OH, CH₂Cl₂, and even boiling water. Powder X-ray diffraction (PXRD) patterns show that all of the experimental diffraction peaks matched well those in the simulated pattern, as shown in Figure 2. The result demonstrates that the structure of **1**·Cd was retained after treatment with solvents.

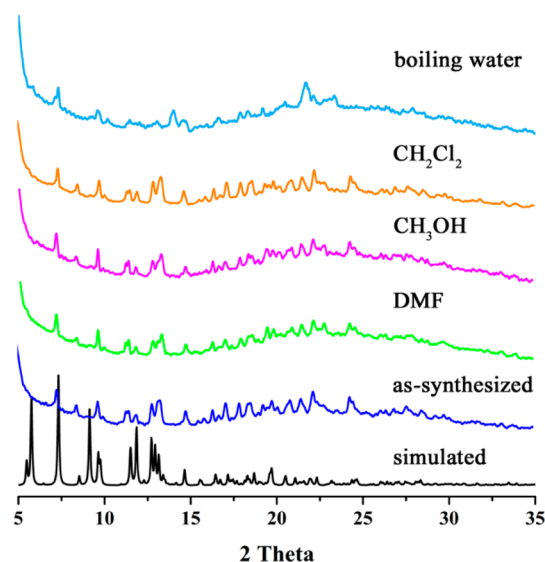


Figure 2. PXRD patterns of the simulation of **1**·Cd (black) and samples as synthesized (blue) and soaked in different solvents.

Cyanosilylation of Aldehydes. Cyanohydrins, as a class of important organic intermediates for both biological processes and organic synthesis, could be prepared by cyanosilylation of aldehydes or ketones.³⁹ The cyanosilylation reaction is well-known as Lewis acid catalyzed C–C bond formation. In the past decades, numerous homogeneous catalysts, such as metal salts, amines, and alkaline-earth-metal oxides, have been extensively utilized for cyanosilylation reactions of aldehydes or ketones.^{10–12} Moreover, some porous MOFs with open metal sites have also shown high catalytic efficiencies for the cyanosilylation reactions in the presence of organic solvents.^{40,41} Nevertheless, solvent-free cyanosilylation reactions catalyzed by MOFs remain rarely evaluated as an environmentally favorable strategy.^{42,43} Given the rich unsaturated Cd^{II} confined in MOF **1**·Cd, catalytic performance of the cyanosilylation of aldehydes and ketones was investigated with low catalyst loading and mild temperature under solvent-free conditions.

As shown in Figure 3, the cyanosilylation of benzaldehyde was utilized as a model reaction to explore the effect of various parameters on the catalytic performance. The product yields after the catalytic reaction were calculated by GC and ¹H NMR analyses (Figures S1 and S2 in the Supporting Information). Before the catalytic reaction, **1**·Cd was fully activated under vacuum to remove the solvents and provide accessible active sites for the substrates. The PXRD pattern of the activated sample presents a good agreement with the calculated pattern, indicating that the framework was well retained after activation (Figure S3 in the Supporting Information). To optimize the reaction conditions, the time-dependent catalytic performance was studied for the reaction of benzaldehyde (1 mmol) and trimethylsilyl cyanide (TMSCN, 2 mmol) by using **1**·Cd as catalyst (0.6 mol %) at room temperature. As shown in Figure 3, only 26% of the

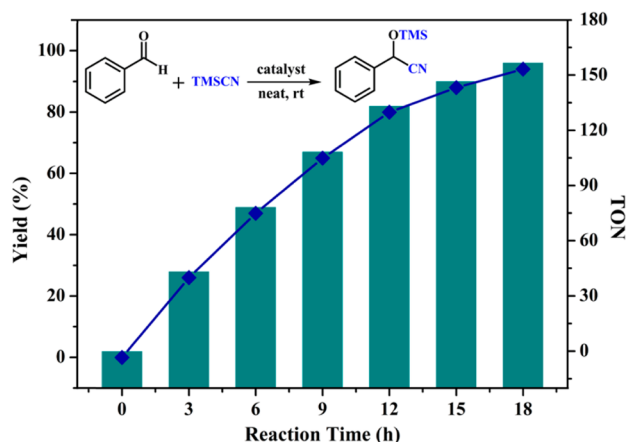


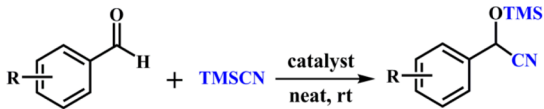
Figure 3. Yields (line) and TON values (bars) of the product 2-phenyl-2-trimethylsilyloxyacetonitrile with the reaction time. Reaction conditions: benzaldehyde (1 mmol), TMSCN (2 mmol), **1**·Cd (0.006 mmol), room temperature.

benzaldehyde was converted to 2-phenyl-2-trimethylsilyloxyacetonitrile in the first 3 h, and the turnover number (TON) was 43 per mole of catalyst **1**·Cd. After 18 h of the reaction, a very high yield (94%) of 2-phenyl-2-trimethylsilyloxyacetonitrile was achieved with a TON value of 156.7 (Table 1, entry 2). In contrast, a control experiment was conducted without a catalyst under otherwise identical condition. The corresponding yields of the product drastically decreased from 95% to 38%, demonstrating the excellent catalytic effect of **1**·Cd on the cyanosilylation reactions (Table 1, entry 1). Moreover, homogeneous control experiments were also performed using Cd(NO₃)₂·4H₂O and Cd^{II}-tipp as catalysts. Under homogeneous conditions, benzaldehydes can be completely converted to the corresponding product 2-phenyl-2-trimethylsilyloxyacetonitrile, demonstrating the high catalytic activity of Cd sites (Table 1, entries 3 and 4).

To further explore the general applicability of **1**·Cd to the catalysis of the cyanosilylation reaction, a family of benzaldehyde derivatives with electron-withdrawing (–Cl, –CN, and –NO₂) and -donating groups (–Me, –Et, and –OMe) were selected as substrates in the following reactions (Table 1). It is noted that the benzaldehyde derivatives bearing electron-withdrawing groups were completely converted to the corresponding cyanosilylation products after 18 h (Table 1, entries 5–7). Nevertheless, when the benzaldehyde derivatives with electron-donating groups were utilized as the substrates, the corresponding product yields clearly decrease under the same conditions (Table 1, entries 8–10). The observable difference in the catalytic performance of **1**·Cd toward the benzaldehyde derivatives could be attributed to their electron-donating and -withdrawing groups. For example, the electron-withdrawing groups of the benzaldehyde derivatives make the electropositive charge on the aldehyde group much higher, leading to excellent conversions in the nucleophilic reactions.⁴⁴ Notably, the 4-ethylbenzaldehyde and anisic aldehyde showed much lower conversion yields (61% and 57%) in comparison to that of the 4-methylbenzaldehyde (89%), indicating that the electron-donating group types also have an effect on the catalytic performance.

To expand the scope of substrates, various aldehydes with alkyl, cyclohexyl, naphthyl, and cinnamyl groups were also employed for the cyanosilylation reactions (Table 1). Significantly, for the cyanosilylation reaction of hexanal and cyclohexanecarbaldehyde with TMSCN, the catalytic yields can reach >99% and 96%, respectively (Table 1, entries 11 and 12). Nevertheless, for

Table 1. Cyanosilylation of Aldehydes and Ketones Catalyzed by **1**·Cd^a



Entry	Substrate	Product	Yield(%) ^b	TON ^c
1 ^d			38	63.3
2			94	156.7
3 ^e			>99	166.7
4 ^f			>99	166.7
5			99	165
6			98	163.4
7			>99	166.7
8			89	148.4
9			61	101.7
10			57	95.2
11			>99	166.7
12			96	160.3
13			6	10
14			5	8.3
15			trace	0
16			trace	0

^aReaction conditions unless specified otherwise: aldehydes or ketones (1 mmol), TMSCN (2 mmol), **1**·Cd (0.006 mmol), 18 h, room temperature. ^bYields were calculated by GC and ¹H NMR. ^cMoles of trimethylsilyl product per mole of catalyst **1**·Cd. ^dThe same reaction conditions without catalyst **1**·Cd. ^eThe same reaction conditions using catalyst Cd(NO₃)₂·4H₂O. ^fThe same reaction conditions using catalyst Cd^{II}-tipp.

2-naphthaldehyde and cinnamaldehyde, only trace catalytic products were achieved using **1**·Cd as catalyst (Table 1,

entries 13 and 14). Moreover, ketones such as acetophenone and 4-methylacetophenone were also utilized as substrates in the cyanosilylation reactions. However, no catalytic products were achieved using acetophenone and 4-methylacetophenone as substrates catalyzed by **1**·Cd (Table 1, entries 15 and 16).⁴⁵

To clarify the heterogeneity of the catalytic reaction, catalyst **1**·Cd was separated by filtration after the product yield reached 47% (6 h) and then the reaction was continued further. The product yields increase only slightly after 18 h, as shown in Figure 4. At the end of the reaction, porphyrin leaching in the

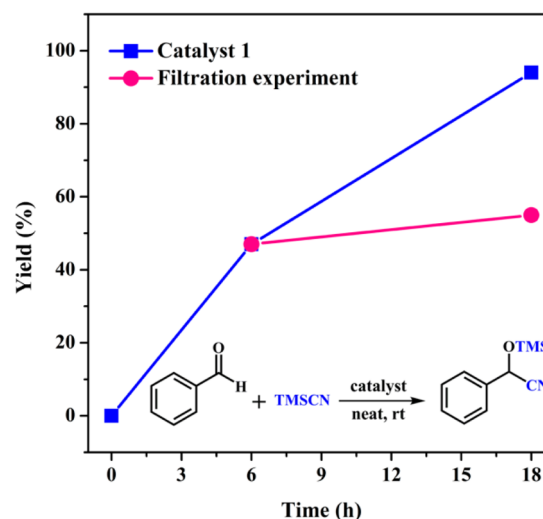


Figure 4. Yields of 2-phenyl-2-(trimethylsilyloxy)acetonitrile in the cyanosilylation reaction catalyzed by **1**·Cd (blue) and by the filtrate of **1**·Cd after 3 h of the reaction (pink). Reaction conditions: benzaldehyde (1 mmol), TMSCN (2 mmol), **1**·Cd (0.006 mmol), room temperature.

reaction filtrate was not observed from the UV–vis absorption spectra, demonstrating that the present catalytic reaction is indeed heterogeneous (Figure S4 in the Supporting Information).

Remarkably, the samples of **1**·Cd can be easily recovered from the reaction mixture by filtering and drying. The PXRD patterns of **1**·Cd matched well before and after the catalytic reactions (Figure S3 in the Supporting Information), demonstrating that the structure of **1**·Cd does not change. Thereby, the reusability of **1**·Cd was further examined and recycling experiments were performed using benzaldehyde as the substrate. As illustrated in Figure 5, the conversions of the benzaldehyde in five successive runs were still retained and only a slight decrease was observed in the last four runs, indicating the good reusability of **1**·Cd.

Notably, the cyanosilylation reactions by utilizing MOFs as the heterogeneous catalysts has been intensely studied in the presence of organic solvents.^{46,47} However, solvent-free catalysis for cyanosilylation reactions employing MOF catalysts still remains in its infancy.⁴⁸ To our knowledge, no solvent-free cyanosilylation reactions have been studied using crystalline porphyrin-based MOFs. In contrast, much higher product yields were achieved with a small amount of **1**·Cd loading under solvent-free conditions.

Knoevenagel Condensation Reaction. Knoevenagel condensation, as a crucial member of the C–C bond formation reaction family, is continually employed in the syntheses of pharmaceutical products and fine chemicals.^{49–51} Very recently, crystalline MOFs have been used as catalysts for Knoevenagel condensation reactions to yield various malononitrile derivatives.^{52,53} Herein, we performed a Knoevenagel condensation reaction by using **1**·Cd as a catalyst under solvent-free conditions.

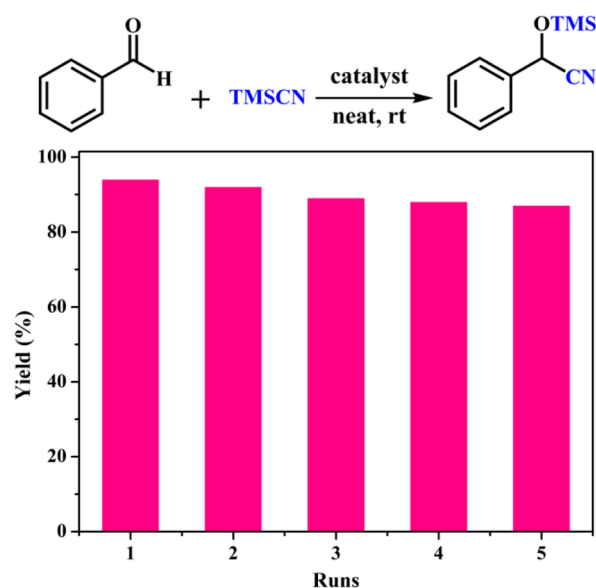


Figure 5. Recycling experiments for the cyanosilylation of benzaldehyde catalyzed by **1•Cd**. Reaction conditions: benzaldehyde (1 mmol), TMSCN (2 mmol), **1•Cd** (0.006 mmol), room temperature.

As shown in Table 2, the initial reaction was performed using 0.6% **1•Cd** relative to the benzaldehyde. The catalytic reactions with **1•Cd** were conducted at 60 °C without using any organic solvents. The catalytic product yields were calculated by GC and further confirmed by ¹H NMR (Figures S5 and S6 in the Supporting Information). As illustrated in Table 2, benzaldehyde reacted with malononitrile to give a 95% yield of 2-benzylidenemalononitrile with a high turnover frequency (TOF) of 158.4 h⁻¹ after 1 h (entry 2). Noticeably, when the reaction was carried out without catalyst, no target products were achieved (Table 2, entry 1), demonstrating the excellent catalytic performance of **1•Cd** for the Knoevenagel condensation reaction. In addition, to verify the active sites, Cd(NO₃)₂·4H₂O and Cd^{II}-tipp were utilized as homogeneous catalysts in the Knoevenagel condensation reaction. For the substrate benzaldehyde, a moderate conversion yield (70%) was achieved with Cd(NO₃)₂·4H₂O as a homogeneous catalyst, while a much higher yield was observed using Cd^{II}-tipp catalyst (Table 2, entries 3 and 4).

Considering the high catalytic activity of **1•Cd** toward the condensation of the benzaldehyde with malononitrile, other benzaldehyde derivatives were further selected as reaction substrates. Since nucleophilic addition is a rate-determining step in the Knoevenagel condensation, benzaldehyde derivatives with electron-withdrawing groups are more reactive than those with electron-donating groups.⁴⁴ As shown in Table 2, benzaldehyde derivatives bearing electron-withdrawing groups (–Cl, –CN, –NO₂) are fully converted to the catalytic products with the highest TOF of 166.7 h⁻¹ after 1 h (entries 5–7). Nevertheless, malononitrile reacted with electron-donating benzaldehyde derivatives, such as 4-ethylbenzaldehyde and 4-methoxybenzaldehyde, to give relatively low product yields (entries 8–10). Obviously, the substituents of the benzaldehyde derivatives have a significant effect on the catalytic yields in the condensation reaction of aldehydes with malononitrile. Moreover, we further enriched the variety of the substrates. As shown in Table 2, hexanal, cyclohexanecarbaldehyde, 2-naphthaldehyde, and cinnamaldehyde were selected to react with malononitrile under the same conditions (entries 11–14). The substrates hexanal, cyclohexanecarbaldehyde, and 2-naphthaldehyde afford the

Table 2. Knoevenagel Condensation Reaction of Malononitrile with Various Benzaldehyde Derivatives Catalyzed by **1•Cd**^a

Entry	Substrate	Product	Yield(%) ^b	TOF(h ⁻¹) ^c
1 ^d			trace	0
2			95	158.4
3 ^e			70	116.7
4 ^f			>99	166.7
5			>99	166.7
6			>99	166.7
7			>99	166.7
8			91	151.7
9			58	96.7
10			55	91.7
11			95	158.4
12			90	150
13			96	160
14			60	100

^aReaction conditions unless specified otherwise: aldehydes (1 mmol), malononitrile (2 mmol), **1•Cd** (0.006 mmol), 1 h, 60 °C. ^bYields were calculated by GC and ¹H NMR. ^cMoles of condensation product per mole of catalyst **1•Cd** per hour. ^dThe same reaction conditions without catalyst **1•Cd**. ^eThe same reaction conditions using catalyst Cd(NO₃)₂·4H₂O. ^fThe same reaction conditions using catalyst Cd^{II}-tipp.

corresponding products in excellent yields (90–96%), whereas cinnamaldehyde only gives a moderate yield of 60%.

In previous reports, porphyrin derivatives have been utilized as homogeneous catalysts in Knoevenagel condensation reactions.⁵⁴ To determine if the leaching porphyrin ligand from **1•Cd** was responsible for the present catalytic performance, we performed an experiment to estimate the contribution of the leaching ligand to the catalytic activity (Figure 6). Typically, the organic phase was separated from the reaction mixture by

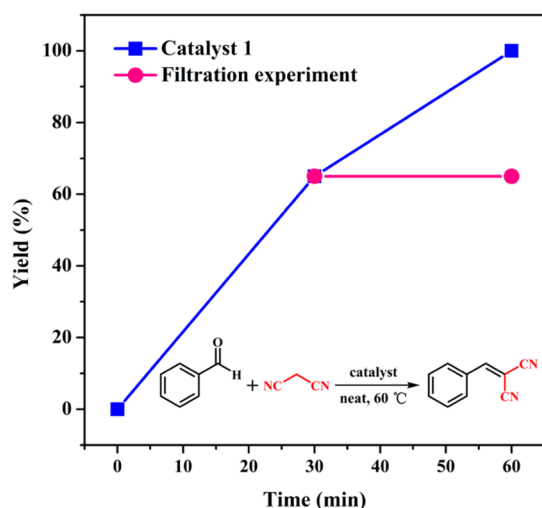


Figure 6. Conversion of the benzaldehyde in the Knoevenagel condensation reactions catalyzed by **1·Cd** (blue) and by the filtrate of **1·Cd** after 30 min of the reaction (pink). Reaction conditions: benzaldehyde (1 mmol), malononitrile (2 mmol), **1·Cd** (0.006 mmol), 60 °C.

filtration after 30 min of the catalytic reaction, and the filtrate was then stirred for a further 30 min. GC analysis revealed that no additional 2-benzylidenemalononitrile products were formed in the filtrate. Moreover, the porphyrin ligand was not observed from the UV–vis spectra of the filtrate, indicating that the present condensation reaction is indeed heterogeneous (Figure S4 in the Supporting Information).

The stability and recyclability of **1·Cd** were further investigated by using benzaldehyde as a substrate. After 30 min of the catalytic reaction, **1·Cd** was isolated by filtration and washed with methanol and reused for the next condensation reaction. As shown in Figure 7, more than 95% conversion of the

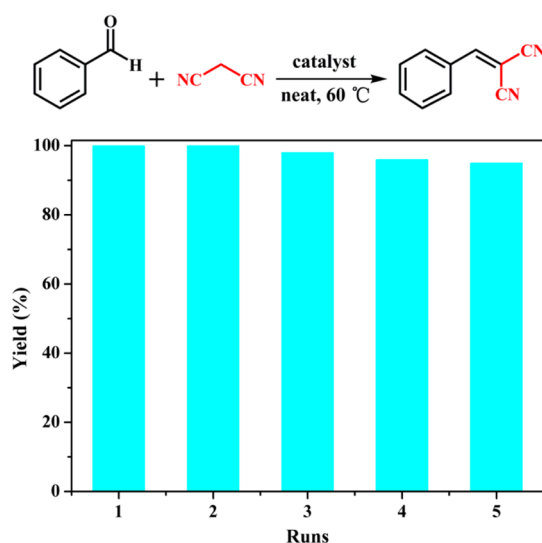


Figure 7. Recycling experiments of the Knoevenagel condensation reaction using catalyst **1·Cd**. Reaction conditions: benzaldehyde (1 mmol), malononitrile (2 mmol), **1·Cd** (0.006 mmol), 60 °C.

benzaldehyde was still maintained even after five consecutive runs. Moreover, the PXRD patterns taken before and after the catalytic reactions indicate that the structure of **1·Cd** remains unchanged (Figure S3 in the Supporting Information).

Remarkably, organic solvents always served as the reaction media in the Knoevenagel condensation catalyzed by MOFs.^{55,56}

To our knowledge, only a few MOFs have been utilized as heterogeneous catalysts for Knoevenagel condensation reactions under solvent-free conditions.⁵⁷ In contrast, our catalyst **1·Cd** exhibits superior catalytic performance under solvent-free conditions with very little catalyst loading.

CONCLUSION

In summary, we reported the highly stable porphyrin-based porous **mog** MOF **1·Cd**. Such a MOF catalyst exhibits rich open Lewis acid sites and Lewis basic moieties, and it was then applied as an efficient heterogeneous catalyst for the cyanosilylation of aldehydes and Knoevenagel condensation reactions with very little catalyst loading. Importantly, **1·Cd** shows much higher catalytic activities to the benzaldehyde derivatives with electron-withdrawing groups in comparison to those with electron-donating groups in the catalytic process. Most strikingly, catalytic reactions by **1·Cd** were accomplished under solvent-free conditions. The excellent catalytic activity, good stability, and recyclability demonstrate that **1·Cd** is an efficient heterogeneous MOF catalyst for C–C bond formation under solvent-free conditions.

EXPERIMENTAL SECTION

Materials and Methods. All reagents and solvents were purchased from commercial sources. FT-IR spectra were measured in the 4000–400 cm^{-1} range on a Mattson Alpha-Centauri spectrometer. Elemental analysis (C, H, N) was performed on a VarioEL III Elemental Analyzer. PXRD patterns were recorded on a Rigaku Dmax 2000 X-ray diffractometer with graphite-monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). TG measurements were determined on a PerkinElmer TG-7 analyzer under nitrogen gas. The catalytic products were measured by GC equipment with a capillary (30 m long \times 0.25 mm i.d., WondaCAP 17) and FID detector (GC-2014C, Shimadzu, Japan). All UV/vis spectra were tested by a Cary TU-1900 double beam UV–vis spectrophotometer. ^1H NMR spectra were recorded on a Varian 500 MHz spectrometer.

Synthesis of $[\text{Cd}_3(\text{tipp})(\text{bpdc})_2]\cdot\text{DMA}\cdot 9\text{H}_2\text{O}$. A mixture of H_2tipp (18 mg, 0.02 mmol), H_2bpdc (24 mg, 0.099 mmol), $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (24 mg, 0.078 mmol), DMA (4 mL), DMSO (1 mL), and isopropyl alcohol (1 mL) was sealed in a 15 mL Teflon reactor and heated to 150 °C for 3 days. Dark purple crystals were achieved in a yield of 38% based on H_2tipp . Anal. Calcd for $\text{C}_{88}\text{H}_{79}\text{Cd}_3\text{N}_{13}\text{O}_{18}$: C, 54.37; H, 4.09; N, 9.36. Found: C, 54.16; H, 3.90; N, 9.22. IR (KBr pellet, cm^{-1}): 3118 (w), 2924 (w), 1667 (s), 1578 (s), 1520 (s), 1383 (s), 1303 (m), 1249 (m), 1197 (w), 1091 (w), 1061 (m), 992 (m), 961 (w), 931 (w), 851 (w), 807 (w), 771 (m), 681 (w), 656 (m).

Synthesis of $\text{Cd}^{\text{II}}\text{-tipp}$. In a typical procedure, a mixture of H_2tipp (0.876 g, 1 mmol) and $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (1.542 g, 5 mmol) in acetic acid (100 mL) was refluxed for 8 h. After removal of the acetic acid, the precipitates were washed with water several times and then a dark purple product was obtained.^{58,59}

Sample Activation. Before the catalytic experiments, the as-synthesized samples of **1·Cd** were washed with DMF and soaked in methanol for 2 days. Further, the samples were filtrated and dried at 100 °C under vacuum to remove the solvent molecules.

Catalytic Study for Cyanosilylation Reactions. In a 15 mL round-bottom flask were placed successively aldehyde or ketone (1 mmol), trimethylsilyl cyanide (TMSCN, 2 mmol), and activated **1·Cd** (0.006 mmol, 10 mg). Then the mixture was stirred for 18 h at room temperature. The yields were determined by GC and ^1H NMR spectra with tridecane as an internal standard.

Catalytic Study for Knoevenagel Condensation Reactions. In a typical procedure, aldehyde (1 mmol), malononitrile (2 mmol), and activated **1·Cd** (0.006 mmol, 10 mg) were placed in a 15 mL round-bottom flask. Then the mixture was heated to 60 °C and stirred for 1 h.

The yields were determined by GC and ^1H NMR spectra with tridecane as an internal standard.

X-ray Crystallography. Crystallographic data of $1\cdot\text{Cd}$ were determined on an Oxford Diffraction Gemini R CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Absorption correction was performed by a multiscan technique. The structure was solved by direct methods with SHELXS-97 and refined on F^2 by full-matrix least squares using the SHELXTL-97 program within WINGX.^{60–62} Non-hydrogen atoms were refined anisotropically, and hydrogen atoms on carbon were generated geometrically.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available: figures, tables, and crystallographic data in CIF See DOI: 10.1039/x0xx00000x The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b03174.

GC spectra, ^1H NMR spectra, additional characterization and crystallographic data, and mechanistic details (PDF) Crystallographic data (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*J.Y.: e-mail, yangj808@nenu.edu.cn.

*S.-Y.S.: e-mail, songsy@ciac.ac.cn.

*J.-F.M.: e-mail, majf247@yahoo.com; fax, +86-431-85098620.

ORCID

Jian-Fang Ma: 0000-0002-4059-8348

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21277022, 21371030, 21301026, and 21471029)

■ REFERENCES

- (1) Gregory, R. J. H. Cyanohydrins in nature and the laboratory: biology, preparations, and synthetic applications. *Chem. Rev.* **1999**, *99*, 3649–3682.
- (2) Denmark, S. E.; Beutner, G. L. Lewis base catalysis in organic synthesis. *Angew. Chem., Int. Ed.* **2008**, *47*, 1560–1638.
- (3) Kikukawa, Y.; Suzuki, K.; Sugawa, M.; Hirano, T.; Kamata, K.; Yamaguchi, K.; Mizuno, N. Cyanosilylation of carbonyl compounds with trimethylsilyl cyanide catalyzed by an yttrium-pillared silicotungstate dimer. *Angew. Chem., Int. Ed.* **2012**, *51*, 3686–3690.
- (4) Zeng, X.-P.; Cao, Z.-Y.; Wang, X.; Chen, L.; Zhou, F.; Zhu, F.; Wang, C.-H.; Zhou, J. Activation of chiral (Salen)AlCl complex by phosphorane for highly enantioselective cyanosilylation of ketones and enones. *J. Am. Chem. Soc.* **2016**, *138*, 416–425.
- (5) Park, B. Y.; Ryu, K. Y.; Park, J. H.; Lee, S.-g. A dream combination for catalysis: highly reactive and recyclable scandium(III) triflate-catalyzed cyanosilylations of carbonyl compounds in an ionic liquid. *Green Chem.* **2009**, *11*, 946–948.
- (6) Huh, S.; Chen, H.-T.; Wiench, J. W.; Pruski, M.; Lin, V. S.-Y. Cooperative catalysis by general acid and base bifunctionalized mesoporous silica nanospheres. *Angew. Chem., Int. Ed.* **2005**, *44*, 1826–1830.
- (7) Dang, D.; Wu, P.; He, C.; Xie, Z.; Duan, C. Homochiral metal-organic frameworks for heterogeneous asymmetric catalysis. *J. Am. Chem. Soc.* **2010**, *132*, 14321–14323.
- (8) Kurono, N.; Yamaguchi, M.; Suzuki, K.; Ohkuma, T. Lithium chloride: an active and simple catalyst for cyanosilylation of aldehydes and ketones. *J. Org. Chem.* **2005**, *70*, 6530–6532.

(9) Iwanami, K.; Choi, J.-C.; Lu, B.; Sakakura, T.; Yasuda, H. Remarkable acceleration of cyanosilylation by the mesoporous Al-MCM-41 catalyst. *Chem. Commun.* **2008**, *44*, 1002–1004.

(10) North, M.; Usanov, D. L.; Young, C. Lewis acid catalyzed asymmetric cyanohydrin synthesis. *Chem. Rev.* **2008**, *108*, 5146–5226.

(11) Brunel, J.-M.; Holmes, I. P. Chemically catalyzed asymmetric cyanohydrin syntheses. *Angew. Chem., Int. Ed.* **2004**, *43*, 2752–2778.

(12) Evans, D. A.; Truesdale, L. K.; Carroll, G. L. Cyanosilylation of aldehydes and ketones. A convenient route to cyanohydrin derivatives. *J. Chem. Soc., Chem. Commun.* **1973**, 55–56.

(13) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. Preparation, clathration ability, and catalysis of a two-dimensional square network material composed of cadmium(II) and 4,4'-bipyridine. *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152.

(14) Xie, Y.; Wang, T.-T.; Liu, X.-H.; Zou, K.; Deng, W.-Q. Capture and conversion of CO_2 at ambient conditions by a conjugated microporous polymer. *Nat. Commun.* **2013**, *4*, 1960.

(15) Tu, W.; Zhou, Y.; Zou, Z. Photocatalytic conversion of CO_2 into renewable hydrocarbon fuels: state-of-the-art accomplishment, challenges, and prospects. *Adv. Mater.* **2014**, *26*, 4607–4626.

(16) Crossley, S.; Faria, J.; Shen, M.; Resasco, D. E. Solid nanoparticles that catalyze biofuel upgrade reactions at the water/oil interface. *Science* **2010**, *327*, 68–72.

(17) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C.-Y. Applications of metal-organic frameworks in heterogeneous supramolecular catalysis. *Chem. Soc. Rev.* **2014**, *43*, 6011–6061.

(18) Peng, Y.; Gong, T.; Zhang, K.; Lin, X.; Liu, Y.; Jiang, J.; Cui, Y. Engineering chiral porous metal-organic frameworks for enantioselective adsorption and separation. *Nat. Commun.* **2014**, *5*, 4406.

(19) Nagarkar, S. S.; Joarder, B.; Chaudhari, A. K.; Mukherjee, S.; Ghosh, S. K. Highly selective detection of nitro explosives by a luminescent metal-organic framework. *Angew. Chem., Int. Ed.* **2013**, *52*, 2881–2885.

(20) Hu, Z.; Lustig, W. P.; Zhang, J.; Zheng, C.; Wang, H.; Teat, S. J.; Gong, Q.; Rudd, N. D.; Li, J. Effective detection of mycotoxins by a highly luminescent metal-organic framework. *J. Am. Chem. Soc.* **2015**, *137*, 16209–162015.

(21) Gao, W.-Y.; Wu, H.; Leng, K.; Sun, Y.; Ma, S. Inserting CO_2 into aryl C-H bonds of metal-organic frameworks: CO_2 utilization for direct heterogeneous C-H activation. *Angew. Chem., Int. Ed.* **2016**, *55*, 5472–5476.

(22) Johnson, J. A.; Zhang, X.; Reeson, T. C.; Chen, Y.-S.; Zhang, J. Facile control of the charge density and photocatalytic activity of an anionic indium porphyrin framework via in situ metalation. *J. Am. Chem. Soc.* **2014**, *136*, 15881–15884.

(23) Wang, K.; Lv, X.-L.; Feng, D.; Li, J.; Chen, S.; Sun, J.; Song, L.; Xie, Y.; Li, J.-R.; Zhou, H.-C. Pyrazolate-based porphyrinic metal-organic framework with extraordinary base-resistance. *J. Am. Chem. Soc.* **2016**, *138*, 914–919.

(24) Jiang, H.-L.; Feng, D.; Wang, K.; Gu, Z.-Y.; Wei, Z.; Chen, Y.-P.; Zhou, H.-C. An exceptionally stable, porphyrinic Zr metal-organic framework exhibiting pH-dependent fluorescence. *J. Am. Chem. Soc.* **2013**, *135*, 13934–13938.

(25) Jiang, W.; Yang, J.; Liu, Y.-Y.; Ma, J.-F. Porphyrin-based mixed-valent Ag(I)/Ag(II) and Cu(I)/Cu(II) networks as efficient heterogeneous catalysts for the azide-alkyne “click” reaction and promising oxidation of ethylbenzene. *Chem. Commun.* **2016**, *52*, 1373–1376.

(26) Johnson, J. A.; Petersen, B. M.; Kormos, A.; Echeverria, E.; Chen, Y.-S.; Zhang, J. A new approach to non-coordinating anions: Lewis acid enhancement of porphyrin metal centers in a zwitterionic metal-organic framework. *J. Am. Chem. Soc.* **2016**, *138*, 10293–10298.

(27) Comito, R. J.; Fritzsche, K. J.; Sundell, B. J.; Schmidt-Rohr, K.; Dincă, M. Single-site heterogeneous catalysts for olefin polymerization enabled by cation exchange in a metal-organic framework. *J. Am. Chem. Soc.* **2016**, *138*, 10232–10237.

(28) Wang, K.; Feng, D.; Liu, T.-F.; Su, J.; Yuan, S.; Chen, Y.-P.; Bosch, M.; Zou, X.; Zhou, H.-C. A series of highly stable mesoporous metalloporphyrin Fe-MOFs. *J. Am. Chem. Soc.* **2014**, *136*, 13983–13986.

- (29) Feng, D.; Chung, W.-C.; Wei, Z.; Gu, Z.-Y.; Jiang, H.-L.; Chen, Y.-P.; Darensbourg, D. J.; Zhou, H.-C. Construction of ultrastable porphyrin Zr metal-organic frameworks through linker elimination. *J. Am. Chem. Soc.* **2013**, *135*, 17105–17110.
- (30) Park, J.; Feng, D.; Yuan, S.; Zhou, H.-C. Photochromic metal-organic frameworks: reversible control of singlet oxygen generation. *Angew. Chem., Int. Ed.* **2015**, *54*, 430–435.
- (31) Jiang, W.; Yang, J.; Liu, Y.-Y.; Song, S.-Y.; Ma, J.-F. A porphyrin-based porous *rtl* metal-organic framework as an efficient catalyst for the cycloaddition of CO₂ to epoxides. *Chem. - Eur. J.* **2016**, *22*, 16991–16997.
- (32) Yang, X.-L.; Xie, M.-H.; Zou, C.; He, Y.; Chen, B.; O’Keeffe, M.; Wu, C.-D. Porous metalloporphyrinic frameworks constructed from metal 5,10,15,20-tetrakis(3,5-biscarboxylphenyl)porphyrin for highly efficient and selective catalytic oxidation of alkylbenzenes. *J. Am. Chem. Soc.* **2012**, *134*, 10638–10645.
- (33) Lu, K.; He, C.; Guo, N.; Chan, C.; Ni, K.; Weichselbaum, R. R.; Lin, W. Chlorin-based nanoscale metal-organic framework systemically rejects colorectal cancers via synergistic photodynamic therapy and checkpoint blockade immunotherapy. *J. Am. Chem. Soc.* **2016**, *138*, 12502–12510.
- (34) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. A catalytically active, permanently microporous MOF with metalloporphyrin struts. *J. Am. Chem. Soc.* **2009**, *131*, 4204–4205.
- (35) Zhang, Z.; Zhang, L.; Wojtas, L.; Nugent, P.; Eddaoudi, M.; Zaworotko, M. J. Templated synthesis, postsynthetic metal exchange, and properties of a porphyrin-encapsulating metal-organic material. *J. Am. Chem. Soc.* **2012**, *134*, 924–927.
- (36) Spek, A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
- (37) Johnson, J. A.; Lin, Q.; Wu, L.-C.; Obaidi, N.; Olson, Z. L.; Reeson, T. C.; Chen, Y.-S.; Zhang, J. A “pillar-free”, highly porous metalloporphyrinic framework exhibiting eclipsed porphyrin arrays. *Chem. Commun.* **2013**, *49*, 2828–2830.
- (38) Feng, D.; Wang, K.; Wei, Z.; Chen, Y.-P.; Simon, C. M.; Arvapally, R. K.; Martin, R. L.; Bosch, M.; Liu, T.-F.; Fordham, S.; Yuan, D.; Omary, M. A.; Haranczyk, M.; Smit, B.; Zhou, H.-C. Kinetically tuned dimensional augmentation as a versatile synthetic route towards robust metal-organic frameworks. *Nat. Commun.* **2014**, *5*, 5723.
- (39) Hatano, M.; Yamakawa, K.; Kawai, T.; Horibe, T.; Ishihara, K. Enantioselective cyanosilylation of ketones with lithium(I) dicyanotrimethylsilicate(IV) catalyzed by a chiral lithium(I) phosphoryl phenoxide. *Angew. Chem., Int. Ed.* **2016**, *55*, 4021–4025.
- (40) Khan, N.-u. H.; Kureshy, R. I.; Abdi, S. H. R.; Agrawal, S.; Jasra, R. V. Metal catalyzed asymmetric cyanation reactions. *Coord. Chem. Rev.* **2008**, *252*, 593–623.
- (41) Yang, H.; Zhang, L.; Wang, P.; Yang, Q.; Li, C. The enantioselective cyanosilylation of aldehydes on a chiral VO(Salen) complex encapsulated in SBA-16. *Green Chem.* **2009**, *11*, 257–264.
- (42) Liu, F.; Xu, Y.; Zhao, L.; Zhang, L.; Guo, W.; Wang, R.; Sun, D. Porous barium-organic frameworks with highly efficient catalytic capacity and fluorescence sensing ability. *J. Mater. Chem. A* **2015**, *3*, 21545–21552.
- (43) D’Vries, R. F.; Iglesias, M.; Snejko, N.; Gutiérrez-Puebla, E.; Monge, M. A. Lanthanide metal-organic frameworks: searching for efficient solvent-free catalysts. *Inorg. Chem.* **2012**, *51*, 11349–11355.
- (44) Bhunia, A.; Dey, S.; Moreno, J. M.; Diaz, U.; Concepcion, P.; Hecke, K. V.; Janiak, C.; Voort, P. V. D. A homochiral vanadium-salen based cadmium bpdc MOF with permanent porosity as an asymmetric catalyst in solvent-free cyanosilylation. *Chem. Commun.* **2016**, *52*, 1401–1404.
- (45) Gustafsson, M.; Bartoszewicz, A.; Martín-Matute, B.; Sun, J.; Grins, J.; Zhao, T.; Li, Z.; Zhu, G.; Zou, X. A family of highly stable lanthanide metal-organic frameworks: structural evolution and catalytic activity. *Chem. Mater.* **2010**, *22*, 3316–3322.
- (46) Mo, K.; Yang, Y.; Cui, Y. A homochiral metal-organic framework as an effective asymmetric catalyst for cyanohydrin synthesis. *J. Am. Chem. Soc.* **2014**, *136*, 1746–1749.
- (47) Zhu, C.; Xia, Q.; Chen, X.; Liu, Y.; Du, X.; Cui, Y. Chiral metal-organic framework as a platform for cooperative catalysis in asymmetric cyanosilylation of aldehydes. *ACS Catal.* **2016**, *6*, 7590–7596.
- (48) Fernández de Luis, R.; Urriaga, M. K.; Mesa, J. L.; Larrea, E. S.; Iglesias, M.; Rojo, T.; Arriortua, M. I. Thermal response, catalytic activity, and color change of the first hybrid vanadate containing bpe guest molecules. *Inorg. Chem.* **2013**, *52*, 2615–2626.
- (49) Freeman, F. Properties and reactions of ylidenemalononitriles. *Chem. Rev.* **1980**, *80*, 329–350.
- (50) Gascon, J.; Aktay, U.; Hernandez-Alonso, M. D.; Klink, G. P. M. v.; Kapteijn, F. Amino-based metal-organic frameworks as stable, highly active basic catalysts. *J. Catal.* **2009**, *261*, 75–87.
- (51) List, B. Emil Knoevenagel and the roots of aminocatalysis. *Angew. Chem., Int. Ed.* **2010**, *49*, 1730–1734.
- (52) Hasegawa, S.; Horike, S.; Matsuda, R.; Furukawa, S.; Mochizuki, K.; Kinoshita, Y.; Kitagawa, S. Three-dimensional porous coordination polymer functionalized with amide groups based on tridentate ligand: selective sorption and catalysis. *J. Am. Chem. Soc.* **2007**, *129*, 2607–2614.
- (53) Liu, H.; Xi, F.-G.; Sun, W.; Yang, N.-N.; Gao, E.-Q. Amino- and sulfo-bifunctionalized metal-organic frameworks: one-pot tandem catalysis and the catalytic sites. *Inorg. Chem.* **2016**, *55*, 5753–5755.
- (54) Modak, A.; Mondal, J.; Bhaumik, A. Porphyrin based porous organic polymer as bi-functional catalyst for selective oxidation and Knoevenagel condensation reactions. *Appl. Catal., A* **2013**, *459*, 41–51.
- (55) Aguirre-Díaz, L. M.; Gándara, F.; Iglesias, M.; Snejko, N.; Gutiérrez-Puebla, E.; Monge, M. A. Tunable catalytic activity of solid solution metal-organic frameworks in one-pot multicomponent reactions. *J. Am. Chem. Soc.* **2015**, *137*, 6132–6135.
- (56) Park, J.; Li, J.-R.; Chen, Y.-P.; Yu, J.; Yakovenko, A. A.; Wang, Z. U.; Sun, L.-B.; Balbuenab, P. B.; Zhou, H.-C. A versatile metal-organic framework for carbon dioxide capture and cooperative catalysis. *Chem. Commun.* **2012**, *48*, 9995–9997.
- (57) Lee, L.-C.; Lu, J.; Weck, M.; Jones, C. W. Acid-base bifunctional shell cross-linked micelle nanoreactor for one-pot tandem reaction. *ACS Catal.* **2016**, *6*, 784–787.
- (58) Liu, Y.; Zhang, H.-J.; Lu, Y.; Cai, Y.-Q.; Liu, X.-L. Mild oxidation of styrene and its derivatives catalyzed by ionic manganese porphyrin embedded in a similar structured ionic liquid. *Green Chem.* **2007**, *9*, 1114–1119.
- (59) Zou, C.; Zhang, Z.; Xu, X.; Gong, Q.; Li, J.; Wu, C.-D. A multifunctional organic-inorganic hybrid structure based on Mn^{III}-porphyrin and polyoxometalate as a highly effective dye scavenger and heterogenous catalyst. *J. Am. Chem. Soc.* **2012**, *134*, 87–90.
- (60) Sheldrick, G. M. *SHELXS-97, Programs for X-ray Crystal Structure Solution*; University of Göttingen, Göttingen, Germany, 1997.
- (61) Sheldrick, G. M. *SHELXL-97, Programs for X-ray Crystal Structure Refinement*; University of Göttingen, Göttingen, Germany, 1997.
- (62) Farrugia, L. J. *WINGX: A Windows Program for Crystal Structure Analysis*; University of Glasgow, Glasgow, U.K., 1988.