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Five porous zinc(II) coordination polymers functionalized with amide groups: cooperative and size-selective catalysis

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Abstract: Five functionalized porous coordination polymers **1–5** with highly ordered amide groups in the channels show notable interaction with the guest molecules. The amide groups functioned as trigger sites and catalytic driven forces to activate the substrate proximity with the pore. Catalytic studies on catalyst with different porous radii and substrates with different molecular size revealed that these porous materials are heterogeneous, efficient and reusable catalysts for the size-selective Knoevenagel condensation reaction. The solids were stable after the reactions and were easily recycled and reused under the reaction conditions. Most importantly, compound **3** with two different functionalities decorated the porous wall displays an elegant example of cooperative catalysis.

Keywords: porous coordination polymers; heterogeneous catalysis; Knoevenagel reaction;

1. Introduction

Nowadays, porous coordination polymers (PCPs) have gained tremendous attention, mainly because of their potential applications in gas storage,[1] separation,[2] heterogeneous catalysis,[3] and so on.[4] Many PCPs have unique characteristic features such as well-defined cavity sizes and shapes, open Lewis acid sites, and active functional organic sites. Thus they can potentially serve as high efficient catalysts to promote organic transformations with size-, regio-, and stereo-selectivities, in a manner similar to inorganic zeolites.[5–10] As heterogeneous and recyclable catalysts, many functional PCPs have been explored to promote cyanosilylation of aldehyde,[11] alkylation of aromatics,[12] ring-opening reaction of epoxide,[13] Knoevenagel condensation,[14] transesterification of esters,[15] and so on. Although impressive progress has been achieved in the fields of catalysis, to improve the functions of the pores in PCPs for better catalytic performance and selectivity still remains a major challenge.

To create functional PCPs, some practical strategies, such as direct synthesis and post-synthetic modification, were used to produce guest accessible sites inside the well-defined spaces, and to introduce functional organic sites to decorate channel surfaces.[16–18] Here, incorporating active ligands including additional functional moieties as guest-accessible sites within pores of PCPs is a powerful approach to achieve functional flasks to facilitate their applications.[17b] An outstanding feature of these PCPs is their chemical functionality that could be achieved by the uncoordinated active organic groups. To date, there are only few examples of amide-, pyridyl-, hydroxyl-, or amino-containing Metal-Organic Frameworks (MOFs) obtained by direct synthesis, among more 10000 MOFs reported.[19]

For functional application, amide-functionalized ligands are good candidates, because amide group has two types of hydrogen bonding sites: the -NH moiety acts as an electron acceptor and the carbonyl group acts as an electron donor. Thus, this amide group can be use as base-type catalytic driving force to prompt several important reactions.[20] For example, Kitagawa et al.[17b] have first

reported that a size-selective Knoevenagel condensation reaction catalyzed by compound $\{[Cd(4\text{-btapa})_2(NO_3)_2]\cdot 6H_2O\cdot 2DMF\}_n$ (4-btapa = 1,3,5-benzene tricarboxylic acid tris[N-(4-pyridyl)amide]). Next, Su et al. have demonstrated that two amide-functionalized lead PCPs display size- and shape-selective catalytic activity towards the Knoevenagel condensation reaction.[10b] On the other hand, incorporation of $-NH_2$ functionality on the pore surface can also yield active catalysts for the Knoevenagel condensation.[9b,14c,21] It is noted that the weak basicity of amide groups implied only very low activities. Thus, a smart strategy is to combine two different basic groups, such as amide and amine groups, exposing in the pores of PCPs so as to exhibit higher catalytic capacity. However, to the best of our knowledge, PCPs with two different active organic functionalities are rare.

To our delight, our research group has recently provided five structural isomorphic PCPs that possess two different active organic functionalities within the cavities.[22] Moreover, our research results reveal that $Zn(L)(aip)\cdot(H_2O)$ (L = $N^4,N^{4'}$-di(pyridin-4-yl)biphenyl-4,4'-dicarboxamide, H_2aip = 5-aminoisophthalic acid) shows the biggest CO_2 adsorption ability among the five isomorphic PCPs due to the combined effect from both amide group and amine group. The interesting result promotes us to study other promising applications. As is well known, cooperative catalysis on a pore of PCP requires the control of the relative spatial arrangement and the relative molar ratio of two functionalities at the channel surface. Moreover, the distance and spatial organization of the two active functionalities have to be carefully adjusted in such a way that they can act synergistically as cooperative catalysts. Indeed, the previous literatures have reported that some catalysts bearing two different active functionalities are able to individually activate each of the two reaction partners in a cooperative manner.[23] Based on the above-mentioned facts, in order to find the best candidate for catalyzing the Knoevenagel condensation reaction, it is necessary to screen the catalytic capacities of the five PCPs. Herein, we report catalytic performance of the five PCPs toward the Knoevenagel condensation reaction. The catalytic result reveals that, among the five catalysts, $Zn(L)(aip)$ shows the highest catalytic active due to the cooperation catalysis from

both amide group and amine group. Furthermore, all the five PCPs display the shape- and size-selective catalytic activity in the Knoevenagel condensation reaction.

2. Experimental Section

2.1. General procedures

All reagents and starting material were commercially available and used as received unless special notice. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8-ADVANCE X-ray diffractometer with Cu–Kα (λ = 1.5418 Å). The products were identified by NMR analysis in comparison with authentic samples. ^{1}HNMR spectra were recorded on a Varian UNITY/NOVA 400 NMR spectrameter using $CDCl_3$or DMSO-d_6 as the solvent at room temperature. Chemical shifts are given in δ relative to TMS. The coupling constants J are given Hz.

2.2. Typical procedure for the Knoevenagel condensation reaction

A 10 mL round-bottomed flask was charged with aldehyde compound (0.2 mmol), malononitrile (0.6 mmol) and catalyst (0.004 mmol). The reaction mixture was stirred for the required time under solvent-free condition. The reaction was monitored by the thin layer chromatography. After the reaction finished, 10 mL of ethanol was added to the reaction mixture. The mixture was stirred for another 5 min. Then the catalyst was filtered off, and the filtrate was concentrated under reduced pressure. The crude product was purified by recrystallization from aqueous ethanol to afford pure compounds. All isolated pure products were fully characterized by NMR analysis. The recovered catalyst was washed with ethyl acetate, dried, and reused without further purification or regeneration. Moreover, the recovered catalysts were characterized by the X-ray powder diffraction and showed identical results to those of the fresh samples.

2.4. Experimental procedure for reusability tests

The reusability of compound **3** was tested for the Knoevenagel condensation reaction. When the reaction finished, the mixture was centrifuged, the filtrate was decanted, and the catalyst was dried under vaccum at room temperature for 8 h, and then reused directly without further purification for the second run with fresh aldehyde and malononitrile. It was used for four consecutive runs with minor loss in activity.

3. Results and Discussion

According to our previous method,[22] we synthesized five structural isomorphic PCPs.，namely, $Zn(L)(ip)·(DMF)(H_2O)_{1.5}$ (**1a**), $Zn(L)(hip)·(DMF)(H_2O)$ (**2a**), $Zn(L)(aip)·(H_2O)$ (**3a**), $Zn(L)(nip)·(DMF)_{0.5}(H_2O)_{0.5}$ (**4a**), $Zn(L)(HBTC)·(H_2O)_2$ (**5a**) (H_2ip = isophthalic acid, H_2hip = 5-hydroxyisophthalic acid, H_2aip = 5-aminoisophthalic acid, H_2nip = 5-nitroisophthalic acid, and H_3BTC = 1,3,5-benzenetricarboxylic acid). The structural analysis reveals that the 1-D hexagonal channels of the five PCPs not only possess abundant amide groups but also is decorated by different functional groups of –H, –OH, $–NH_2$, $–NO_2$, and –COOH, respectively. TGA data indicated that PCPs **1a, 2a, 4a,** and **5a** are lease completely water and DMF molecules exceed 200 °C except PCPs **3a** in the temperature range of 30–150°C, to form a guest-free phase $Zn(L)(ip)$ (**1**), $Zn(L)(hip)$ (**2**), $Zn(L)(aip)$ (**3**), $Zn(L)(nip)$ (**4**), and $Zn(L)(HBTC)$ (**5**), respectively. The powder X-ray diffraction (PXRD) patterns of the guest-free phase **1**–**5** are almost identical with that of the as-synthesized **1a**–**5a**, respectively, indicating that the basic 3D framework is retained and thus the 1D hexagonal channels are accessible to guest molecules.

The previous studies demonstrated that PCPs with amide groups could function as the catalytic interaction sites on the channel wall. We also expected the amide groups in the channels of the resulting five PCPs can provide guest interaction sites as base sites (Figure 1). The selective accommodation and activation of reactants by the five PCPs were confirmed by selective adsorption experiments toward three active methylene compounds. Three methylene compounds chosen for the reaction were malononitrile (molecular size, 6.9 ×4.5 Å²), ethyl cyanoacetate (10.3

$\times$ 4.5 Å^2), and cyano-acetic acid tert-butyl ester (10.3 $\times$5.8 Å^2).   As-synthesized five PCPs were immersed in the benzene containing corresponding reagent and stirred, respectively. The powders were filtered and dried in air. The resulting powers were characterized by ^{1}H NMR and IR analyses. The corresponding data of compound **3** will be representatively discussed in detail, as shown in Figures 2 and 3. The ^{1}H NMR spectra showed that compound **3** adsorbs 3.8, 1.6, and 0.5 molecular stoichiometric amounts of malononitrile, ethyl cyanoacetate, and cyano-acetic acid tert-butyl ester per **3**, respectively (Figure 2). The result indicates the smallest malononitrile molecule was most easily introduced in the channels of **3**, and the inclusion amount of malononitrile for **3** was 2-8 times larger than those of the other reagents. The IR analysis also reveals that only malononitrile interacted with **3** (Figure 3). Some conclusions can be deduced from these results: 1) if an active methylene compound interacts with part of the α-H atom, the IR band attributed to the C$\equiv$N stretching vibration shifts to a lower wavenumber and υ^s_{CN}-υ^{as}_{CN} splitting appears;[24] 2) the υ^s_{CN}-υ^{as}_{CN} splitting at 2183 and 2202 cm^{-1} was observed for malononitrile in **3**, whereas the other reagents showed only the original peak; 3) the IR spectrum of **3** containing malononitrile shows two types of guests: one interacting with the host **3** and the other not interacting. Based on the above two analyses, the channels of **3** can selectively adsorb and activate the smallest malononitrile molecule, similar to the previous report.[14a]

PCPs with base properties are important heterogeneous catalysts for base-catalyzed reaction due to their unique reactivity and selectivity under mild reaction conditions. One of the most important base-catalyzed reaction is the Knoevenagel condensation reaction. In this reaction, the C–C bond-forming is promoted by the activation of the carbonyl carbon and the addition of the active methylene compounds to give rise to α,β-unsaturated compounds, a kind of precursors of fine chemicals and biological compounds.

In a typical reaction, a mixture of benzaldehyde (0.1 mmol) and malononitrile (0.3 mmol) was added into a 50 mL flask containing the catalyst (0.003 mmol, 3 mol %). The resulting mixture was stirred at room temperature. The progress of the reaction was monitored by checking

TLC from the reaction mixture at regular time intervals.

First of all, the reactivity of the five PCPs (**1–5**) as catalysts was studied. The results reveal that catalyst **3** yields the product almost quantitatively after 3 h, while the yields for catalysts **1**, **2**, **4** and **5** were lower than 80, 70, 72 and 60%, respectively (Figure 4). It is noted that all the five PCPs display good catalytic efficiency towards to the Knoevenagel reaction because the amide groups are introduces as trigger sites to achieve efficient guest interactions, a powerful catalytic driving force, and good signal responding communications. The active differences found between **3** and other four polymers (**1**, **2**, **4**, and **5**) cannot be attributed to the differences in diffusion rate, because all structural frameworks contained similar pore openings, but must be due to difference in the basicity strength of the active groups. Possibly the amide and amine groups of **3** in a cooperative manner show a higher basicity than those groups at the windows of the other four PCPs, because except for amide groups, the pendent NH_2 groups of **3** present at the pore surface can also promote the Knoevenagel reaction, which has been identified by the previous reports.[16b, 21a] Indeed, the distance and organization of the amide and amine functionalities in **3** can be precisely adjusted in such a way that they can act synergistically as cooperative catalysts. Accordingly, **3** shows a remarkably superior activity (1.2 times higher than that of **1**). However, the lower activity of **5** might be ascribed to the decrease of base by the acid pendent COOH groups. Notably, the activity observed for **3** catalyzed the Knoevenagel reaction of benzaldehyde with malononitrile is superior to those found for [Cd(4-btapa)$_2$(NO$_3$)$_2$] (4 mol% loading, 98% yield and 12 h),[17b] the porous BF-COF-1 (5 mol% loading, 96% yield and 10 h),[17d] and the multi-functional PCN-12 (5 mol% loading, 99% yield and 12 h).[17e]
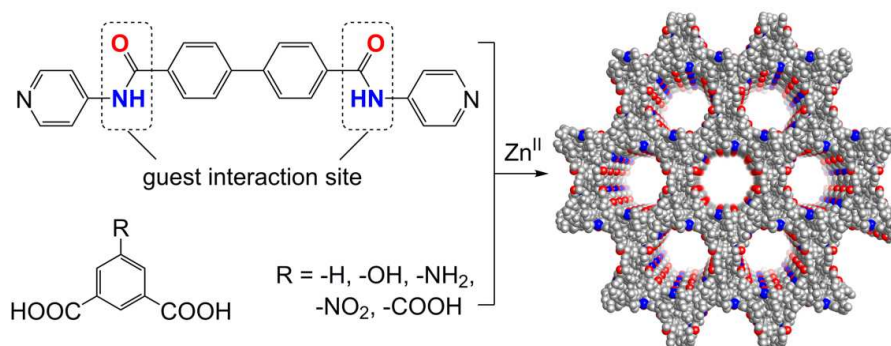
Figure 1. Perspective views of channels within multifunctional PCPs **1–5** showing the constructional fragments.
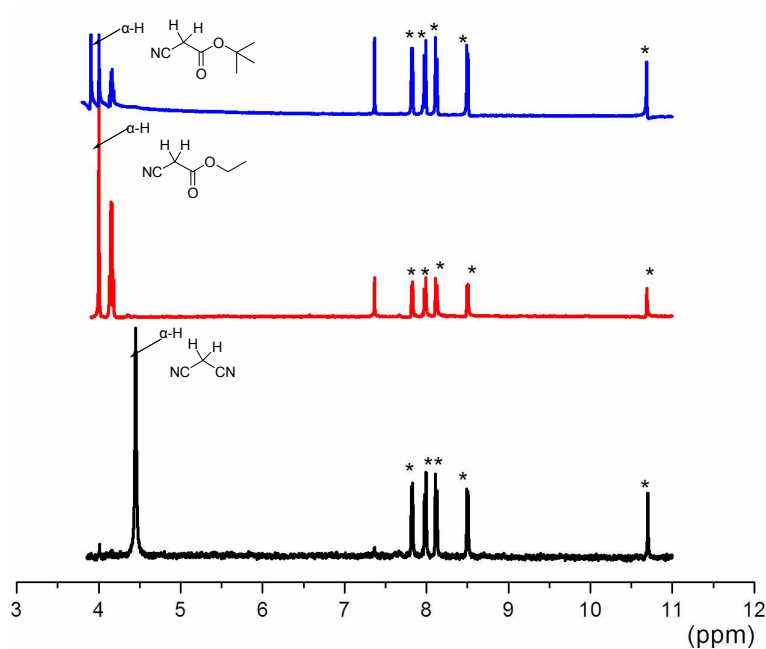

Figure 2. ^{1}H-NMR (DMSO-d$_6$) spectra of **3** that adsorbed each guest molecule: (a) malononitrile, (b) ethyl cyanoacetate, and (c) cyano-aceticacidtert-butyl ester. The peaks marked with an asterisk indicate the L and nip ligands.
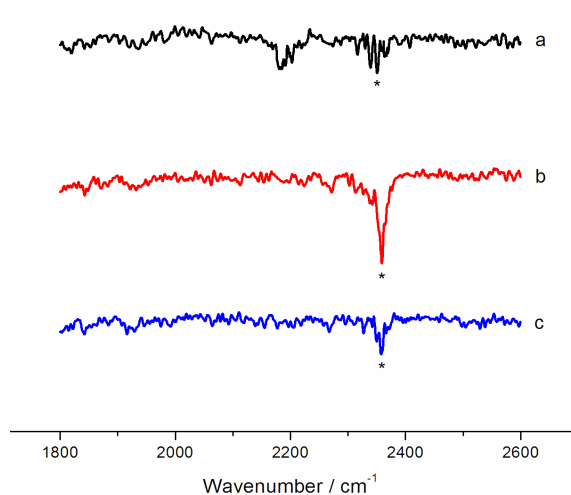
Figure 3. IR spectra in the region of C≡N stretching vibration bands of (a) **3** containing malononitrile, (b) **3** containing ethyl cyanoacetate, and (c) **3** containing cyano-acetic acid tert-butyl ester. The bands marked with an asterisk indicate the C≡N stretching vibration bands due to each substrate that is not activated.
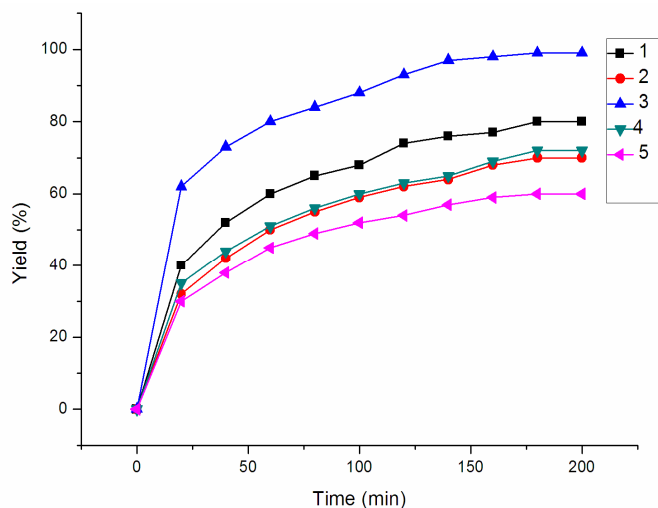
Figure 4. Kinetic profiles for Knoevenagel condensation reaction of for PCPs **1–5**.

To investigate the advantageous role of the neat conditions, we carried out the above reaction in different solvents, such as water, CH_2Cl_2, MeCN, and benzene under identical conditions to obtain the corresponding α,β-unsaturated compounds in 40%, 60%, 85%, and 30% yields, respectively. It is remarkable that the reaction carried out under neat conditions by using catalyst **3**

affords the corresponding α,β-unsaturated compounds in excellent yield (99%), which is significantly higher than that in organic solvents.
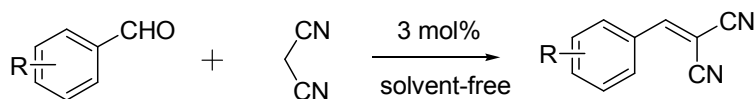
Considering the possibility of those compounds containing amide or amine groups to catalyze the Knoevenagel condensation reaction, we performed control tests with 5-aminoisophthalic acid or $N^4,N^{4'}$-di(pyridin-4-yl)biphenyl-4,4'-dicarboxamide as catalysts instead of **3**. As in the case of **3**, the reaction of benzaldehyde with malononitrile in the presence of 5-aminoisophthalic acid gave the same products with little lower yields under similar reaction conditions (e.g., 92% for H$_2$aip vs 99% for **3**). However, the $N^4,N^{4'}$-di(pyridin-4-yl)biphenyl-4,4'-dicarboxamide ligand is very less efficient to prompt the catalytic transformation, affording the corresponding α,β-unsaturated compounds with 32% yields. When the 5-aminoisophthalic acid was used as catalyst, all the Knoevenagel condensation reaction did not exhibit any selectivity toward the reaction substrates. And, the process involving **3** was heterogeneous, catalytic reaction in the presence of H$_2$aip was partially homogeneous, but without achieving complete dissolution of H$_2$aip. Therefore, compared to H$_2$aip, higher activity of **3** may be caused by better accessibility of the catalyst's active sites. Taken together, these results indicate that the catalytic activity of **3** is superior to its corresponding components.
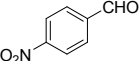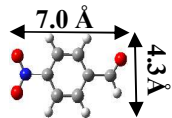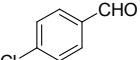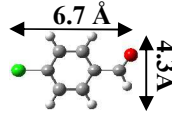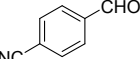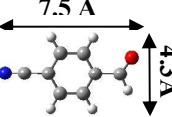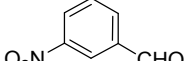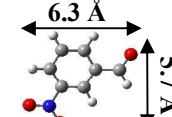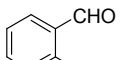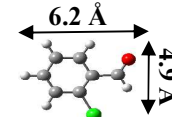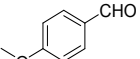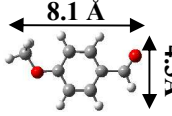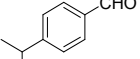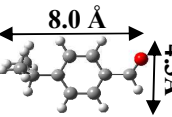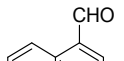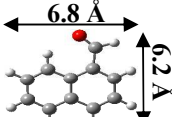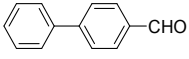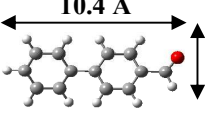
Next, the remarkably simple and convenient reaction conditions, easy work up, and high yield for the transformation prompted us to extend the scope of **3** as heterogeneous catalyst for the Knoevenagel condensation reaction of a wide variety of aromatic aldehydes. It gave the corresponding α,β-unsaturated compounds in good-to-excellent yields (Table 1). On the one hand, it seems that the nature of the substituent on the aromatic ring had dramatic effect on the reaction yield; the lowest yield was obtained for an electron donor group like p-methoxybenzaldehyde. On the other hand, in order to test the size selectivity of **3**, a systematic approach must be performed by varying the size and shape of aldehyde. In the case of 4-phenylbenzaldehyde, a slightly elongated, linear molecule (4.3 × 10.4 Å^2), afforded a 90% yield. As for 1-naphthaldehyde with

entry	substrate	molecular size	time	yield[a]
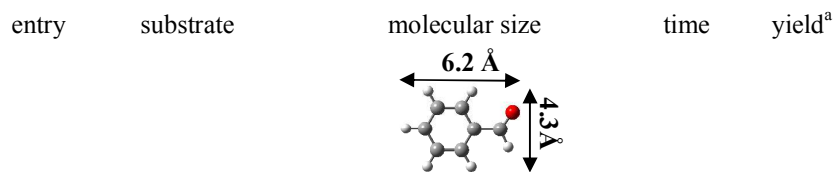
molecular dimensions of 6.8 × 6.2 Å², the yield was reduced to 70%. These results suggest that the

Knoevenagel condensation reactions catalyzed by **3** are closely dependent on its pore sizes (7.0 ×

8.7 Å). Under similar experimental conditions, we have attempted ketones instead of

benzaldehyde derivatives to carry out Knoevenagel condensation reactions. Unfortunately,

ketones seem to not react with malononitrile.

Table 1. Knoevenagel condensation reactions catalyzed by **3**

1			3	99
2		7.0 Å / 4.3 Å	2	99
3		6.7 Å / 4.3 Å	3	99
4		7.5 Å / 4.3 Å	2	99
5		6.3 Å / 5.7 Å	3	99
6		6.2 Å / 4.9 Å	5	98
7		8.1 Å / 4.3 Å	4	98
8		8.0 Å / 4.3 Å	4	99
9		6.8 Å / 6.2 Å	4	70
10		10.4 Å / 4.3 Å	4	90

[a]Yield of pure isolated product

To further probe whether the Knoevenagel reaction occurred inside the pores or on the surface of the solid catalyst, active methylene substrates of increasing dimensions were tested for the catalyst **3**. In the case of ethylcyanoacetate, a slightly elongated molecule (4.5×10.3 Å^2), the

conversions of these Knoevenagel condensations with benzaldehyde decreased obviously to 70%

under the same conditions. As for even larger tert-butyl cyanoacetate (5.8 × 10.3 $Å^2$), the

condensation reactions with benzaldehyde did not proceed (Table 2). Since the pore sizes of **3** are

7.0 × 8.7 Å which exhibits the confined sizes and cavity, the large substrates might be excluded in

the catalysis due to difficulty in diffusion into the channels of **3**. The guest-selective reaction

clearly demonstrates that the reaction occurs in the channels and not on the surface of **3**.

Finally, the heterogeneity, recyclability and stability of **3** in the Knoevenagel reaction of

benzaldehyde and malononitrile were examined. After the reaction mixture was stirred for 2 h,

removal of the catalysts via filtration resulted in the complete shut down of the reaction, which

verifies the heterogeneous catalysis of **3**. In order to examine the recyclability and stability of **3** in

this Knoevenagel reaction, they were recycled in four consecutive experiments. As mentioned

before, a corresponding product yield of 99% is achieved in the first run. In the second, third, and

fourth run the product yields, determined after the same reaction conditions, decrease to 98%,

95% and 93%, respectively. Meanwhile, elemental analyses along with powder X-ray analysis

were applied to characterize catalyst **3** before and after catalytic application. Elemental analysis of

the recyclic catalyst **3** showed good agreement between the calculated and experimentally

determined compositions, as summarized in Table 3. The PXRD patterns of catalysts **3** measured

after the reactions show the same profiles as the as-synthesized samples, indicating the unchanged

coordination frameworks although the crystallinity in the fourth run seems to be weakened due to

decreasing dramatically intension of the diffraction peaks, as depicted in Figure 5.
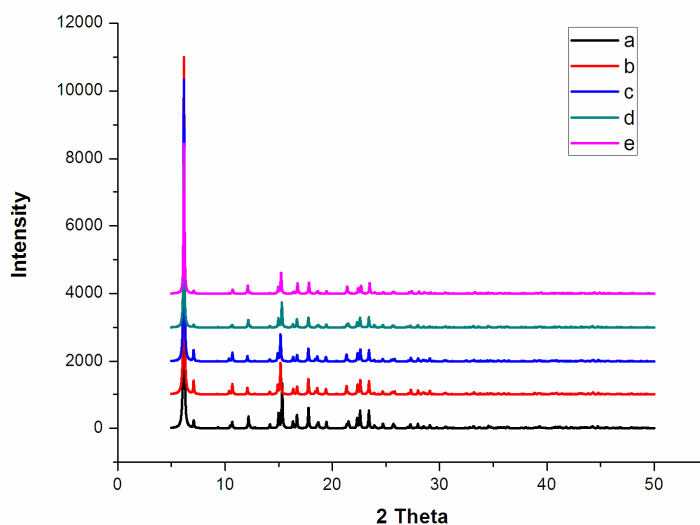
Figure 5. XRD patterns of **3**: (a) the simulated XRD pattern, (b) the first run, (c) after the second run, (d) after the third run, and (e) after the fourth run.

Table 2. Knoevenagel Condensation Reaction of Benzlaldehydewith Substrates

entry	substrate	molecular size	catalyst	yield (%)[a]
1	NC⌒CN	6.9 Å / 4.5 Å	3	100
2	NC⌒C(=O)O⌒	10.3 Å / 4.5 Å	3	70
3	NC⌒C(=O)O-C(CH₃)₃	10.3 / 5.8 Å	3	0

[a]Yield of pure isolated product

Table 3. Elemental analysis of **3**

	C	H	N
Calculated	60.15	3.63	10.96
Found	60.38	3.65	11.03
First recycling	60.43	3.67	11.05
Second recycling	60.56	3.69	11.09
Third recycling	60.62	3.72	11.12
Fourth recycling	60.78	3.74	11.16

Conclusions

In conclusion, we have developed five desolvated PCPs, which are mild and efficient heterogeneous catalysts for the Knoevenagel condensation reaction. The amide groups in the five PCPs work as trigger sites and catalytically driven forces to achieve efficient guest interactions, enforcing the reaction components proximity within the pore, resulting in excellent size-selective towards the substrate. Most importantly, the results clearly demonstrated that compound **3** is the efficient base catalyst for the Knoevenagel condensation reaction among the five PCPs under solvent-free conditions, because the distance and spatial organization of the amide and amine groups in **3** can site in such a way that they can act synergistically as cooperative catalysts. Therefore, the present study is significant, because it displays an elegant example of two different functionalities decorated the porous wall with cooperative catalysis.

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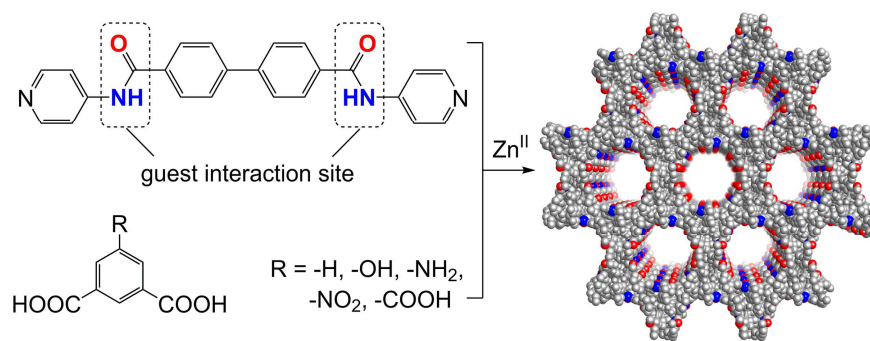
Five desolvated PCPs exhibit efficient base catalysts for the Knoevenagel condensation reaction and show size selectivity under solvent-free conditions.