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MOF materials as new emerged catalyst have been demonstrated to show high catalytic activity and size-, regio-, and stereo-selectivity. However, how to artifically controlling the catalytic process by convenient external stimulus such as light is still unexploited. Such photocontrol over organic reaction may enable switchable catalytic activities and/or selectivities, consequently producing desired products from a pool of building blocks according to the order and type of stimuli applied. In this work, we present a novel MOF catalyst, which not only offers ultrahigh photocontrol with the ON/OFF ratio as high as 407, but also displays disparate photomodulation in reaction kinetics towards various aldehyde substrates in light of their sizes, thus creating the first example in MOFs showing photoswitchable catalysis. The origin, as unveiled by photoswitching adsorption experiments and density functional theory calculations, is due to photoswitching storage of guest molecules in metal-organic framework (MOF).

## Introduction

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Metal-organic frameworks (MOFs), constructed by metal ions and organic ligands through coordination bonds, owning several outstanding merits such as high specific surface area, regular pore, adjustable aperture, and functionalized pore wall, are recently extensively pursued, due to not only their topological aesthetics, but also broad applications in storage, separation, sensor, catalysis, and so on.<sup>1-4</sup> Among these applications MOF materials as catalyst are highly attractive and have been demonstrated to catalyze a great deal of chemical reactions involving in, but not limited to, Knoevenagel condensation, Aza-Michael condensations, cyclohexene oxidation, Suzuki-Miyaura coupling. CO oxidation. cvclooctene hvdrogenation.5-8

Note that once the reaction conditions are chosen, all established MOF catalysts are inherently limitted to a fixed catalytic rate and/or selecitivity, which means that such synthesis process could not be artifically controlled by external stimulus. However, as we know, even in simple living organisms many essential functions such as photosynthesis are highly controllable by external factor.<sup>9</sup> In this regard, to meet future catalysis we have to focus on the development of switchable catalysis, especially photoswitchable catalysis, as light stimulus is non-invasive and can offers excellent temporal and spatial resolution.<sup>10-12</sup>

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In this work, as an ongoing work in photoactive MOFs,18-19 we attempt to develop a new conceptually MOF based photoswitchable catalysis. To implement such goal, three crucial pre-requisites such as porosity, photoresponse unit, and catalytic-active site are initially considered. Accordingly, we make a precise choice in organic ligands and 4,4'-diazene-1,2-divldibenzoate acid (H2AzDC) ligand is selected, because, i) the long carboxylate ligand of H<sub>2</sub>AzDC facilitates to coordinate with metal ions and enables to generate porous framework;<sup>20</sup> ii) as a typical T-type photochrome, azobenzene system often provides good stability, good photomechanical properties, fast reversible photoisomerization, and E-Zand exquisite photoisomerization with a large geometrical change from d<sub>4-4</sub> ~9Å of the co-planar E (tans) configuration to  $d_{4-4} \approx 6 \text{\AA}$  of the non-planar Z (cis) configuration, suggesting it as a good candidate to play a photoresponse role;<sup>21</sup> iii) the -N=N- group of H<sub>2</sub>AzDC is also a fascinating functional group capable of acting as a base-type catalyst. As a result, the new prepared MOF,  $[In(AzDC)_2]$   $[H_2N(CH_3)_2]$ , namely ECUT-50, shows regular 1D channel of 8.4Å×8.4Å along a axis, excellent catalysis performance for the Knoevenagel condensation reactions, and unique photoswitchable catalysis.

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## **Results and discussion**

The Structure of ECUT-50. Reacting InCl<sub>3</sub> and H<sub>2</sub>AzDC in DMF at 110°C for three days yields large block crystals of ECUT-50 with high yield (92%) and purity. Its structure is determined by single crystal X-ray diffraction, giving the Orthorhombic, Pnna space group. The In(III) site displays a somewhat distorted square-antiprismatic geometry finished by eight oxygen atoms from four AzDC<sup>2-</sup> ligands (Fig. 1a). The AzDC<sup>2-</sup> ligand takes the *trans* configuration and bi(bidentate) mode. As shown in Fig. 1b, the combination of In(III) ions and AzDC<sup>2-</sup> ligands builds a 3D framework with large open channel, which further allows to occur four-fold interpenetration in the [2+2] fashion.<sup>22</sup> Thereby the resulted open window with the consideration of atom radius is estimated to be 8.4Å×8.4Å (Fig. 1c), giving a solvent-accessible volume of 66.3%.<sup>23</sup> Topology analysis suggests dia net with four-fold interpenetration (Fig. 1d).22



Fig. 1 The structure of ECUT-50. a) the coordination surrounding of In(III) site; b) the 3D open framework constructed by In(III) and  $AzDC^{2-}$  ligands; c) four-fold interpenetrating framework with the open window of  $8.4\text{\AA} \times 8.4\text{\AA}$ ; d) topological view of the **dia** net with four-fold interpenetration in the [2+2] fashion. All hydrogen atoms are omitted for clarity. Color code: In/purple, O/red, C/gray, N/blue. The interpenetration is respectively distinguished by color of black, green, blue, and red.

**Porosity of ECUT-50**. Thermal gravimetric analysis (TG, Fig. S1) plus powder X-ray diffraction (PXRD, Fig. S2) is employed to confirm the thermostability and robust framework of **ECUT-50**. The first major weight loss of 37% before 200°C belongs to the loss of free DMF molecules. The PXRD patterns of activated samples, **ECUT-50a**, match with that of as-synthesized samples, indicative of maintenance of its framework integrality after degassing. The permanent porosity of **ECUT-50a** is evaluated by N<sub>2</sub> adsorption at 77K. The results are presented in Fig. S3, giving a Brunauer-Emmett-Teller (BET) surface area of 175 m<sup>2</sup>/g and Langmuir surface area of 223 m<sup>2</sup>/g. The pore size distribution (PSDs) is calculated using the well-known method of nonlocal density functional theory (NLDFT),<sup>24</sup> and a narrow pore width of ca. 0.98 nm is observed, comparable with the predicted value of 0.84 nm from crystal data.

Catalysis Performance. We note that the Knoevenagel condensation reaction, typically presenting a base-catalyzed model reaction is an important methodology in organic synthesis for formation of new C-C bond. It has been demonstrated that both MOFs and COFs (covalent organic frameworks),<sup>25</sup> containing certain base-like catalysis position in the pore wall, could not only catalyze such reaction but also perform size-selectivity. To characterize its base properties of ECUT-50a stemming from the -N=N- segment of AzDC2- ligands, we systematicly studied it as a catalyst for the Knoevenagel condensation reaction, involving dosage of catalyst (Fig. S4), reaction temperature (Fig. S5), and various aldehyde substrates. Table 1 shows the catalytic results of the condensation between aldehyde substrates and cyanoethylacetate over the MOF catalyst, ECUT-50a. Higher catalytic performance is observed for these substrates with the size of less than 6.7 Å, and especially the substrates of more than 7.2 Å even could not be converted to corresponding product. The results imply high size-selectivity of ECUT-50a. And as suggested in the literature,<sup>11</sup> such size-selectivity should be mainly dependent on the open window of MOFs. For ECUT-50a, although it provides about 0.84 nm open window, however the location of charge-balance ions of [H<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>] inside the channel would reduce the size of open window, consequently leading to that the large substrates with the size of more than 7.2 Å is excluded from the channel of ECUT-50a.

To attest its heterogeneity, a hot filtration experiment was carried out for 5h, however no further conversion of substrate was observed (Fig. S6). Moreover, **ECUT-50a**, as heterogeneous catalyst, can be readily isolated from the reaction system *via* filtration and further reused at least three times just with a little drop in activity (Fig. S7).





<sup>a</sup>Reactions were performed with 1mmol substrates and 1mmol cyanoethylacetate in 10 mL C<sub>2</sub>H<sub>5</sub>OH with 15 mg catalyst of **ECUT-50a** for 6 h at 60°C.

<sup>b</sup> The size of substrate was calculated as the longest distance of these molecules. <sup>c</sup> Pure isolated product from recrystallization is obtained and characterized by GC.

<sup>d</sup> No product from recrystallization is obtained.

Photoswitchable Catalysis. As we know, azobenzene derivates are an excellent photochromic candidate, due to its large geometrical change of E-Z photoisomerization and some unique merits, which is well realized in photoswitching catalysis of organic synthesis<sup>10-12</sup> or photomodulating host-guest behavior in MOFs.14 In this regard, we carried out photoswichting catalytic experiments and the results are shown in Fig. 2 and Table 2. For these selected aldehyde substrates, the conversion of salicylaldehyde under UV (365 nm) is completely rejected with only negligible conversion to product (<6% by GC, commonly referred as the OFF state), giving a significant decrease of more than 86.6%, relative to its high conversion (92.6%, commonly referred as the ON state) in the dark. The reaction with a third-order rate constant in the dark ( $k_{on}$ ) or UV ( $k_{off}$ ) is estimated to be 6.1×10<sup>-4</sup> mmol<sup>-1</sup> s<sup>-1</sup> and 1.5×10<sup>-6</sup> mmol<sup>-1</sup> s<sup>-1</sup>, respectively. Such observed 407fold (kon/koff) decrease in activity upon UV irradiation presents the highest value in the field of photoswitching catalysis<sup>8</sup> and suggested us that for salicylaldehyde substrate ECUT-50a catalyst is almost inactive under UV irradiation to execute the Knoevenagel condensation reaction. Significant decrease in activity under UV irradiation for other aldehyde substrates are also observed (2chlorobenzaldehyde, *k*<sub>on</sub>/*k*<sub>off</sub>=6.0; 2-nitrobenzaldehyde, *k*<sub>on</sub>/*k*<sub>off</sub>= 19.9; 4-fluorobenzaldehyde,  $k_{on}/k_{off}$ =43), however, where we also notice disparate photomodulation of the reaction kinetics that directly relates to the size of aldehyde substrates, suggesting photoswitching catalytic selectivity. Thus, the results suggest ECUT-50a as a superior catalyst

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for not only photoswitching catalytic activity but also photoswitching catalytic selectivity. DOI: 10.1039/C7TA01388D

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Table 2. The experimental results in the dark and UV (365		
nm) for these selected aldehyde substrates.		
Substrates <sup>a</sup>	Conversion	Reaction rate(mmol <sup>-1</sup> s
		<sup>1</sup> )
Un	dorte 02 60/	k 61×10-4
	UUK . 92.0%	$k_{on:} = 0.1 \times 10^{-6}$
🤇 🗡 сно	$\Delta^{d}$ : 86.6%	$k_{on}/k_{off}$ 407°
Salicylaldehyde		
	doute 96 10/	L 2.07.10-4
	UV·51.4%	$k_{on:} 2.97 \times 10^{-5}$
🤇 🎾 сно	Δ: 34.7%	$k_{off} = 4.97 \times 10$ $k_{off} = 6^{f}$
		-on oy
2-chlorobenzaldehyde		
NO <sub>2</sub>		
	dark: 92.4%	$k_{on:}$ 5.73×10 <sup>-4</sup>
СНО	UV:39.6%	$k_{off} = 2.88 \times 10^{-9}$
	Δ. 32.870	Kon/Koff: 19.9
2-nitrobenzaldehyde		
F——— СНО	dark: 78.4%	$k_{on:}$ 4.17×10 <sup>-4</sup>
$\mathbb{N}$	UV:18.5%	$k_{off:} 9.67 \times 10^{-6}$
4-fluorobenzaldehyde	Δ: 59.9%	$k_{on}/k_{off}$ 43 <sup>r</sup>

<sup>a</sup>Reactions were performed with 1mmol substrates and 1mmol cyanoethylacetate in 10 mL  $C_2H_5OH$  with 15 mg catalyst of **ECUT-50a** for 6 h at 60°C.

<sup>b</sup>Reactions are performed in the dark.

<sup>c</sup> Reactions are performed under UV (365nm).

<sup>d</sup> The difference for conversion of substrates in the dark and UV after reaction for 6h.

<sup>e</sup> Third-order rate constants, see Figure S8

f Second-order rate constants, see Figure S9-11.



Fig. 2 The photoswitching catalysis for these selected aldehyde substrates. a), b), c), d) presents the conversion of these selected aldehyde substrates in the dark or UV (365 nm). e) the difference in

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conversion in the dark or UV after 6 h for these selected aldehyde substrates.

The Mechanism of Catalysis and Size-Selectivity. To disclose the catalysis mechanism several appropriate control experiments were conducted. A homogeneous catalysis of the Knoevenagel condensation reaction between 2-nitrobenzaldehyde and cyanoethylacetate was carried out without catalyst or with the reagent of InCl<sub>3</sub> or H<sub>2</sub>AzDC, giving the conversion of 0%, 29.7%, and 73.8%, respectively (Fig. S12). These results demonstrate that such reaction is not spontaneous, but could be accelerated by both InCl<sub>3</sub> and H<sub>2</sub>AzDC, however, with their catalytic ability far less than the heterogeneous catalyst of **ECUT-50a** that shows the value of 92.4%. In this regard, the catalytic performance of **ECUT-50a** is mainly derived from  $AzDC^2$ - ligands located on its pore wall.

To better understand size-selectivity, both TG and IR characterizations were employed to trace the inclusion of aldehyde substrates inside MOFs. Fig. S13 clearly suggests that the large substrate of 4-biphenylcarboxaldehyde could not be accommodated inside ECUT-50a, whereas on the contrary, ECUT-50a affords considerable adsorption capacity towards the smaller reactants like that of 2-nitrobenzaldehyde (ca. 3 molecules per ECUT-50a) and salicylaldehyde (ca. 5 molecules per ECUT-50a). Infrared spectroscopy of the catalyst also presents the fail in infusing large substrate of 4biphenylcarboxaldehyde inside ECUT-50a, but the success in loading of small substrate of salicylaldehyde (Fig. S14). All the above evidences agree that the size of the open window is the key factor for ECUT-50a to recognize and distinguish these aldehyde substrates with various sizes, consequently leading to the high size selectivity when it is used to catalyze the Knoevenagel condensation reaction.

The Mechanism of Photoswitchable Catalysis. The photoactivity of ECUT-50a was initially evaluated by UV-Vis spectrum (Fig. S15), where a characteristic *E-Z* photoisomerization of  $AzDC^{2-}$  ligands under UV (365nm) irradiation is detected.<sup>14</sup> The photoresponse towards guest molecule was tested by CO<sub>2</sub> adsorption at 293K, where an adsorption capacity of 8.4 cm<sup>3</sup>/g is observed for ECUT-50a at 1 atm in the dark, whereas under UV (365 nm) its adsorption capacity decreases by 17% (Fig. S16). Similarly, its photoresponse towards salicylaldehyde is shown in Figure S13, where under UV(365 nm) ECUT-50a only adsorbs ca. 2.5 molecules *per* ECUT-50a, relative to the adsorption ability of ECUT-50a in the dark, suggesting a 50% decrease in adsorption of salicylaldehyde. The decrease in adsorption of guest molecule was obtained in the dark because of the near-complete conversion of the *cis* form to the *trans* form, consequently leading to the unique photoswitchable catalysis observed above.

H<sub>2</sub>AzDC<sup>2-</sup> ligands as photoswitching catalyst was also measured (Fig. S17), and significant decrease in conversion and catalysis activity of the condensation reaction between 2-nitrobenzaldehyde and cyanoethylacetate from 73.8% and  $k_{on}=1.3\times10^{-4}$  mmol<sup>-1</sup>s<sup>-1</sup> to 25.1% and  $k_{off}=1.2\times10^{-5}$  mmol<sup>-1</sup>s<sup>-1</sup> is observed, giving a 48.7% decrease in conversion and 8.3-fold ( $k_{on}/k_{off}$ ) decrease in catalysis activity. By contrast, **ECUT-50a** affords a 19.9-fold ( $k_{on}/k_{off}$ ) decrease in catalysis activity, almost 2.4 times bigger than that observed for only H<sub>2</sub>AzDC<sup>2-</sup> ligands, implying that the photoswitchable catalysis performed by **ECUT-50a** origins from *E-Z* photoisomerization of AzDC<sup>2-</sup> ligands, but incorporation of photoactivated AzDC<sup>2-</sup> ligands into MOF platform will largely enhance its photocontrol ability.



**Fig. 3.** DFT calculation of the potential of  $H_2AzDC^{2-}$  ligands in the *trans* or *cis*-conformation surrounded by benzaldehyde molecule.

Furthermore, we also carried out DFT calculation to correlate E-Z photoisomerization of AzDC<sup>2-</sup> ligands with photoswitching storage of guest molecules (Fig. 3). We found that each *trans*- H<sub>2</sub>AzDC holds the potential surrounded by four benzaldehyde molecules, whereas due to steric hindrance each *cis*-H<sub>2</sub>AzDC only accommodate three benzaldehyde molecules around it; this suggests that the storage capacity of guest molecules in **ECUT-50a** would be largely decreased if triggered by UV, consistent with the experimental results.

We also note that although the substrates of salicylaldehyde and 2-chlorobenzaldehyde own comparable size, however, their outcome in photoswitchable catalysis is very different. Thereby, the finally products were recrystallized and determination by single crystal X-ray diffraction (Fig. S18). All the aldehyde substrates, except for salicylaldehyde, undergo the Knoevenagel condensation reation with the formation of new carbon-carbon bonds of ~1.32Å, comparable with C=C double bond, and a Econfiguration. Surprisedly, the salicylaldehyde substrate generates an exceptional product, where both the Knoevenagel condensation and Michael addition reaction are observed, leading to the formation of two new carbon-carbon bonds (C2-C3/1.506(3)Å from the Knoevenagel condensation and C3-C10/1.558(3)Å from Michael addition), agreeing with the value of C-C single bond. The results indicate that to conversion of salicylaldehyde, relative to other aldehyde substrates, two-fold amount of salicylaldehyde are needed. In this regard, in conjunction with the TG results, the 50% decrease in loading salicylaldehyde within ECUT-50a under UV irradiation could not meet its conversion criterion, thus leading to the ultrahigh photocontrol in catalysis activity. To the best of our knowledge, the case of showing the coincidence of the Knoevenagel condensation and Michael addition reaction in a single system catalyzed by MOFs or COFs is never documented.

#### Conclusions

In summary, we have conveyed the concept upon MOF platform, for the first time, to control organic reaction by photoswiching catalysis in both catalysis activity and selectivity. The photosensitive H<sub>2</sub>AzDC ligand is the key factor to execute both catalysis and photoresponse performance, while MOF environment is also critical to enhance the catalysis, photoswitchable catalysis, and especially unique catalysis selectivity *via* confined space within the pores of MOF. The results present an excellent example of photoswitchable catalysis and may be transferred to other organic reactions, if with a

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precise molecule design in the pores of MOFs or selecting proper MOFs.

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## Photoswitching storage of guest molecules in metal-organic framework for

photoswitchable catalysis: exceptional product, ultrahigh photocontrol, and

## photomodulated size selectivity

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Photoswitching Catalysis Activity and Selectivity

We present a novel MOF catalyst, which not only offers ultrahigh photocontrol, but also displays disparate photomodulation in reaction kinetics towards various aldehyde substrates, thus creating the first example in MOFs showing photoswitchable catalysis.