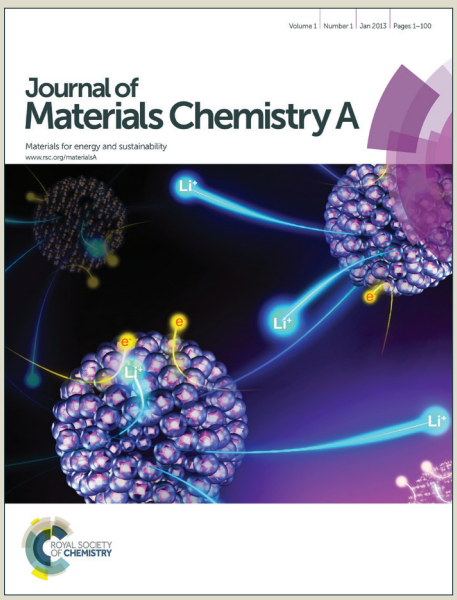
Journal of Materials Chemistry A

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsA

Urea Containing Metal–organic Frameworks as Heterogeneous Organocatalysts

Alireza Azhdari Tehrani,[‡a] Sedigheh Abedi,[‡a] Ali Morsali[*a], Jun Wang[b] and Peter C. Junk[b]

[a] Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

[b] College of Science Technology and Engineering, James Cook University, Townsville Qld, 4811, Australia

ABSTRACT:

Two novel pillared metal-organic frameworks (MOFs) including urea-functional groups are introduced. Herein, urea functional groups were incorporated into the MOF backbone by preparing urea-ditopic ligand. These frameworks (**TMU-1**8 and **TMU-19**) were fabricated using the synthesized urea-containing ligand, 4,4'-Bipyridine (bpy) and 1,2-Bis(4-pyridyl)ethane (bpe), respectively using zinc nitrate as metal source. Subsequently, **TMU-18** and **TMU-19** were characterized by X-ray diffraction, IR spectroscopy, elemental analysis, scanning electron microscopy (SEM) and thermogravimetric analysis. Furthermore, their potential talent as organocatalysts was evaluated in the regioselective methanolysis of epoxides.

Introduction

Supramolecular organocatalysis is an interdisciplinary research area that includes elements from organic chemistry, supramolecular chemistry and biochemistry.[1, 2] The design of a supramolecular catalyst is based on using hydrogen bonding and other intermolecular interactions in recognition and activation of substrates for triggering a variety of chemical transformations.[3, 4] However, supramolecular catalysis often suffer from drawbacks such as the lack of catalyst recycling and low efficiency due to the self-aggregation (self-quenching) of the catalyst.[3] The heterogenization of supramolecular organocatalysts may be a logical solution to overcome these obstacles in extending the applicability of these systems.[5-7] Recently, metal-organic frameworks (MOFs) were introduced as promising candidates for applications in diverse areas.[8-10] Compared to other porous materials, MOFs have given to the chemist the opportunity of tuning the topology, pore size and functionality by rational selection of the organic linkers and inorganic metal centers. Owing to this feature, MOFs with uniform and permeable pores and channels have shown to be particularly promising for catalysis.[11-14] According to the catalytic active sites, these frameworks may be categorized into four distinct groups, namely metal-organic frameworks with coordinatively unsaturated metal sites (group I), MOFs with metalloligands (group II), MOFs with functional organic sites (group III) and metal nanoparticles embedded in the MOF cavities (group IV). Among these, MOFs with catalytically-active functional organic sites have received less attention due to the synthetic complexities in providing guest-accessible functional organic groups in the pore surface of frameworks.[15] In this regard, different organic functional groups, such as proline, amide, binol and pyridyl were successfully incorporated into MOFs.[16] Recently, both Cr-MIL-101 and IRMOF-3 are decorated with activated urea and thiourea functions, respectively using post-synthesis modification

method.[17, 18] The appealing idea of preparing heterogeneous urea-based MOF catalysts was proposed recently by Farha, Hupp and Scheidt et al.[6] They have examined the catalytic activity of the urea-based MOF for the Friedel-Crafts reaction between pyrroles and nitroalkenes. In addition, although high conversion was obtained in the case of small substrates, the yield of the addition product was low (39%) at the optimum reaction condition. They could also successfully synthesize a Zr-based MOF containing urea function used for Morita–Baylis–Hillman reaction.[19] Therefore, designing such a catalytic system based on urea containing MOF is in the early stages and needs further work and development. Ring opening of epoxides is one of the most important reactions produced vital intermediates in organic synthesis. There are some reports for this reaction catalysed by MOF containing Lewis acid sites, especially with Cu, Fe and Hf metal nodes.[20-23] In this regards, there is no report of urea-containing MOFs as hydrogen-bond catalyst in this reaction.

In this paper, we report an extension of these studies aimed at investigating the organocatalytic role of urea-containing MOFs in the activation of epoxides. Our design is based on two following assumptions: (i) synthesis a ditopic oxygen-donor ligand containing a urea functional group, that are capable of forming dual hydrogen bonds with organic substrates. (ii) selection of an appropriate pillaring strut able to form MOFs with dinuclear paddle-wheel SBUs, in which five of the six coordination positions of each Zn(II) ion are anticipated to be occupied for network propagation and the sixth is located inside the zinc cluster. Accordingly, two novel urea-containing MOFs synthesized by combining the ditopic urea "strut", a pillaring strut, and $Zn(NO_3)_2.6H_2O$ using the solvothermal method at 90˚C for 120 h to give suitable X-ray quality crystals of $[Zn_2(ubl)_2(bipy)]\cdot DMF$ (**TMU-18**) and $[Zn_2(ubl)_2(bpe)]\cdot DMF$ (**TMU-19**), where ubl

(urea-based ligand) is 4,4'-(carbonylbis(azanediyl))dibenzoic acid, bipy and bpe are 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethane, respectively, Figure 1.

Experimental Section

Apparatus and Reagents

All starting materials, including 1,1'-Carbonyldiimidazole, 4-Aminobenzoic acid were purchased from commercial suppliers (Sigma-Aldrich, Merck) and used as received. The infrared spectra were recorded on a Nicolet Fourier Transform IR, Nicolet 100 spectrometer in the range 500-4000 cm^{-1} using the KBr disk technique. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using an ECS 4010 CHN made in Costech, Italy. Melting points were obtained by a Bamstead Electrothermal type 9200 melting point apparatus and corrected. Thermogravimetric analyses (TGA) of the compounds were performed on a computer-controlled PL-STA 1500 apparatus. The ^{1}H-NMR spectrum was recorded on a Bruker AC-250 MHz spectrometer at ambient temperature in d_6-DMSO and $CDCl_3$. X-ray powder diffraction (XRPD) measurements were performed using a Philips Xpert diffractometer with monochromated Cu-Kα radiation (λ = 1.54056 Å). The samples were also characterized by field emission scanning electron microscope (FE-SEM) SIGMA ZEISS and TESCAN MIRA (Czech) with gold coating.

Single-Crystal Diffraction.

X-ray crystal structure determinations: Crystals in viscous paraffin oil were mounted on cryoloops and intensity data were collected on the Australian Synchrotron MX1 beamline at 100 K with wavelength (λ = 0.71073 Å). The data were collected using the BlueIce[24] GUI and processed with the XDS[25] software package. The structures were solved by conventional methods and refined by full-matrix least-squares on all F^2 data using SHELX97[26] or SHELX2014

in conjunction with the X-Seed[27] or Olex2[28] graphical user interface. Anisotropic thermal parameters were refined for non-hydrogen atoms and hydrogen atoms were calculated and refined with a riding model.

Crystallographic data: TMU-18: $C_{83}H_{63}N_{13}O_{21}Zn_4$, M= 1839.94 g mol^{-1}, Triclinic, $P\bar{1}$, a= 21.179(4) Å, b= 22.560(5) Å, c= 23.138(5) Å, α= 105.30(3)˚, β= 114.19(3)˚, γ= 102.88(3)˚, V= 9013(4) Å^3, Z=2, ρ_{calc}= 0.678 g cm^{-3}, λ= 0.71073, T=100 K, R_1= 0.0688, wR_2= 0.1817, S= 0.897, ccdc=1041981; TMU-19: $C_{21}H_{16}N_3O_5Zn$, M= 455.74 g mol^{-1}, orthorhombic, *Pnna*, a= 21.035(4) Å, b= 16.064(3) Å, c= 29.891(6) Å, V= 10100(3) Å^3, Z=8, ρ_{calc}= 0.599 g cm^{-3}, λ= 0.71073, T=100 K, R_1= 0.0786, wR_2= 0.2428, S= 1.103, ccdc=1041982.

Synthesis of urea ditopic ligand.

The urea ditopic ligand was synthesized in three steps, starting from commercially available 4-aminobenzoic acid. Detailed synthetic procedures and characterization of the synthesized frameworks are provided in the experimental section and supporting information.

Synthesis and activation of TMU-18

$Zn(NO_3)_2.6H_2O$ (0.297 g, 1 mmol), 4,4'-(carbonylbis(azanediyl))dibenzoic acid (0.300 g, 1 mmol) and 4,4'-Bipyridine (0.078 g, 0.5 mmol) were dissolved in 20 mL DMF. The mixture was placed in teflon-lined stainless steel autoclaves and heated to 90 ˚C for 72 h and then it was gradually cooled to room temperature over 48 h. The crystals were obtained in a 72% yield. The products were characterized by different techniques such as powder X-ray diffraction (PXRD), IR spectroscopy, elemental analysis and SEM microscopy. (Before activation) FT-IR (KBr pellet, cm^{-1}): 3320 (br), 1657 (vs), 1604 (vs), 1530 (vs), 1398 (vs), 1308 (m), 1230 (m), 1171

(m), 856 (w), 779 (m), 626 (w), 500 (w). Anal. calcd for $ZnC_{23}H_{23}N_4O_7$: C, 51.84; H, 4.35; N: 10.51, Found: C, 49.96; H, 4.79, N: 10.85.

The sample was activated by immersing the crystals of **TMU-18** in anhydrous chloroform followed by heating at 80°C in vacuum for 24 h. The activation was also confirmed by PXRD and FT-IR spectroscopy.(after activation) FT-IR (KBr pellet, cm^{-1}): 3390 (br), 1604 (vs), 1532 (vs), 1400 (vs), 1308 (s), 1228 (m), 1172 (m), 856 (w), 779 (m), 628 (w), 500 (w). Anal. calcd for $ZnC_{20}H_{14}N_3O_5$: C, 54.38; H, 3.19; N: 9.51, Found: C, 54.12; H, 3.82, N: 9.94.

Synthesis and activation of TMU-19

$Zn(NO_3)_2.6H_2O$ (0.297 g, 1 mmol), 4,4'-(carbonylbis(azanediyl))dibenzoic acid (0.300 g, 1 mmol) and 1,2-Bis(4-pyridyl)ethane (0.092 g, 0.5 mmol) were dissolved in 20 mL DMF. The mixture was placed in teflon-lined stainless steel autoclaves and heated to 90 ˚C for 72 h and then it was gradually cooled to room temperature over 48 h. The crystals were obtained in a 60% yield. The products were characterized by different techniques such as powder X-ray diffraction (PXRD), IR spectroscopy, elemental analysis and SEM microscopy. (Before activation) FT-IR (KBr pellet, cm^{-1}): 3346 (br), 1655 (vs), 1605 (vs), 1532 (s), 1397 (s), 1308 (m), 1231 (m), 1172 (m), 855 (m), 780 (m), 622 (w), 500 (w). Anal. calcd for $ZnC_{24}H_{25}N_4O_7$: C, 52.71; H, 4.61; N: 10.25, Found: C, 50.99; H, 4.83, N: 11.05.

The sample was activated by exchanging the DMF molecules with chloroform and then evacuating at room temperature for 8 h. The FT-IR spectroscopy confirmed that some of the DMF molecules are removed from TMU-19, while the rest of them could be necessary to stabilize the MOF framework. (after activation) FT-IR (KBr pellet, cm^{-1}): 3346 (br), 1606 (vs),

1527 (s), 1391 (s), 1306 (m), 1227 (m), 1169 (m), 855 (m), 778 (m), 619 (w), 505 (w). Anal. calcd for $ZnC_{21}H_{16}N_3O_5$: C, 55.34; H, 3.54; N: 9.22, Found: C, 55.17; H, 3.88, N: 9.96.

Catalysis Experiments.

In a typical reaction, the urea-based MOFs (25 mg, ca. 0.05 mmol equiv of urea species) were added to a CH_3OH solution (3 mL) containing the epoxide substrate (0.2 mmol). The reaction mixture was stirred at 60℃ for the indicated times mentioned in Table 1 of the manuscript. After the required reaction time, the reaction mixture was cooled to room temperature and analysed by GC analysis using internal-standard method.

Catalyst Recycling.

The reusability of **TMU-18** and **TMU-19** was tested for the methanolysis of styrene oxide. After stirring for 40 h, the heterogeneous mixture was allowed to settle completely followed by decanting the supernatant liquid. The **TMU-18** and **TMU-19** catalysts were filtered off after 40 h reaction, washed with excess MeOH and respectively dried at 80℃ and under vacuum at room temperature. The recovered catalyst was then reused without further purification for the second run with fresh styrene oxide and methanol.

Typical Procedure for the Methanolysis of Styrene Oxide.

The prepared urea MOF (25 mg, ca. 0.05 mmol) catalysts is suspended in a MeOH (3 mL) solution of styrene oxide (25 mg, 2 mmol) and stirred at 60℃ for 140 h. Then, the solid catalyst was filtered off. The reaction mixture was analyzed using gas chromatography. Then excess of solvent was removed under reduced pressure to give the corresponding product. The major product (2-Methoxy-2-phenylethanol) is determined by NMR. ^{1}HNMR (250 MHz, CDCl3):

7.26-7.39 (m, Ph, 5H), 4.3 (dd, J = 3.74, 8.1 Hz, 1H), 3.58-3.72 (m, CH2OH, 2H), 3.31 (s, OMe, 3H), 2.91 (bs, OH, 1H).

Typical Procedure for the Methanolysis of other Epoxides.

The prepared urea MOF catalysts is suspended in a MeOH (3 mL) solution of epoxide (25 mg) and stirred at 60℃ for 110 h. Then, the solid catalyst was filtered off. Determination of the major product was performed based on an internal-standard method. All standards samples for determination of the major products in the reaction mixture were prepared using the separated methanolysis reactions of the epoxides in the presence of catalytic amount of HCl. Since the prominent product in this acidic condition is the adduct owing to steric reasons, their retention time for GC analysis was revealed in this manner. For this reaction, 2 drop of the concentrated HCl was added to the solution of epoxides (2 mmol) and MeOH (5 ml). The reaction solution was stirred at 60℃ for 1 h. The progress of the reaction was monitored using GC analysis.

Results and Discussion

Structural analysis and characterization

TMU-18 and **TMU-19** were synthesized by combining the ditopic urea ligand, a pillaring strut, and $Zn(NO_3)_2.6H_2O$ using the solvothermal method at 90˚C for 120 h to give suitable X-ray quality crystals. X-ray crystallography analyses reveal that TMU**-18** and **TMU-19** crystallize in triclinic *P*$\bar{1}$ and orthorhombic *Pnna*, respectively. In these compounds, the coordination geometry around the Zn(II) can be described as distorted octahedral, with four sites occupied by oxygen atoms of four different urea ligand carboxylate groups in an approximately square configuration and the fifth site occupied by a nitrogen atom of bipy/bpe ligand (Figure 2a and 2d). The remaining coordination site of each metal center is located inside the zinc paddle-wheel cluster.

The Zn-Zn distances are 2.930(1) and 2.9319(7) Å for **TMU-18** and **TMU-19**, respectively. Both compounds are composed of paddle-wheel dinuclear zinc carboxylate clusters ($Zn_2(COO)_4$) bridged by the urea struts to form a two dimensional square grid. The 2D square grids are further linked to each other by pillaring bipy/bpe forming a 3D framework which can be described a doubly-interpenetrated **pcu** network, Figure 2. Both compounds possess large channels (along the *bc*-plane with aperture size of 13.5 × 9.9, for **TMU-18** and along the *b*-axis with aperture size of 12.1 × 10.6 Å for **TMU-19**, including van der Waals radii of the atoms), Figures 2(c) and 2(f). Also, the calculated void space per unit cell for disorder- and guest-free **TMU-18** and **TMU-19** frameworks are 66.3% (5977.6 $Å^3$) and 69.6% (7034.1 $Å^3$), respectively.[29] X-ray crystallography analysis reveals that the N-H groups of **TMU-18** are involved in N-H•••O hydrogen bonding interactions with the oxygen atom of the *N,N*-dimethylformamide (DMF) molecule. In the case of **TMU-19**, the DMF molecule cannot be located in the electron-density map, due to the severe disorder and therefore was squeezed out with the help of PLATON squeeze.[29] However, spectroscopic analyses suggest that **TMU-18** and **TMU-19** may have similar chemical compositions.

Thermogravimetric analysis (TGA) indicates that **TMU-18** has a much better thermal stability compared to **TMU-19**. The TGA data of **TMU-18** shows an initial weight loss (4%, after heating to 120˚C) which is attributed to the loosely bound water molecule. The other weight loss occurred between 120 and 200˚C (13%) corresponding to the removal of DMF. In contrast to **TMU-18**, TGA analysis of **TMU-19**, indicates a large mass loss in two steps in the range of 30 to 260˚C, indicating its low thermal stability. Thus, in order to activate the potential catalytic sites of **TMU-18**, the crystals were immersed in anhydrous chloroform for 72 h, filtered and vacuum-dried at 80˚C for 24 h. The activation was confirmed by FT-IR spectroscopy and PXRD

analysis (see the ESI). An attempt to activate **TMU-19** by the same procedure was unsuccessful probably due to the low thermal stability of this compound at elevated temperatures. Accordingly, this compound was activated by exchanging the DMF molecules with chloroform and then evacuating at room temperature for 8 h. The FT-IR spectroscopy confirmed that some of the DMF molecules are removed from **TMU-19**, while the rest of them may be necessary to stabilize the MOF framework.

Catalytic studies of TMU-18 and TMU-19

The ring-opening reaction of epoxides, by alcoholic compounds known as "alcoholysis", was chosen as a probe to study the catalytic activity of the synthesized urea-containing MOFs. The alcoholysis reaction of epoxides is facile providing 1,2-bifunctional compounds such as 1,2-diols, β-amino alcohols and other interesting compounds for the pharmaceutical and agrochemical points of view.[30, 31] Actually, the activation of the oxygen atom of the epoxides is catalytically performed using either Lewis or Brønsted acids. Methanolysis of epoxides which was traditionally attained using corrosive sulfuric acid,[32] has been widely investigated in heterogeneous catalytic systems including polymers and silica-based materials.[33, 34] In recent years, some noteworthy attempts for the methanolysis reaction using MOFs has been reported, in which the epoxide activation is mostly achieved by the function of metal Lewis acidity centers within the MOF structures.[20, 22, 23] Generally, the coordination talent of the solvent typically MeOH either acts as a nucleophile on the one side, and the requisite free metal center sites within the MOF catalyst, on the other side led to the weak structural stability of these kinds of catalysts even those provided excellent catalytic activity and selectivity.[35] Therefore, incorporating the linkers containing Brønsted acids[36] or hydrogen-bond donating (HBD) moieties upon a MOF

structure which involves locked metal centers such as paddle-wheel nodes can hopefully provide a MOF catalytic system that would be durable even for recycling purposes. According to the only valuable report presented by Hupp and coworkers, incorporating a urea strut within MOF structures can significantly enhance is HBD ability preventing the intrinsic unproductive self-quenching behavior of the urea units.[6]

Regarding to the above synthesized urea-containing MOFs of **TMU-18** and **TMU-19**, we subsequently examined their potential as organocatalyst for methanolysis reaction of epoxides. The ring opening of the styrene oxide in MeOH as a probe reaction was selected to explore the reaction conditions. No methanolysis reaction proceeded at room temperature. Moreover, in the presence of mixed solvent systems including toluene, CH_2Cl_2, $CHCl_3$, THF and CH_3CN in combination with MeOH (1:1 ratio), no additional product was observed during 48 h reaction with styrene oxide. The alcoholysis reaction in the presence of 25 mg (0.05 mmol) of these urea-based MOFs and net MeOH as solvent gave 5% conversion as obtained by GC. However, in the absence of catalyst, when the reaction temperature was increased to 60℃, during 24 and 110 h, the reaction proceeded with 14 and 19% conversions (Table 1, entries 1 and 2) while within 24 h, in the presence of **TMU-18** and **TMU-19**, 35 and 31% of styrene oxide was converted, respectively (entry 4). This observation clearly revealed the catalytic effect of the prepared urea-containing MOFs. In addition, the same reaction runs were carried out for optimization of the catalyst and also solvent amounts. During the survey of the reaction conditions in the presence of 25 mg of the styrene oxide, the best results were obtained by using 25 mg of the catalysts (~25 mol%, indicated by ICP analysis) and at 60 ˚C in 3 ml of MeOH. Through the optimized reaction conditions 45 and 41% of the corresponding products were respectively formed after 40 h (entry 6). It is noteworthy to mention that 15% of methanolysis reaction took place in the presence of

40 mol% of urea powder as catalyst, in a homogeneous system (entry 3). It should be noted that using the original urea-containing ligand could not be appropriate in the control reaction. In this case, the reaction proceeds through the role of this two carboxylic acid groups over the urea species. Considering the paddle-wheel nodes established by X-ray analysis, in these urea-based heterogeneous catalytic systems the self-quenching phenomena raised from aggregation of urea molecules in homogeneous systems has been suppressed through accommodation into MOF structures. Further investigation of heterogeneous character of the catalytic system as well as stability of the structures was carried out using a hot filtration test in addition to ICP analysis. After 40 h of the methanolysis reaction of the styrene oxide, the reaction mixtures were centrifuged and the catalysts were filtered off. Then, the supernatant of methanolic liquids were left stirred at 60℃. Interestingly, within 40 h of further reaction time, no distinguishable changes were recognized in the reaction conversion using GC analysis.

Moreover, in other sets of the same reactions, the catalysts were filtered off after 40 h, washed thoroughly with MeOH and subsequently the filtrates were examined by ICP analysis. 0.13 and 0.19% of residual zinc was identified respectively which significantly confirmed more than 99% of the zinc metal center do not leach into reaction mixture during the methanolysis conditions. Not only all of these observations confirm reliable chemical stability of the prepared MOFs, but also they reject the Lewis acid catalytic role of metal species for epoxide activation. Finally, these observations may confirm the HBD character of the urea moieties through the MOF structure.

The productivity of both catalysts was evaluated by determination of the reaction selectivity for the conversion of styrene oxide to 2-methoxy-2-phenylethanol as the major product in our catalytic system. As Table 1 shows, after 40 h reaction time, 95% selectivity was calculated for

the mentioned major product (entry 6). When the reactions prolonged to 140 h, with **TMU-18**, quantitative conversion of styrene oxide was obtained with 98% selectivity for the 2-methoxy-2-phenylethanol that was characterized by GC and NMR (ESI). During the same time 95% conversion with 98% selectivity was achieved in the presence of **TMU-19** catalyst (entry 7).

The observed catalytic activity as well regioselectivity achieved in methanolysis of styrene oxide encouraged us to examine other epoxides in the reaction. The reaction of three epoxides including γ-phenoxypropylene oxide, allyl(2,3-epoxypropyl)oxide and cyclohexene oxide were screened with both catalysts using the same optimum reaction conditions (Table 1, entries 10-18). However, the reactivity changed in methanolysis of these less reactive substrates especially cyclohexene oxide and the corresponding products which were formed with relatively moderate yield and regioselectivity, even in the presence of twice the amount of the catalysts (entries 12, 15 and 18). Actually, increasing the amount of catalyst, in the case of styrene oxide, did not lead to doubling of catalytic activity (entry 9) and a little improvement was observed (110 h vs. 140 h for completion the reaction). Although more detailed studies need to identify the real cause of this issue, this may be explained by engaging or hiding of some urea functional groups within the complexities of the bulk matrix of the framework. We also checked the reaction with a bulky substrate, *t*-butyl styrene oxide, to clarify the catalysis occurred within the pores of the frameworks. As tabulated in Table 1 (entry 19), the methanolysis of *t*-butyl styrene oxide proceeded negligibly even after 140 h.

In order to further investigate the comparison of the catalytic performance of these heterogeneous urea catalytic systems, the time-conversion for both catalysts were plotted and compared with the control methanolysis reaction of styrene oxide, Figure 3. Although both catalyst systems are carried out with significant diversity relative to the control reaction and

moderately implement the reaction within 140 h, the **TMU-18** catalyst shows somewhat higher activity than **TMU-19** catalyst. The comparison of the PXRD diffraction peaks of the catalysts upon activation, represented in Figure S1(ESI), indicates little change occurred in the **TMU-19** structure. Accompanied with the lower thermal stability of **TMU-19** indicated by TG analysis, these results demonstrate higher catalytic performance of the **TMU-18** compared to **TMU-19** thereafter it was also confirmed through the recycling experiment.

Moreover, to evaluate durability and the catalyst recycling ability, **TMU-18** and **TMU-19** catalysts were filtered off after 40 h reaction, washed with excess MeOH and dried at 80℃ and under vacuum at room temperature, respectively. Methanolysis reaction of styrene oxide with these recovered catalysts proceeded with more diminished catalytic reactivity in the case of **TMU-19** structure (Table 1, entry 8). In addition, the comparison of the PXRD patterns of these catalysts clearly show that a decrease in crystallinity occurred in both recovered catalyst structures (ESI). As shown in Figure S1 (ESI), the prominent changes of the **TMU-19** structure takes place after its activation, while activated **TMU-18** structure has more similar PXRD to the simulated pattern. Considering the instability observed after extraction of entire DMF molecules in **TMU-19**, these data confirm the foundation role of the solvent molecules in preserving the whole skeleton. Although the solvent exchange with the epoxide molecules propels the methanolysis reaction, it seems that remaining DMF within the pores slightly suppresses the orgaocatalytic activity of this structure.

The foundation role of the solvent within the pores was additionally proved for both MOFs by immersing them in deionized water. The catalysts were removed after 48 h, washed with $CHCl_3$ and subsequently the aliquots were monitored using GC. Interestingly no segregated residues of the organic pillars were detected for both samples. Furthermore, preserving of the PXRD

patterns of these two water treatment samples along with their PXRD patterns after 140 h of methanolysis reaction of styrene oxide (Figure S2) explicitly reveals the aforementioned effect. In addition, this data may show the genuine heterogeneous character and actual chemical stability in the reaction.

Conclusion

Two new pillared metal-organic frameworks containing urea functional groups were synthesized aiming at their application as heterogeneous organocataysts. Structural analysis revealed that both **TMU-18** and **TMU-19** could be described as doubly-interpenetrated **pcu** network. These frameworks were characterized by different techniques and were further utilized as organocatalyst in the methanolysis of epoxides. Compared with the previous report,[6] in which the number of electron withdrawing carboxyl groups per urea units is doubled, the results of the methanolysis reaction indicate that **TMU-18** and **TMU-19** have weaker hydrogen bond donating ability, while they are more chemically stable MOF structures. In addition, the elucidation of additional structural features of these organocatalysts to design more active urea-based MOFs structures is an ongoing project in our laboratory and needs further work and refinement.

ASSOCIATED CONTENT

Supporting Information.
Experimental, details, PXRD patterns, TGA, IR spectroscopy, SEM images "This material is available free of charge via the Internet at http://pubs.acs.org."

AUTHOR INFORMATION

Corresponding Author

*Phone: +98-21-82884416. Fax:+98-21-82884416. E-mail: Morsali_a@modares.ac.ir (A. Morsali)

Author Contributions

‡These authors contributed equally.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was funded by Iran National Science Foundation (INSF) (grant number: 92024961), Iran Nano technology Initiative Council (INIC) and Tarbiat Modares University.

REFERENCES

1. P. M. Pihko, *Hydrogen bonding in organic synthesis*, Wiley-VCH, Weinheim, 2009.
2. D. W. MacMillan, *Nature*, 2008, **455**, 304-308.
3. M. Raynal, P. Ballester, A. Vidal-Ferran and P. W. N. M. van Leeuwen, *Chem. Soc. Rev.*, 2014, **43**, 1660-1733.
4. Z. Zhang and P. R. Schreiner, *Chemical Society Reviews*, 2009, **38**, 1187-1198.
5. A. Zamboulis, N. Moitra, J. J. Moreau, X. Cattoën and M. W. C. Man, *J. Mater. Chem.*, 2010, **20**, 9322-9338.
6. J. M. Roberts, B. M. Fini, A. A. Sarjeant, O. K. Farha, J. T. Hupp and K. A. Scheidt, *Journal of the American Chemical Society*, 2012, **134**, 3334-3337.
7. I. Fechete, Y. Wang and J. C. Védrine, *Catalysis Today*, 2012, **189**, 2-27.
8. S. Abedi and A. Morsali, *ACS Catalysis*, 2014, **4**, 1398-1403.
9. L. R. MacGillivray, *Metal-organic frameworks: design and application*, Wiley, Hoboken, N.J, 2010.
10. S. Abedi and A. Morsali, *New J. Chem.*, 2015.
11. T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chemical Reviews*, 2012, **113**, 734-777.

12. A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev. (Washington, DC, U. S.)*, 2010, **110**, 4606-4655.
13. J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chemical Society Reviews*, 2009, **38**, 1450-1459.
14. R. J. Kuppler, D. J. Timmons, Q.-R. Fang, J.-R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang and H.-C. Zhou, *Coordination Chemistry Reviews*, 2009, **253**, 3042-3066.
15. C. M. McGuirk, M. J. Katz, C. L. Stern, A. A. Sarjeant, J. T. Hupp, O. K. Farha and C. A. Mirkin, *Journal of the American Chemical Society*, 2015, **137**, 919-925.
16. J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011-6061.
17. X.-W. Dong, T. Liu, Y.-Z. Hu, X.-Y. Liu and C.-M. Che, *Chem. Commun.*, 2013, **49**, 7681-7683.
18. Y. Luan, N. Zheng, Y. Qi, J. Tang and G. Wang, *Catalysis Science & Technology*, 2014, **4**, 925-929.
19. P. W. Siu, Z. J. Brown, O. K. Farha, J. T. Hupp and K. A. Scheidt, *Chem Commun*, 2013, **49**, 10920-10922.
20. A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *Chemistry – A European Journal*, 2010, **16**, 8530-8536.
21. K. Tanaka, K.-i. Otani, T. Murase, S. Nishihote and Z. Urbanczyk-Lipkowska, *B Chem Soc Jpn*, 2012, **85**, 709-714.
22. D. Jiang, A. Urakawa, M. Yulikov, T. Mallat, G. Jeschke and A. Baiker, *Chem-Eur J*, 2009, **15**, 12255-12262.
23. M. H. Beyzavi, R. C. Klet, S. Tussupbayev, J. Borycz, N. A. Vermeulen, C. J. Cramer, J. F. Stoddart, J. T. Hupp and O. K. Farha, *J Am Chem Soc*, 2014, **136**, 15861-15864.
24. T. M. McPhillips, S. E. McPhillips, H.-J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter and R. P. Phizackerley, *Synchrotron Radiation*, 2002, **9**, 401-406.
25. W. Kabsch, *Journal of applied crystallography*, 1993, **26**, 795-800.
26. G. Sheldrick, University of Göttingen, Germany, 1997.
27. L. J. Barbour, *Journal of Supramolecular Chemistry*, 2001, **1**, 189-191.
28. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, *Journal of applied crystallography*, 2009, **42**, 339-341.
29. A. Spek, *Acta Crystallographica Section D*, 2009, **65**, 148-155.
30. D. Jiang, T. Mallat, F. Krumeich and A. Baiker, *Journal of Catalysis*, 2008, **257**, 390-395.
31. K. Tanaka, S. Oda and M. Shiro, *Chem. Chommun.*, 2008, 820-822.
32. W. Reeve and I. Christoffel, *J. Am. Chem. Soc.*, 1950, **72**, 1480-1483.
33. G. A. Olah, A. P. Fung and D. Meidar, *Synthesis*, 1981, **1981**, 280-282.
34. P. Salehi, M. Dabiri, A. Zolfigol and A. B. Fard, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 2004, **179**, 1113-1121.
35. P. Garcia-Garcia, M. Muller and A. Corma, *Chem. Sci.*, 2014, **5**, 2979-3007.
36. S. J. Garibay, Z. Wang and S. M. Cohen, *Inorg. Chem.*, 2010, **49**, 8086-8091.

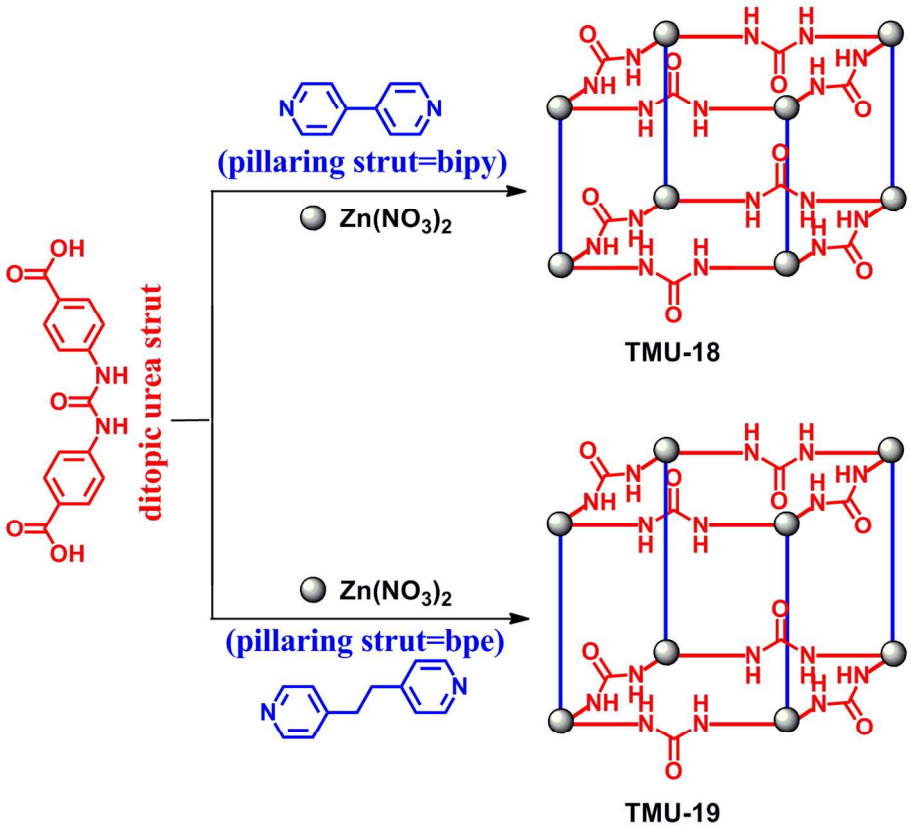


Figure 1. Synthesis of **TMU-18** and **TMU-19** from urea containing dicarboxylate ligand and bipy/bpe as pillar ligand.

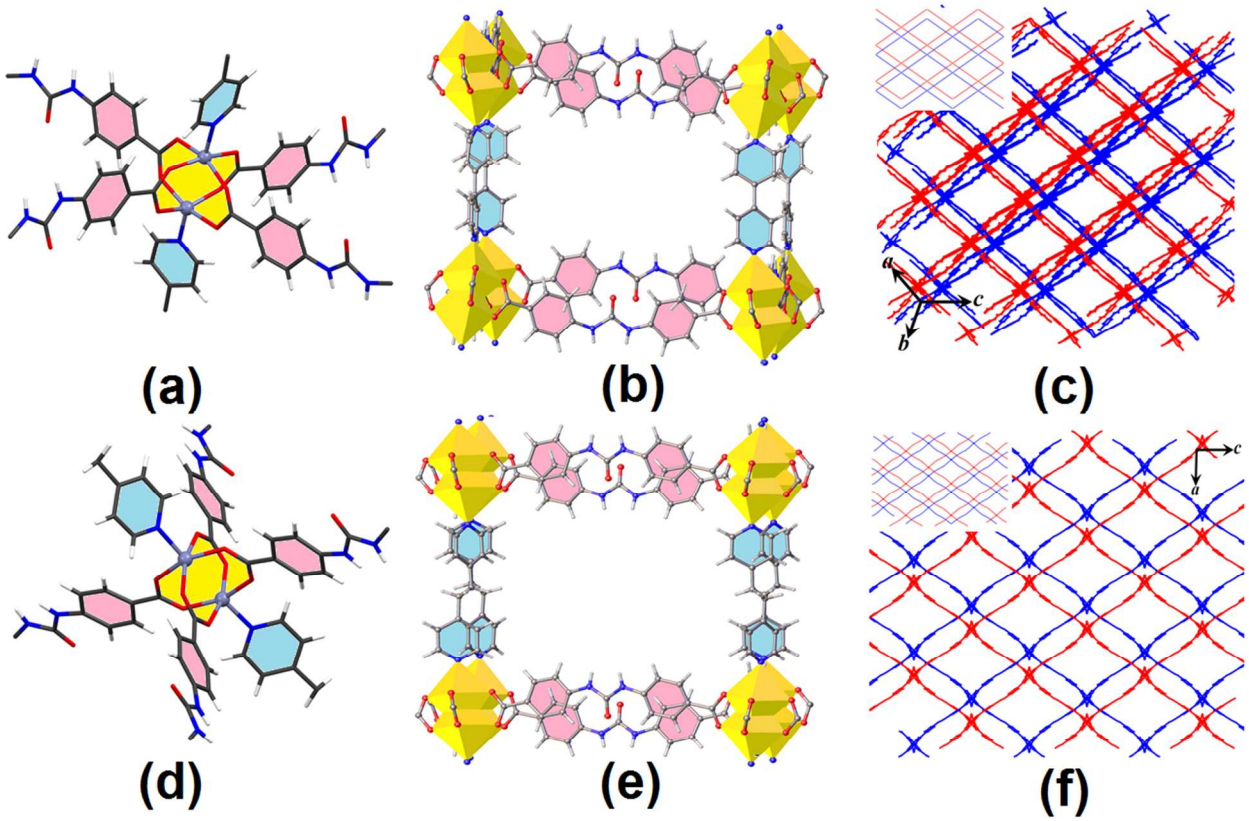


Figure 2. Paddle-wheel dinuclear zinc carboxylate clusters (a) and (d), Representation of the cubic structure (b) and (d) and a view along the pore direction (c) and (f). The two interpenetrating frameworks are shown in red and blue. All guest molecules were omitted for clarity. The left top insert illustrates the simplified interpenetration in **TMU-18** and **TMU-19**, respectively.

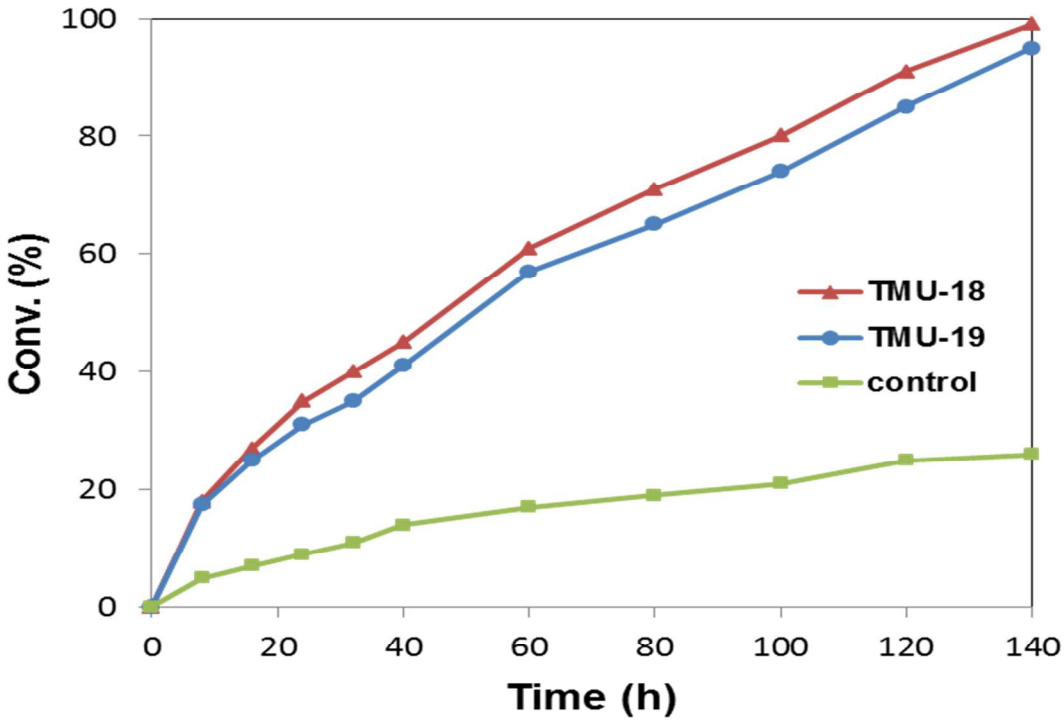
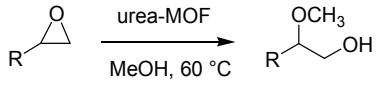
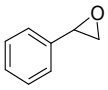
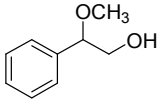
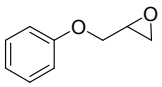
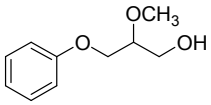
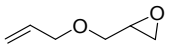
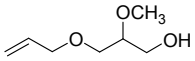
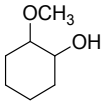
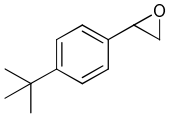
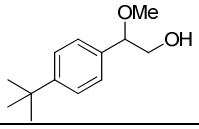


Figure 3. Comparison of time conversion plot for methanolysis of styrene oxide catalyzed by **TMU-18**, **TMU-19** and the reaction control system. Conditions: styrene oxide (25 mg, 0.2 mmol), catalyst (25 mg, 0.05 mmol of urea moiety), 60℃, methanol (3 mL); reaction control (without catalyst)

Table 1. Methanolysis of epoxides by urea-containing MOFs



Entry	Substrate	Major Product	Time [h]	Conversion [%][a] TMU-18	Conversion [%][a] TMU-19
1			24[b]	14	
2			110[b]	19	
3			24[c]	15	
4			24	35	31
5			40	45 (95)[f]	41 (95)
6			110	78 (96)	72 (97)
7			140	100 (98)	95 (98)
8			40[d]	39 (95)	29 (94)
9			110[e]	100 (98)	100 (98)
10			110[b]	22	
11			55	40	33
12			110[e]	78 (96)	67 (91)
13			110[b]	26	
14			55	37	35
15			110[e]	64 (81)	53 (77)
16			110[b]	16	
17			55	34	19
18			110[e]	51 (78)	48 (72)
19			40	<5	<5
			140	9	6

[a] GC yield using internal-standard method; Conditions: styrene oxide (25 mg, 0.2 mmol), catalyst (25 mg, 0.05 mmol of urea moiety, ~ 25 mol%), 60°C, methanol (3 mL). [b] reaction control (without catalyst). [c] with 40 mol% urea in homogeneous system. [d] with recycled catalysts. [e] with 50 mg (0.1 mmol) of the catalysts. [f] The data in parenthesis are the selectivity calculated for the major product.

Table of contents

Urea Containing Metal–organic Frameworks as Heterogeneous Organocatalysts

Two novel pillared MOFs including urea-functional group are introduced and their talent as organocatalysts were evaluated in methanolysis of epoxides.