Electronic Supplementary Information (ESI) For

Microwave-Assisted Synthesis of Urea-Containing Zirconium Metal-Organic Framework for Heterogeneous Catalysis of Henry Reactions

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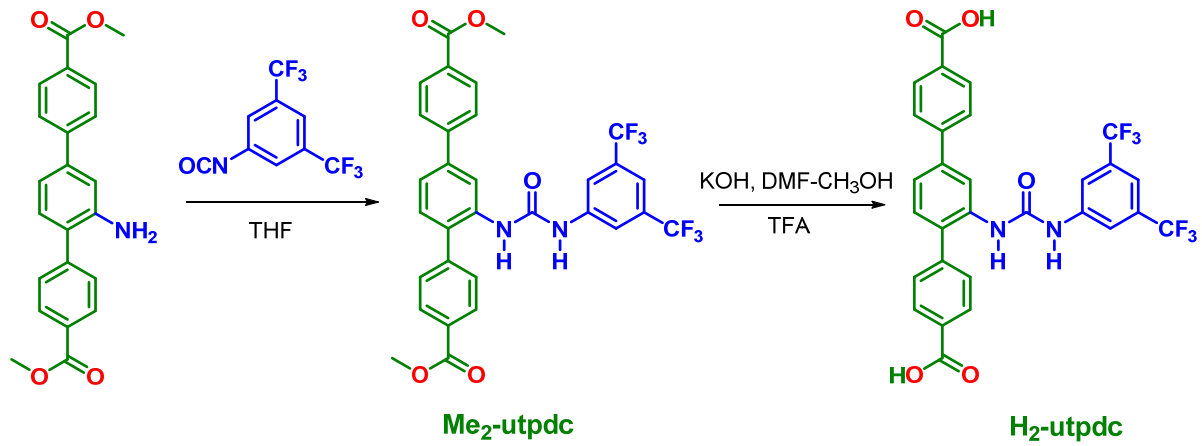
General method and materials

Unless specifically mentioned, all chemicals are commercially available and were used as received. The compounds dimethyl 2'-amino-[1,1':4',1"-terphenyl]-4,4"-dicarboxylate and 2',5'-dimethyl-[1,1':4',1"-terphenyl]-4,4"-dicarboxylic acid were prepared according to our previous papers.[S1,S2] Microwave irradiation was carried out with Initiator 2.5 Microwave Synthesizers from Biotage, Uppsala, Sweden. The reaction temperatures were measured by infrared detector during microwave heating. NMR spectra were taken on a Bruker AV400 at room temperature. The powder X-ray diffraction (PXRD) measurements were taken on a Bruker D8 diffractometer using Cu-K_α radiation (λ = 1.5418 Å) at room temperature. Field-emission scanning electron microscopy (FE-SEM) images were obtained on a HITACHI S-8010 instrument operating at 10 kV. Low-pressure gas sorption measurements were performed by using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with the extra-high pure gases. The as-prepared MOF (~45 mg) was immersed in ethanol (10 mL) for 2 day, during which time fresh ethanol was replaced six times. The sample was then moved into a sample cell and dried under vacuum at 80 °C and 120 °C by using the "out-gasser" function of the machine for 3 h and 12 h before the measurement, respectively. Brunauer-Emmett-Teller (BET) surface area and pore size distribution were calculated from the N_2 sorption isotherms at 77 K based on Non-Local Density Functional Theory (NL-DFT) model in the Quantachrome ASiQwin 2.01 software package. *Digestion of MOF*: Approximately 10 mg activated MOF samples were digested under sonication in 1 mL DMSO and 10 µl HF aqueous solution. After that, water was added to the resulting solution until no further precipitate was detected. The precipitate was collected by centrifugation, washed with and dried in vacuum.

Synthesis and Characterizations

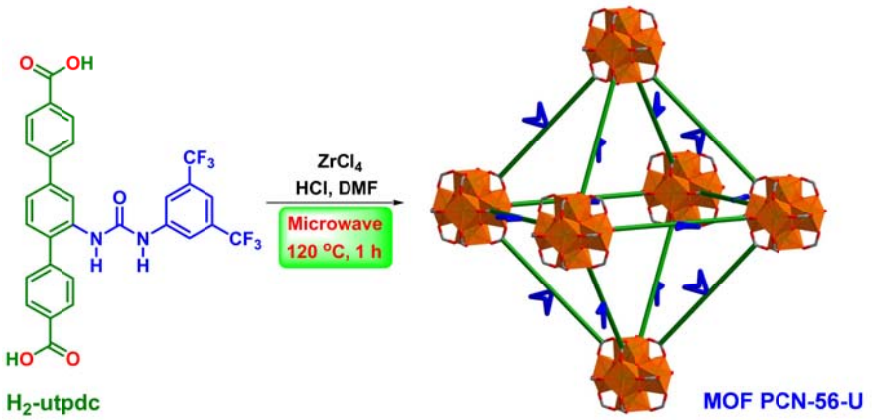


Scheme S1 The synthetic route for **H_2-utpdc**.

Compound Me_2-utpdc: Dimethyl 2'-amino-[1,1':4',1"-terphenyl]-4,4"-dicarboxylate (0.50 g, 1.38 mmol) in 60 mL THF at 0 ^oC was added 3,5-bis(trifluoromethyl)phenyl isocyanate (0.36 ml, 2 mmol). The reaction was slowly warmed up to room temperature and stirred overnight. The mixture was concentrated under reduced pressure, washed with Et_2O and dried under high vacuum to yield a white solid (0.70 g, 1.19 mmol, yield: 86%). ^1H NMR (400 MHz, d_6-DMSO) δ 9.63 (s, 1H), 8.25 (d, J = 1.8 Hz, 1H), 8.16 (s, 1H), 8.11 – 8.05 (m, 4H), 8.01 (s, 2H), 7.90 – 7.86 (m, 2H), 7.66 – 7.60 (m, 4H), 7.45 (d, J = 8.0 Hz, 1H), 3.89 (d, J = 1.3 Hz, 6H).

Ligand H_2-utpdc: To a 10 mL DMF solution of the precursor methyl ester **M_2-utpdc** (0.50 g, 0.8 mmol) was added KOH (0.66 g, 12 mmol) in 5 mL MeOH, this reaction mixture was heated for 1 h at 80 ^oC. After cooling to room temperature, 2 mL TFA was added into the solution. The resulting precipitate was isolated by filtration and washed with water, MeOH and dried under vacuum (0.41 g, 0.70 mmol, yield: 87%). ^1H NMR (400 MHz, d_6-DMSO) δ 12.99 (br, 2H), 9.67 (s, 1H), 8.26 (s, 1H), 8.13 (s, 1H), 8.09 – 8.00 (m, 6H), 7.85 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.1 Hz, 4H), 7.44 (d, J = 8.0 Hz, 1H).

Preparation for MOF PCN-56-U: Organic ligand H_2-utpdc (46 mg, 0.078 mmol) and $ZrCl_4$ (20 mg, 0.085 mmol) were dissolved in DMF (5 mL), which was added into a 20 ml Pyrex vial. Then, concentrated HCl (0.5 mL) was added to the Pyrex vial and the reaction mixture was heated at 120 ^oC for 1 h under microwave condition. After cooling to room temperature, the product was separated by centrifugal to afford the white solid, which was washed with DMF (10 mL x 3) and EtOH (10 mL x 3), respectively. The sample was dried in vacuum. The powder XRD pattern of product was very broad (Fig. S1), suggesting its poor crystalline. The main peaks in XRD pattern of MOF PCN-56-U are still matches the simulated one from UiO-68, confirming its UiO-68 framework.



Scheme S2 Preparation for pure strut MOF PCN-56-U only containing organic linker H_2-utpdc.

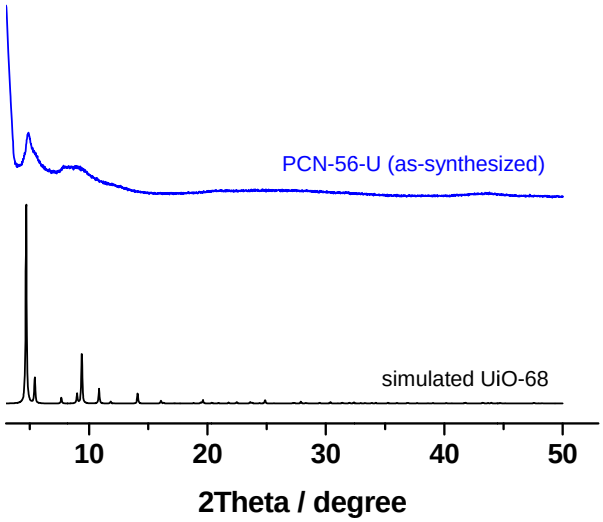
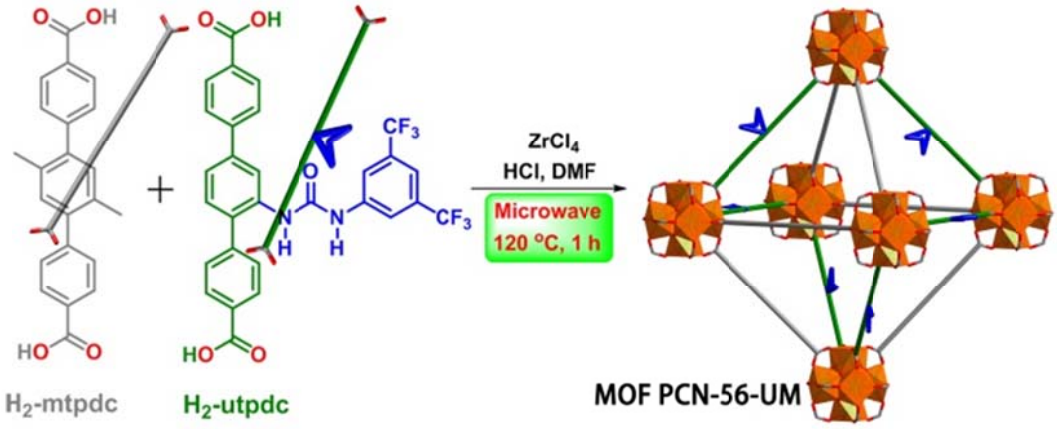


Fig. S1 Powder XRD pattern of MOF PCN-56-U.

Preparation for MOF PCN-56-UM: Organic struts H_2-mtpdc (12 mg, 0.035 mmol), H_2-utpdc (21 mg, 0.035 mmol) and $ZrCl_4$ (20 mg, 0.085 mmol) were dissolved in DMF (5 mL), which was added into a 20 ml Pyrex vial. Then, concentrated HCl (0.5 mL) was added to the Pyrex vial and the reaction mixture was heated at 120 ^oC for 1 h under microwave condition. After cooling to room temperature, the product was separated by centrifugal to afford the white solid, which was washed with DMF (10 mL x 3) and EtOH (10 mL x 3), respectively. The sample was dried in vacuum. The powder XRD pattern of product was similar to the simulated pattern generated from crystal data of MOF UiO-68 (Fig. S2), confirming its UiO-68 topological framework and the phase purity. The molar ratio of H_2-utpdc to H_2-mtpdc in MOF PCN-56-UM was determined to be ~1:1.1 (Fig. S3).



Scheme S3 Rapid preparation for the mixed strut MOF PCN-56-UM with TPDC linkers of H_2-mtpdc and H_2-utpdc *via* a microwave method.

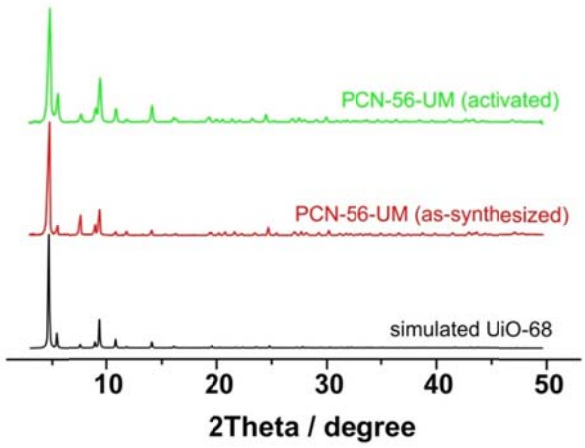


Fig. S2 Powder XRD pattern of MOF PCN-56-UM, indicating the framework was retained after the activation process.

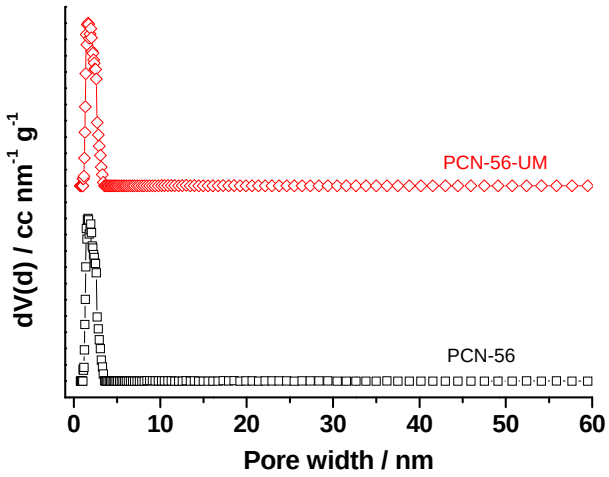


Fig. S3 Pore size distribution plot of PCN-56 and PCN-56-UM calculated from experimental N_2 adsorption isotherm using the nonlocal density functional theory.

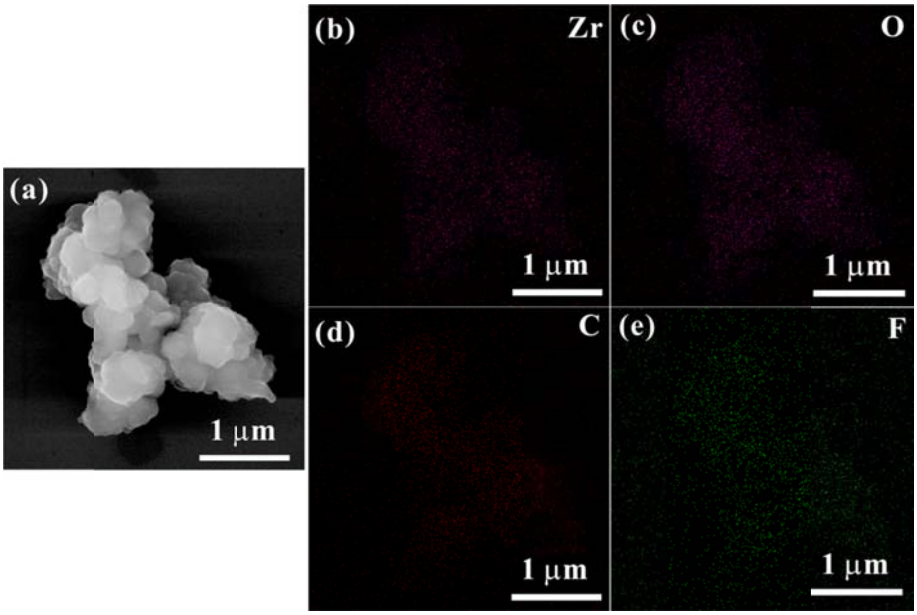


Fig. S4 SEM image for MOF PCN-56-UM and its elemental mapping images; the distribution of fluorine element from H_2-uptdc ligand matches well with other elements, suggesting the single phase instead of mere physical mixtures of separated PCN-56 and PCN-56-U phases.

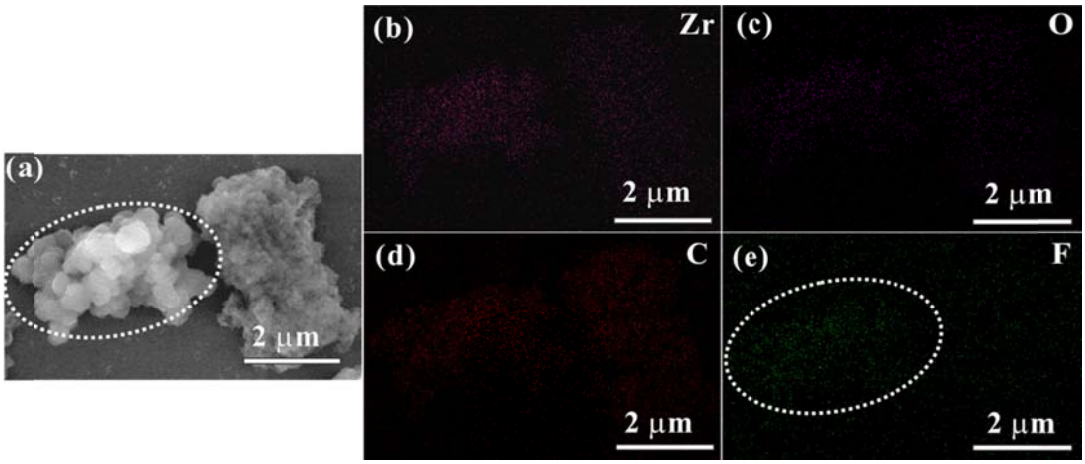


Fig. S5 SEM image for the physical mixture of MOF PCN-56 and PCN-56-U, as well as elemental mapping images. There is the distinct phase separation in both morphology and elemental distribution, as indicated by the uneven fluorine distribution. Sample in circle should be PCN-56-U as confirmed by F mapping.

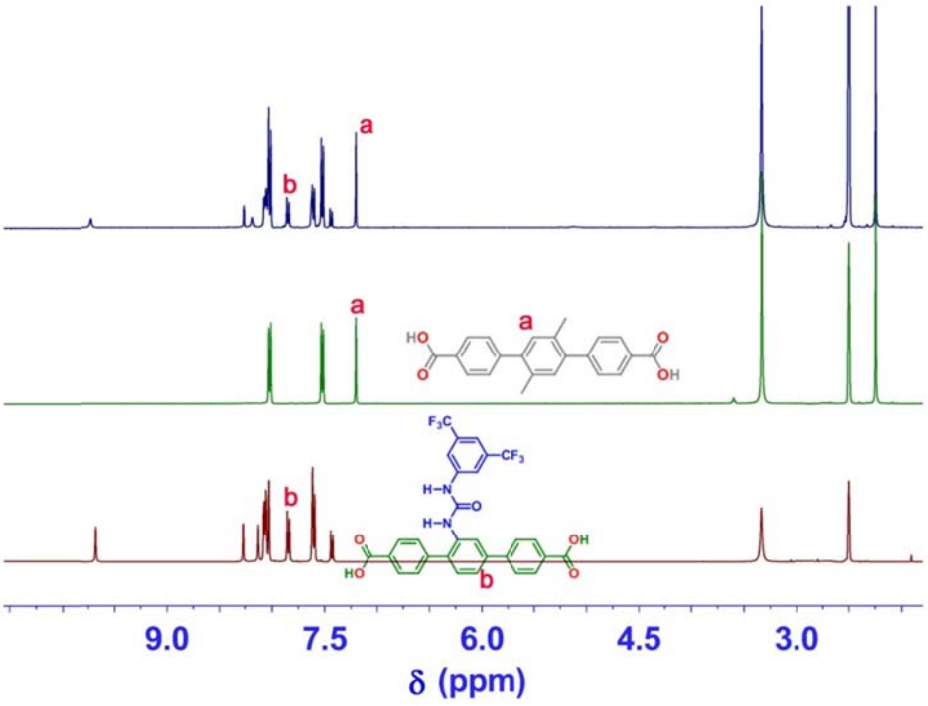


Fig. S6 ^{1}H NMR of digested MOF PCN-56-UM by HF in DMSO-d_6. The molar ratio of linkers H_2-utpdc and H_2-mtpdc in as-prepared MOF was calculated from the integration of Ha (H_2-mtpdc) and Hb (H_2-utpdc), giving the ratio of around 1:1.1, which is almost same to the initial ratio of 1:1 in preparation of MOF. The slightly higher content of H_2-mtpdc linker in MOF should be ascribed to the steric bulk of H_2-utpdc linker.

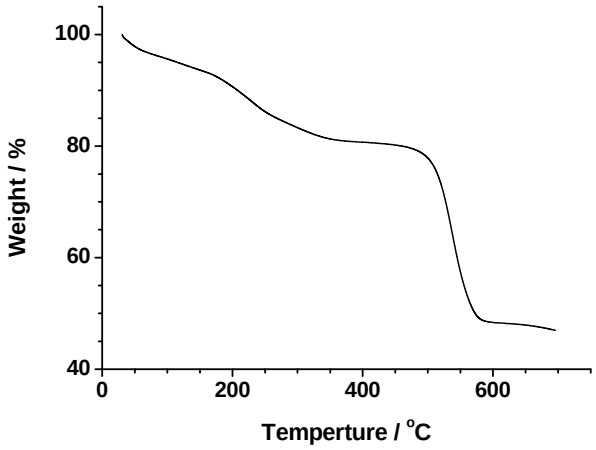


Fig. S7 TGA plot of as-synthesized MOF PCN-56-UM, suggesting the framework can be stable up to ~550 °C.

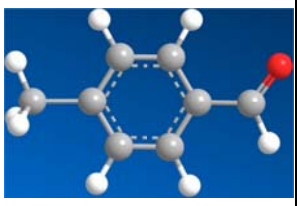
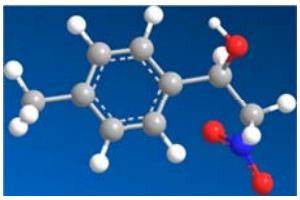
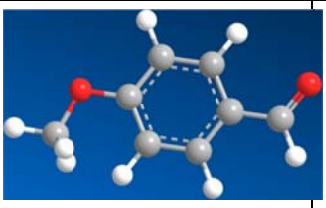
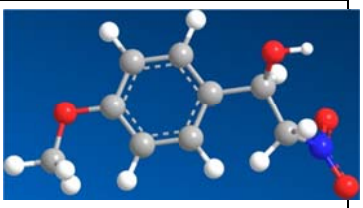
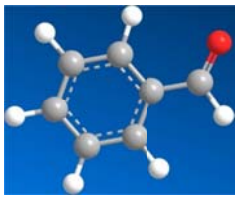
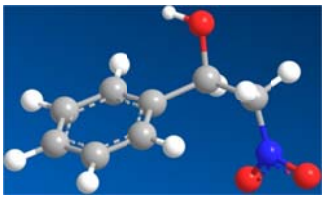
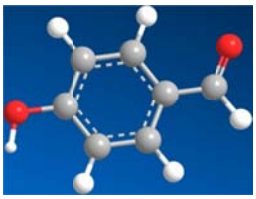
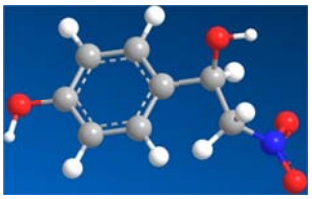
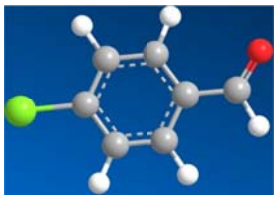
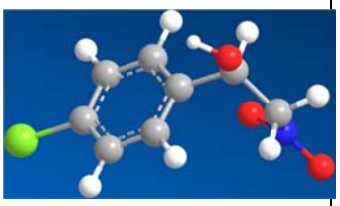
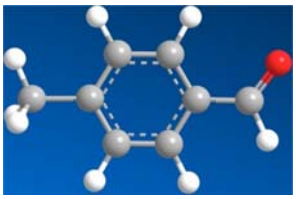
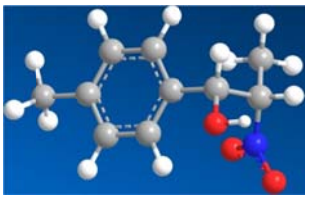
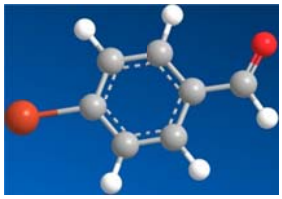
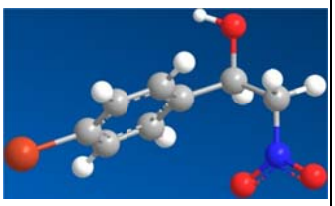
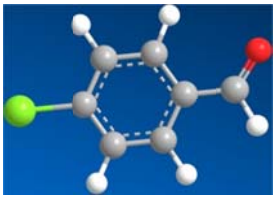
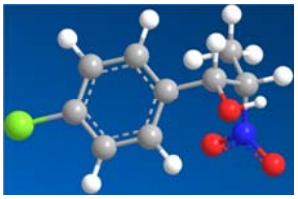
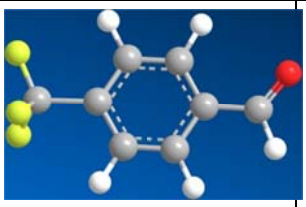
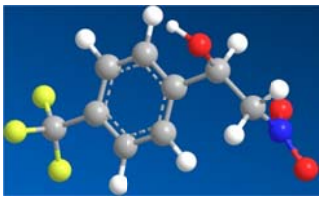
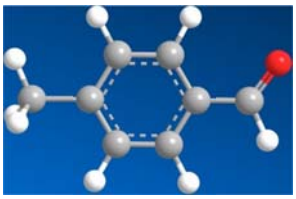
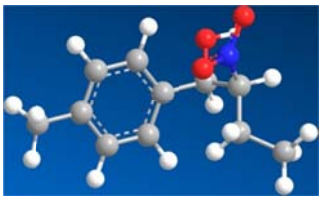
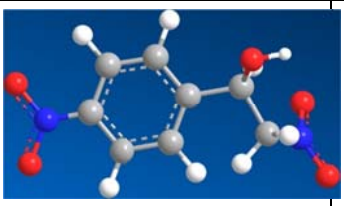
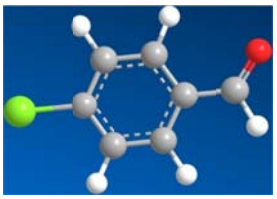
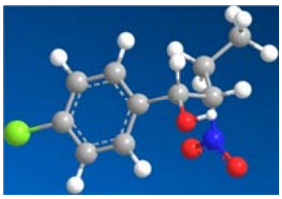
General Procedure for Catalysis

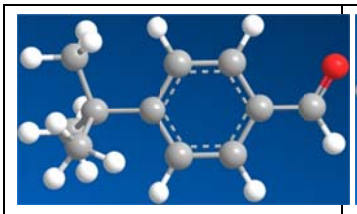
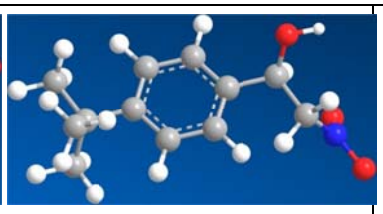
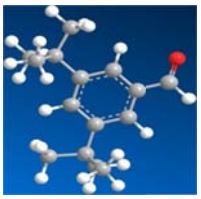
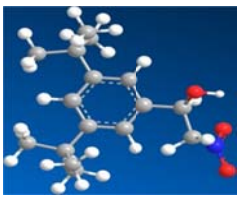
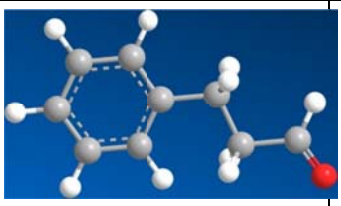
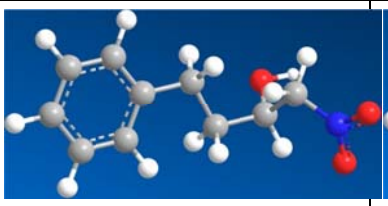
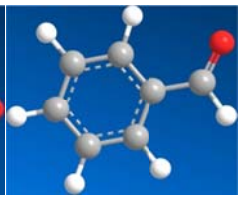
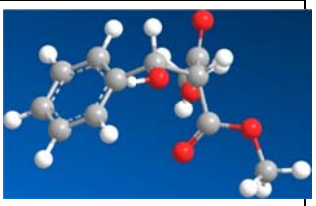
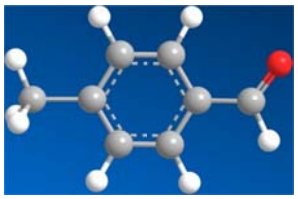
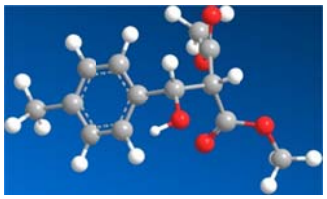
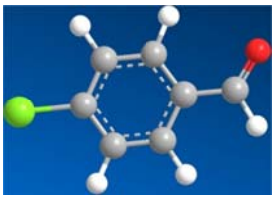
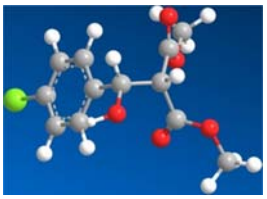
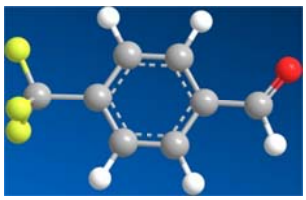
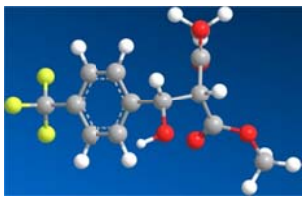
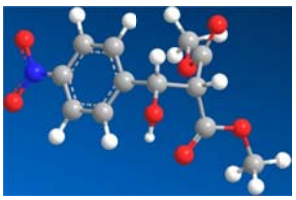
The weighed as-synthesized MOF PCN-56-UM was exchanged with THF for 2 days, respectively. During the period, fresh solvent was exchanged several times a day. To a solution of benzaldehydes (0.5 mmol) and nitroalkanes (5 mmol) was added 5% molar MOF catalyst and 20% molar $^{i}Pr_2EtN$ in 0.5 mL THF of a vial. Then, the vial was placed in a vortex mixer and shook at room temperature for 24 h. The MOF catalyst for next round reaction was recycled by centrifugation at 10 000 rpm and washed by fresh THF two times.

Table S1 Comparison for Henry reaction of *p*-tolualdehyde and nitromethane.

Entry	Catalyst	Time	Yield
1	PCN-56-UM	24	90%
2	UiO-67-Urea/bpdc[S3]	24	65%
3	Me_2-utpdc	24	56%
4	PCN-56	24	14%
5	PCN-56-U	24	41%
6	PCN-56+PCN-56-U	24	29%
7	ground PCN-56-UM	24	50%
8	ground PCN-56-U	24	39%

Table S2 The estimated molecular size of substrates and products.

Benzaldehydes	Products	Benzaldehydes	Products
 **1a**, 0.64 nm	 **3a**, 0.85 nm	 **1g**, 0.81 nm	 **3g**, 0.96 nm
 **1b**, 0.60 nm	 **3b**, 0.74 nm	 **1h**, 0.66 nm	 **3h**, 0.77 nm
 **1c**, 0.66 nm	 **3c**, 0.75 nm	 **1a**, 0.64 nm	 **3i**, 0.81 nm
 **1d**, 0.67 nm	 **3d**, 0.76 nm	 **1c**, 0.66 nm	 **3j**, 0.78 nm
 **1e**, 0.70 nm	 **3e**, 0.85 nm	 **1a**, 0.64 nm	 **3k**, 0.92 nm
 **1f**, 0.68 nm	 **3f**, 0.90 nm	 **1c**, 0.66 nm	 **3l**, 0.87 nm

 **1m**, 0.82 nm	 **3m**, 1.0 nm	 **1n**, 0.90 nm	 **3n**, 1.04 nm
 **1o**, 0.84 nm	 **3o**, 0.99 nm	 **1b**, 0.60 nm	 **3p**, 0.94 nm
 **1a**, 0.64 nm	 **3q**, 1.05 nm	 **1c**, 0.66 nm	 **3r**, 0.98 nm
 **1e**, 0.70 nm	 **3s**, 1.07 nm	 **1f**, 0.68 nm	 **3t**, 0.99 nm

All of them are smaller than 1.1 nm, while the pore size of PCN-56-UM was calculated to be ~1.6 nm. Thus, this will facilitate the diffusion of substrates and products into and out of framework for efficient heterogeneous catalysis.

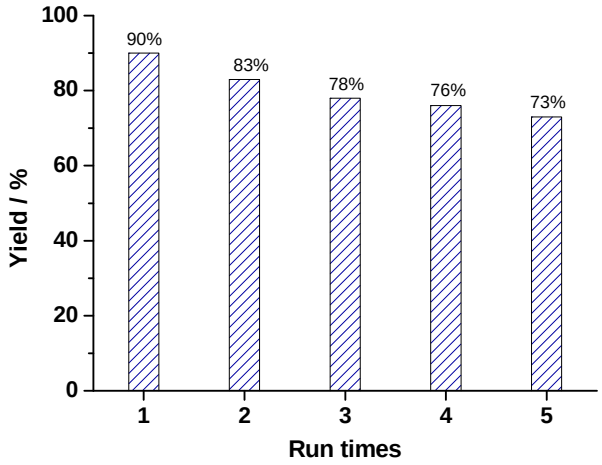


Fig. S8 Recycling experiments of PCN-56-UM for the reaction of benzaldehyde and CH_3NO_2.

X-ray crystallography.

The single crystal **Me_2-utpdc** for X-ray analysis was grown from the mixture of THF-hexane and picked up under a microscope from a freshly synthesized solution and then mounted immediately. The diffraction data were collected at room temperature using graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) on a Bruker CCD APEXII diffractometer. The collected frames were processed with the software SAINT. The data were corrected for absorption by using the SADABS program. The structure was solved by the direct methods and refined by full-matrix least-squares analyses on F^2. Crystallographic data is summarized in Table S2.

CCDC 1889711 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S3 Crystal data and structure refinement for **Me_2-utpdc**.

Empirical formula	$C_{31}H_{22}F_6N_2O_5$
Formula weight	616.50
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	12.036(7)
b/Å	12.533(7)
c/Å	14.010(13)
α /°	109.014(10)
β /°	97.412(10)
γ /°	118.495(7)
Volume/Å^3	1650(2)
Z	2
ρ_{calc}g/cm^3	1.241
μ /mm^{-1}	0.107
F(000)	632.0
Crystal size/mm^3	0.19 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.794 to 50.998
Index ranges	-14 ≤ h ≤ 14, -13 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	10166
Independent reflections	6032 [R_{int} = 0.0657, R_{sigma} = 0.0912]
Data/restraints/parameters	6032/573/453
Goodness-of-fit on F^2	0.941
Final R indexes [I>=2σ (I)]	R_1 = 0.0689, wR_2 = 0.1676

Final R indexes [all data]	$R_1 = 0.1343$, $wR_2 = 0.1884$
Largest diff. peak/hole / e Å^{-3}	0.23/-0.22

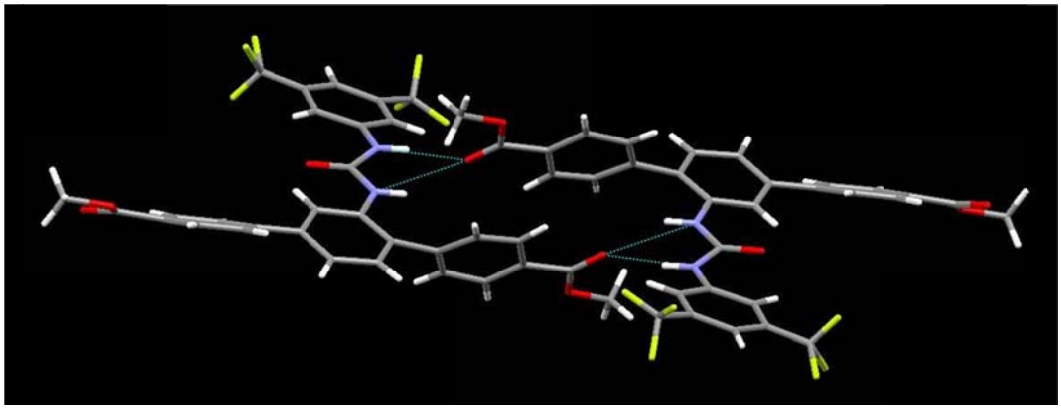


Fig. S9 A dimer was formed through the hydrogen bonding between urea N-H and C=O of ester in Me2-utpdc.

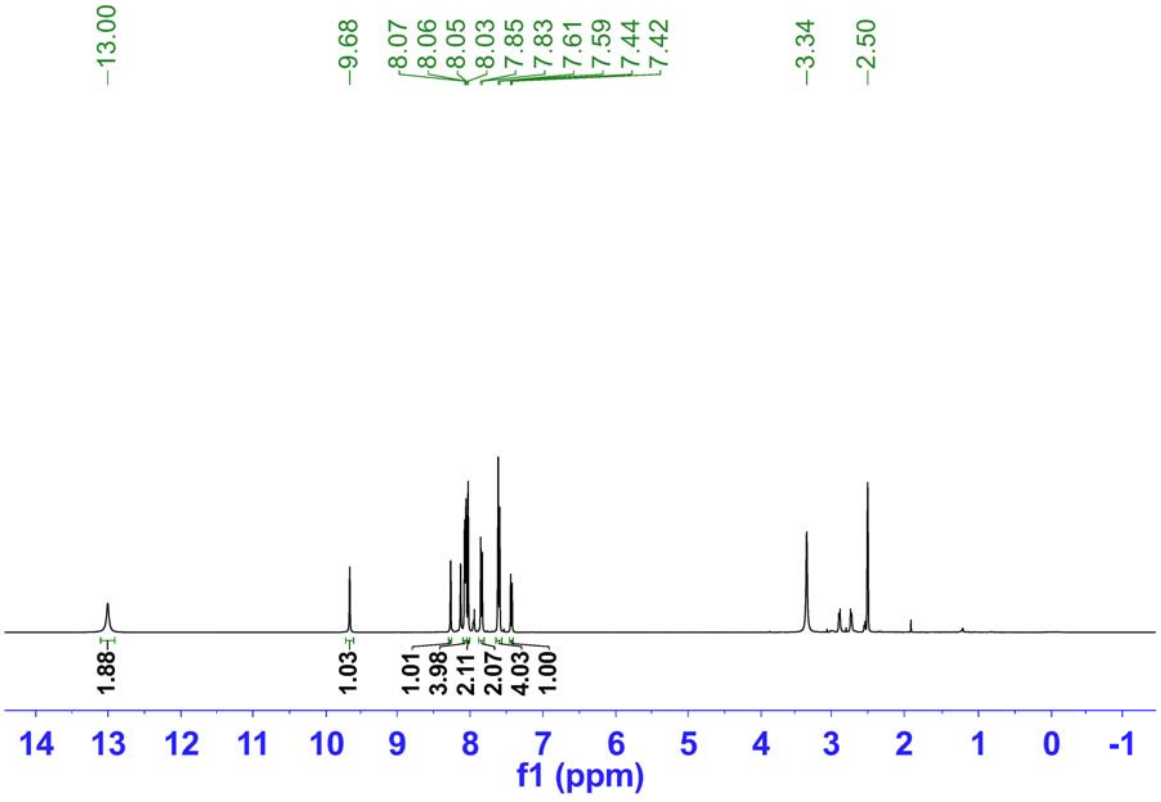


Fig. S10 ^{1}H NMR spectra of H_2-utpdc (DMSO-d_6).

References:

[S1] Y. Quan, Q.-Y. Li, Q. Zhang, W.-Q. Zhang, H. Lu, J.-H. Yu, J. Chen, X. Zhao and X.-J. Wang, *RSC Adv.*, 2016, **6**, 23995-23999.

[S2] W.-Q. Zhang, Q.-Y. Li, Q. Zhang, Y. Lu, H. Lu, W. Wang, X. Zhao and X.-J. Wang, *Inorg. Chem.*, 2016, **55**, 1005-1007.

[S3] P. W. Siu, Z. J. Brown, O. K. Farha, J. T. Hupp and K. A. Scheidt, *Chem. Commun.*, 2013, **49**, 10920-10922.