Electronic Supplementary Information (ESI)

Isomer of Linker for NU-1000 Yields a New *She*-type, Catalytic, and Hierarchically Porous, Zr-based Metal–Organic Framework

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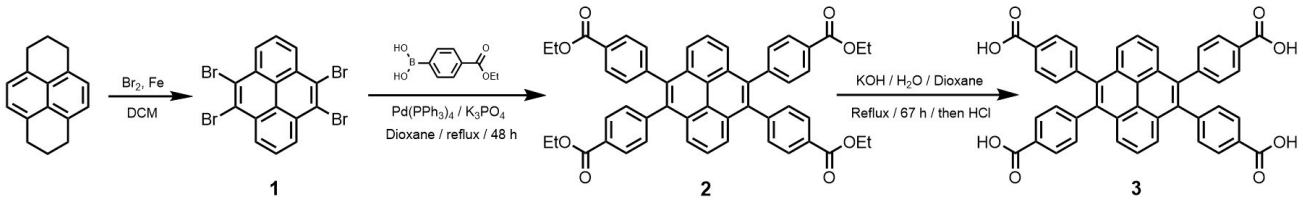
SECTION S1. Linker Synthesis and Characterization



Scheme S1. The synthetic procedure of H_4TBAPy-2.

4,5,9,10-tetrabromopyrene (1). 1,2,3,6,7,8-hexahydropyrene (3.12 g, 15.0 mmol), Bromine (27.17 g, 170 mmol), iron powder (0.59 g, 10.6 mmol) and 100 ml dichloromethane were added to a 250 ml round bottom flask and refluxed overnight. The precipitate was filtered and washed with acetone (3×200 ml) and boiling chloroform (3×200 ml). 3.2 g 4,5,9,10-tetrabromopyrene was obtained in the yield of 41.2%. ^{1}H NMR (500MHz, $CDCl_3$-*d*, δ ppm): 8.80 (d, 4H, $-CH_2-$), 8.09 (t, 2H, $-CH_2-$).

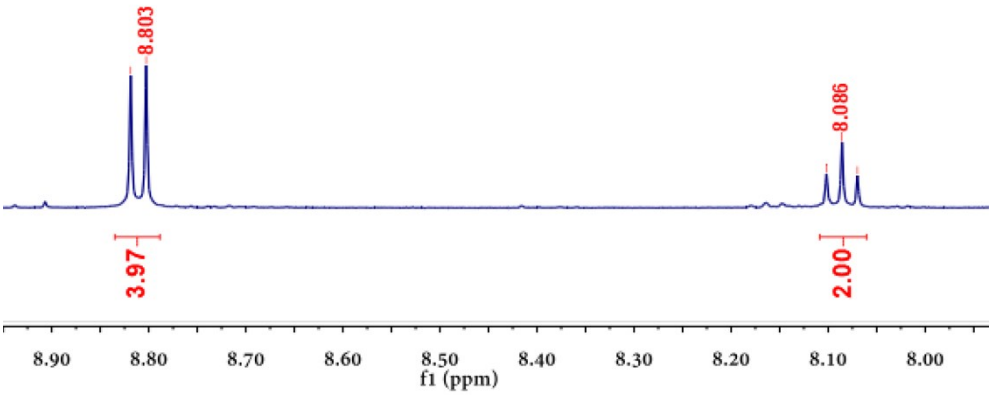


Figure S1. ^{1}H NMR spectrum of 4,5,9,10-tetrabromopyrene in $CDCl_3$-*d* solution.

4,5,9,10-tetrakis(4-(ethoxycarbonyl)phenyl)pyrene (2). Into a flask flushed with N_2, (4-(ethoxycarbonyl)phenyl)boronic acid (4.125 g, 21.26 mmol), 4,5,9,10-tetrabromopyrene (2.500 g, 4.85 mmol), and potassium tribasic phosphate (8.25 g, 38.87 mmol) were added to dry dioxane (200 mL). After stirring for half an hour, tetrakis(triphenylphosphine) palladium(0) (0.375 g 0.325 mmol) was

added. The system was purged with N_2 for an additional 5 min. The solution was then refluxed at 90 °C for 3 days under nitrogen atmosphere. The reaction mixture was evaporated to dryness and the solid residue was washed with water to remove inorganic salts. The insoluble material was extracted with chloroform (three times by 50 mL), the extract was dried over magnesium sulfate, and the solvent volume was reduced under vacuum. The crude dark product was further purified by column chromatography on silica gel with 3:10 CH_2Cl_2/hexane to give pale yellow solid. This procedure gave 0.88 g of 4,5,9,10-tetrakis(4-(ethoxycarbonyl)phenyl)pyrene (22.8% yield). ^{1}H NMR (500MHz, $CDCl_3$-*d*, δ ppm): 8.03 (d, 8H, Ar−H), 7.83 (m, 6H, Pyrene−H), 7.40 (d, 8H, Ar−H), 4.41 (q, 8H, $-CH_2-$), 1.44 (t, 2H, $-CH_3$).

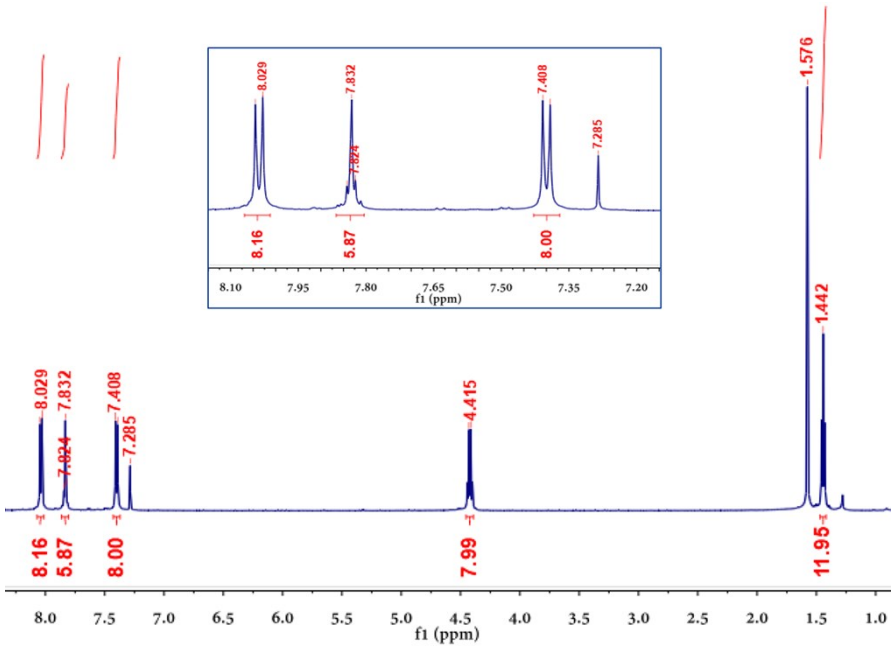
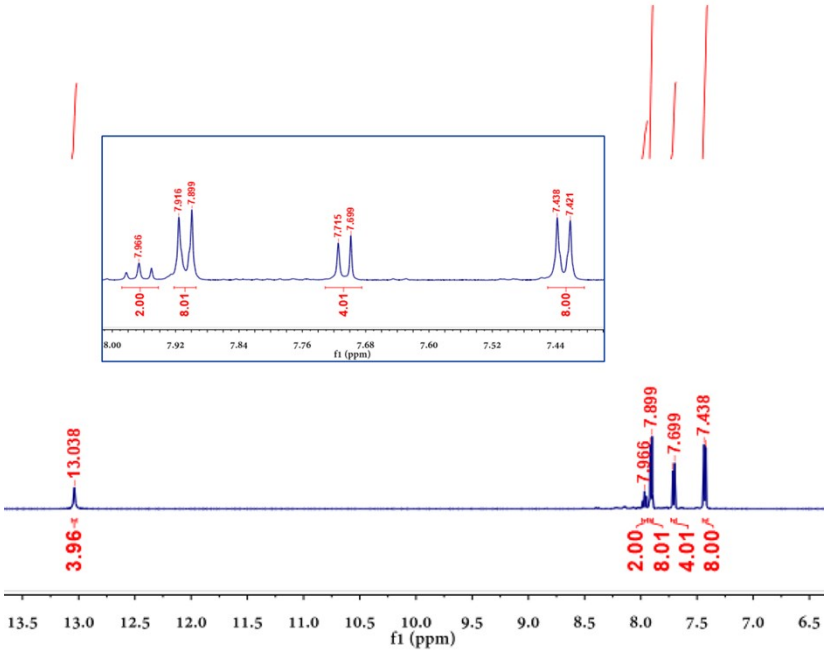


Figure S2. ^{1}H NMR spectrum of 4,5,9,10-tetrakis(4-(ethoxycarbonyl)phenyl)pyrene in $CDCl_3$-*d* solution.

4,5,9,10-tetrakis(p-benzoic acid)pyrene (3). To a 250 mL round bottom flask containing 0.88 g (1.1 mmol) of solid 4,5,9,10-tetrakis(4-(ethoxycarbonyl)phenyl)pyrene, a solution containing 1.5 g

(37.5 mmol) NaOH in 100 mL of a THF/water (ratio 1:1) mixture was added and the resultant suspension was vigorously stirred under reflux overnight. The solvents were removed under vacuum and water was added to the residue which formed a clear solution. The solution was added concentrated HCl to adjust pH value to 1 . The resulting light-pink solid was collected by filtration, and washed with water several times, and then dried in vacuum oven. This gave 0.69 g (92%) of the pure product H_4TBAPy-2. ^{1}H NMR (500MHz, DMSO-d_6, δ ppm): 13.04 (s, 4H, −COOH), 7.97 (t,



2H, Pyrene−H), 7.90 (d, 8H, Ar−H), 7.70 (d, 4H, Pyrene−H), 7.43 (d, 8H, Ar−H).

Figure S3. ^{1}H NMR spectrum of 4,5,9,10-tetrakis(p-benzoic acid)pyrene in DMSO-d_6 solution.

SECTION S2. Synthesis and Activation of NU-601.

Synthesis of NU-601-as-syn (single crystals). 12.3 mg of $ZrOCl_2 \cdot 8H_2O$ (0.069 mmol) and 250 mg (2.05 mmol) of benzoic acid were mixed in 1 mL of DMF and ultrasonically dissolved. The clear solution was incubated in an oven at 100 °C for 1h. In the meantime, H_4TBAPy-2 (5 mg, 0.0073 mmol) was added to 0.5 mL DMF and heated to 100 °C for 1 h. After cooling down to room

temperature, H_4TBAPy-2 solution and trifluoroacetic acid (TFA) (5 uL, 0.065 mmol) were added to pre-made Zr node containing solution and sonicated for 10 min. The yellow suspension was placed in a pre-heated oven at 120 °C for 24 h. This method yields 50~100 micron **NU-601** single crystals.

Synthesis of NU-601-p (powder, 1-2 μm). 8.75 mg of $ZrCl_4$ (0.038 mmol) and 0.14 ml formic acid were added in 0.75 mL of DEF and ultrasonically dissolved. The clear solution was incubated in an oven at 80 °C for 1h. In the meantime, H_4TBAPy-2 (5 mg, 0.0073 mmol) was added to 0.5 mL DEF and sonicate for well-dispersion. After cooling down to room temperature, H_4TBAPy-2 solution and formic acid (20 μL) were added to pre-made Zr node containing solution and sonicated for 5 min. The yellow suspension was heated in an oven at 120 °C for 3 h. After cooling down to room temperature, pale yellow polycrystalline material was isolated by filtration (4 mg of activated material, 54% yield) and washed with DMF.

Synthesis of NU-601-p (powder, 4-5 μm). 8.75 mg of $ZrCl_4$ (0.038 mmol) and 0.14 ml formic acid were added in 0.75 mL of DEF and ultrasonically dissolved. The clear solution was incubated in an oven at 80 °C for 1h. In the meantime, H_4TBAPy-2 (5 mg, 0.0073 mmol) was added to 0.5 mL DEF and the solution was put in an oven at 80 °C for 1h. After cooling down to room temperature, H_4TBAPy-2 solution and formic acid (20 μL) were added to pre-made Zr node containing solution and sonicated for 5 min. The yellow suspension was heated in an oven at 120 °C for 13 h. After cooling down to room temperature, pale yellow polycrystalline material was isolated by filtration (4 mg of activated material, 54% yield) and washed with DMF.

Synthesis of NU-601-p (powder, 8-10 μm). 8.75 mg of $ZrCl_4$ (0.038 mmol) and 0.14 ml formic acid were added in 0.75 mL of DEF and ultrasonically dissolved. The clear solution was incubated in an oven at 80 °C for 1h. In the meantime, H_4TBAPy-2 (5 mg, 0.0073 mmol) was added to 0.5 mL DEF and the solution was put in an oven at 80 °C for 1h. After cooling down to room temperature, H_4TBAPy-2 solution and formic acid (100 μL) were added to pre-made Zr node containing solution and sonicated

for 5 min. The yellow suspension was heated in an oven at 120 °C for 13 h. After cooling down to room temperature, pale yellow polycrystalline material was isolated by filtration (4 mg of activated material, 54% yield) and washed with DMF.

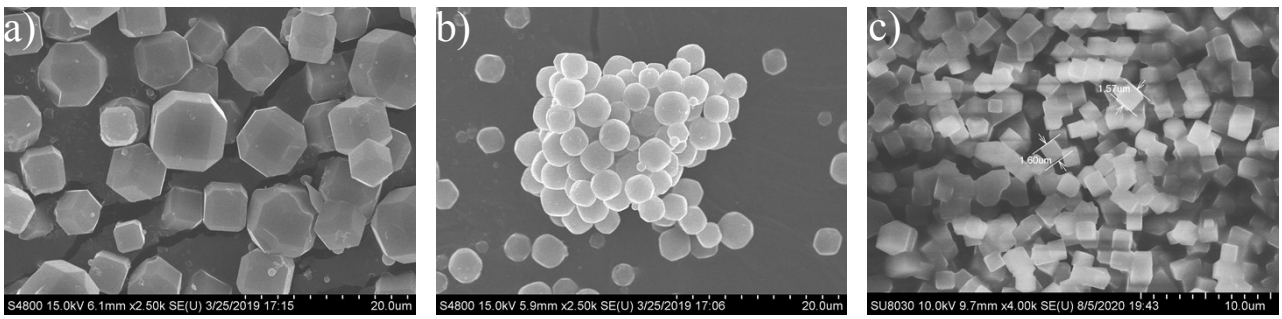


Figure S4. SEM images of **NU-601-p** with different particles sizes. a) 8-10 μm; b) 4-5 μm; c) 1-2 μm.

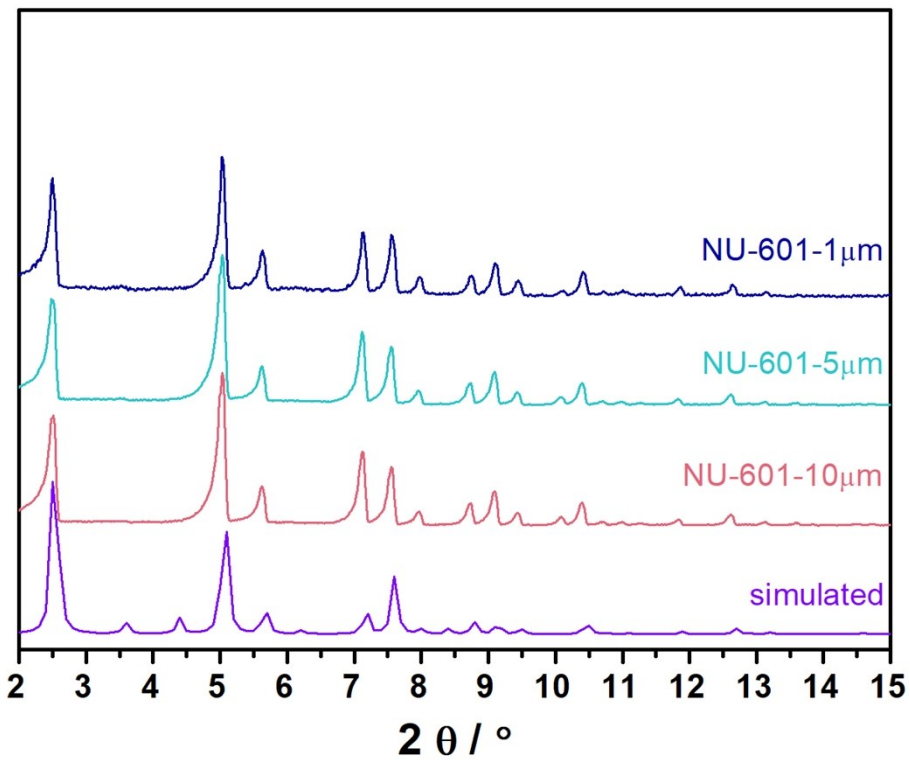


Figure S5. PXRD patterns of **NU-601-p** with different particles sizes.

SECTION S3. Activation procedure for NU-601

Approximately 40 mg of **NU-601-as-syn** was soaked in 12 ml of DMF and 0.5 ml of 8 M aqueous HCl was added. This mixture was heated in an oven at 100 °C overnight. After cooling to room temperature, the solution was removed and the material was washed twice with DMF to remove HCl impurities. Subsequently the solid residue was washed twice with acetone and soaked in acetone for additional 12 h. **NU-601** was filtered, briefly dried on a filter paper and activated at 120 °C under vacuum for 12h. Shown below, the activated **NU-601** sample was characterized by ^{1}H NMR, and DRIFTS. The data are consistent with the removal of benzoic acid from the Zr_6 node and the incorporation of formate groups.

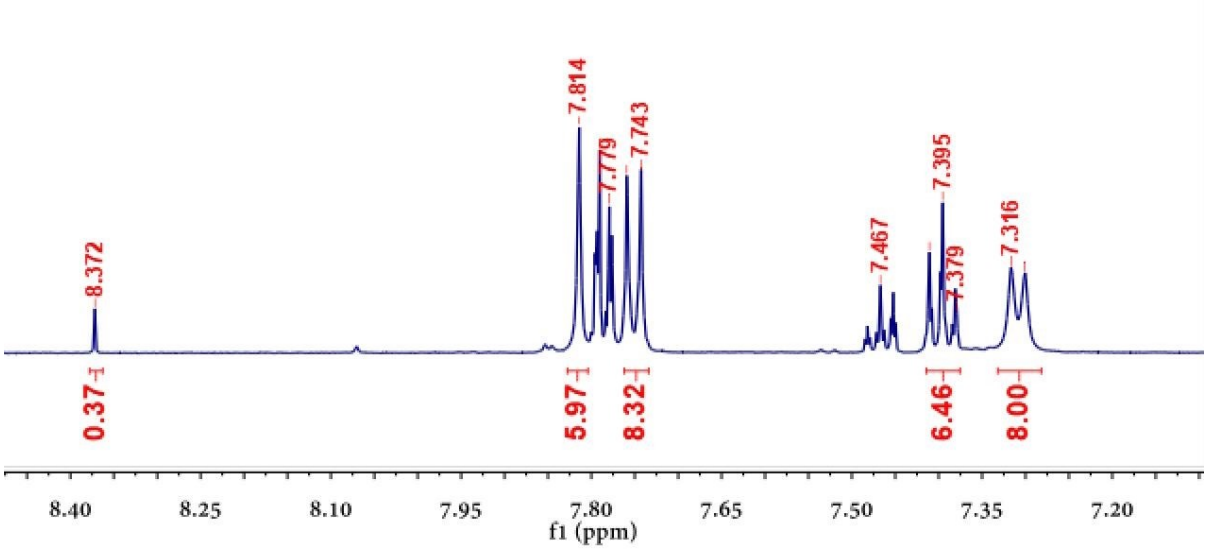


Figure S6. ^{1}H NMR spectrum of **NU-601-as-syn** with modulator in NaOD/D_2O solution.

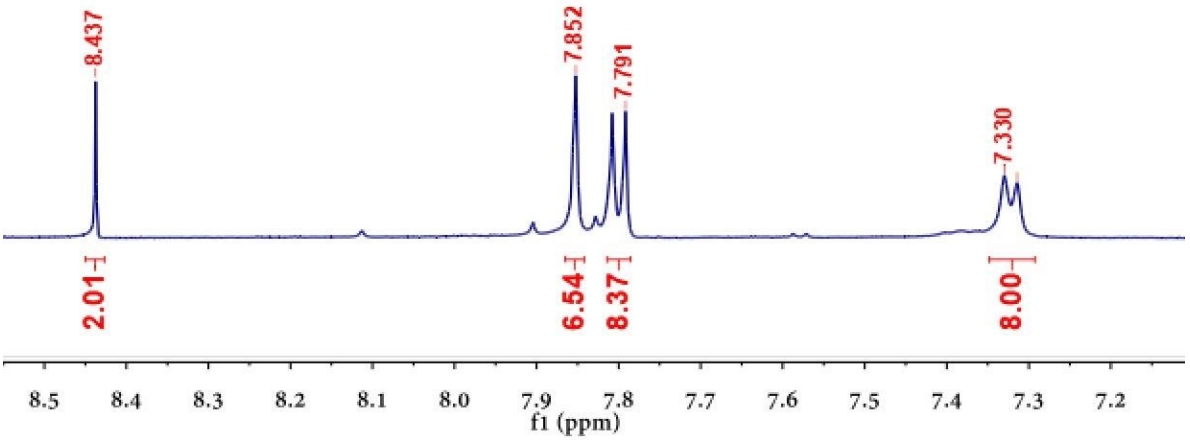


Figure S7. ^{1}H NMR spectrum of **NU-601-Activated** in NaOD/D_2O solution.

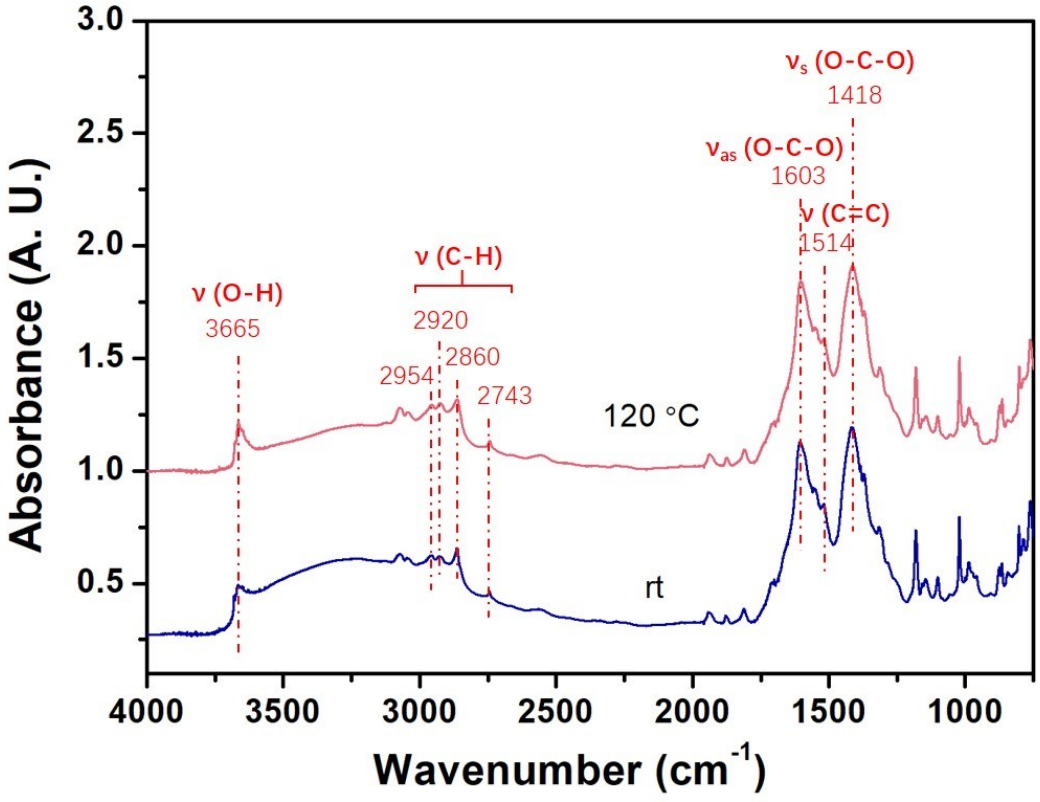


Figure S8. DRIFTS spectra of **NU-601-p** at room temperature and at 120 °C

SECTION S4. Crystal structure

Single-crystal X-ray diffraction data of NU-601-as-syn was measured on a Bruker Apex II CCD diffractometer at 100 K using graphite monochromated Mo/Kα radiation (λ = 0.71073 Å). Data reduction was made with the Bruker SAINT programs. Single-crystal X-ray diffraction data of NU-601-activated was measured on Rigaku Oxford Diffraction XtaLAB Synergy-S at 100 K using graphite monochromated Cu/Kα radiation (λ = 1.54184 Å). Data reduction was made with the Rigaku CrysAlisPro programs. The structures were solved by direct (SHELXS) and intrinsic phasing (SHELXT) methods and refined with full-matrix least squares technique using the SHELXL package. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2 × Ueq of the attached atom. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules and thereby, to produce a set of solvent-free diffraction intensities; structures were then refined again using the data generated. Crystallographic data for the NU-601-as-syn and NU-601-activated, crystal structures in CIF format have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC-2015123-2015124. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.)

Table S1. Crystal Data for **NU-601**.

	NU-601-as-syn	**NU-601-activated**
CCDC number	2015123	2015124
Empirical formula	$C_{90}\ H_{51}\ O_{32}\ Zr_6$ [+solvent]	$C_{66}\ H_{33}\ O_{32}\ Zr_6$ [+ solvent]
Formula weight	2191.63	1885.24
crystal system	Cubic	Cubic
Space group	*P m -3 m*	*P m -3 m*
a [Å]	34.8374(5)	34.8119(1)
b [Å]	34.8374(5)	34.8119(1)
c [Å]	34.8374(5)	34.8119(1)
α [deg]	90	90
β [deg]	90	90
γ [deg]	90	90
V [Å^3]	42280.2(18)	42187.4(4)
Z	8	8
T [K]	100	101
ρ_{calc} [g cm^{-3}]	0.689	0.594
R1, wR2[a] [$I>2\sigma(I)$]	0.0937; 0.2965	0.0467; 0.1282
R1, wR2[a] [all data]	0.1213; 0.3184	0.0523; 0.1320

[a] $R1 = \Sigma||F_o| - |F_c||/|F_o|$; $wR2 = [\Sigma w(\Sigma F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

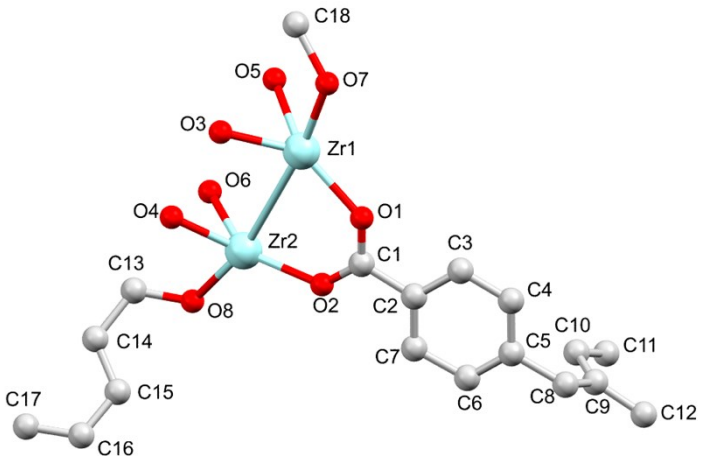


Figure S9. The asymmetric structural unit of **NU-601-as-syn**.

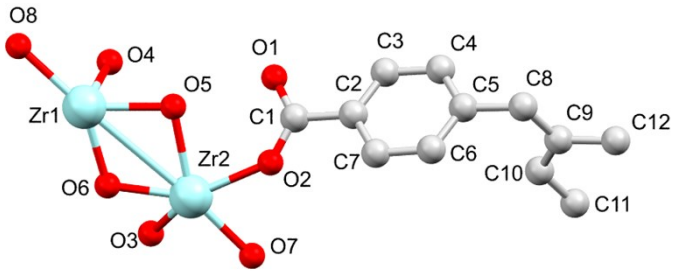


Figure S10. The asymmetric structural unit of **NU-601-activated**.

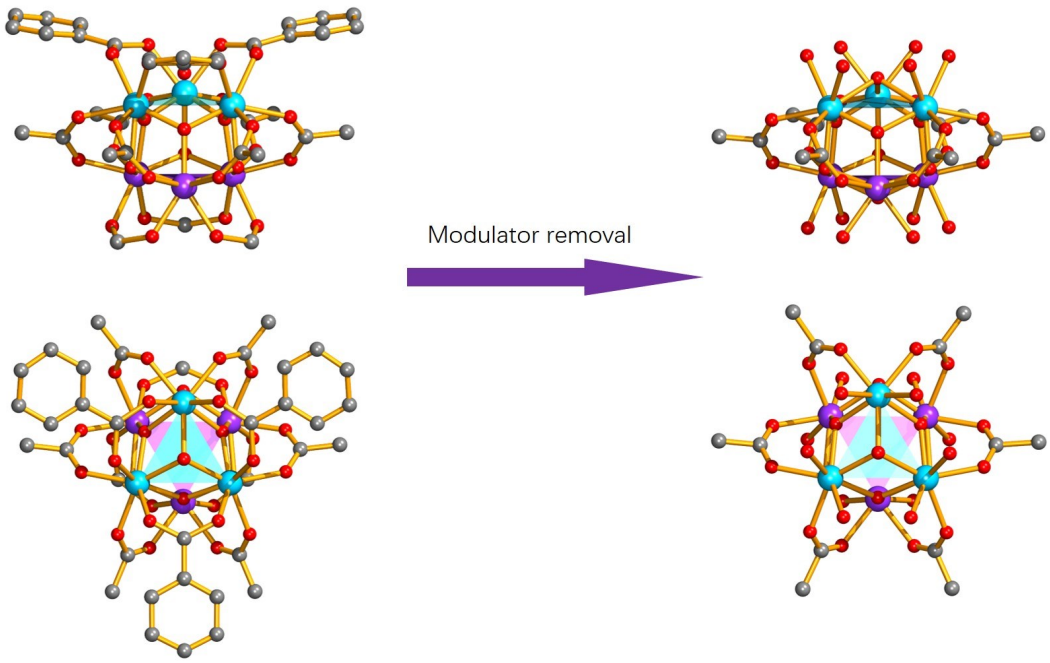


Figure S11. Node coordination environment after modulator removal

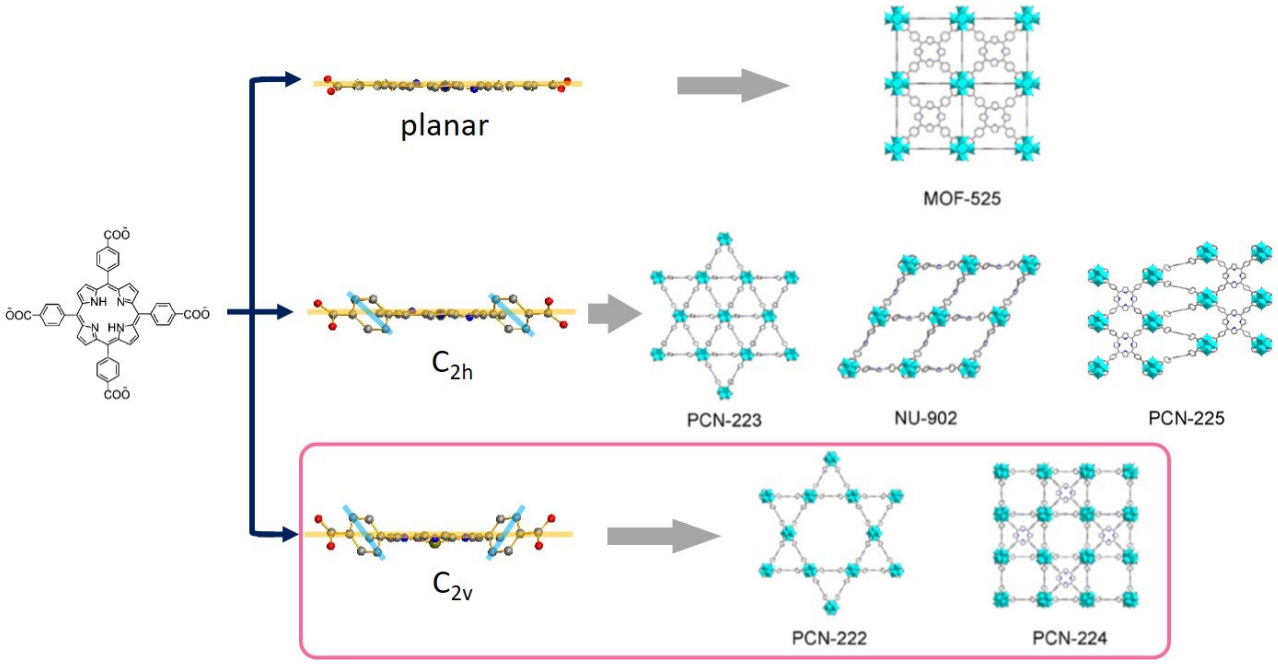


Figure S12. An illustration of symmetry and geometry of H_4TCPP leading to Zr-MOFs with various topologies.

Table S2 φ_{cc} and φ_{cb} in different *csq*-type Zr-MOFs

csq-type MOFs	φ_{cc} / °	φ_{cb} / °	References
NU-1000	61.3	59.3	[1]
PCN-128	57.5	60.0	[2]
PCN-608-OH	56.1	50.2	[3]
NU-1008	54.1	79.6	[4]
PCN-808	51.1	46.0	[5]

SECTION S5. PXRD patterns and water stability

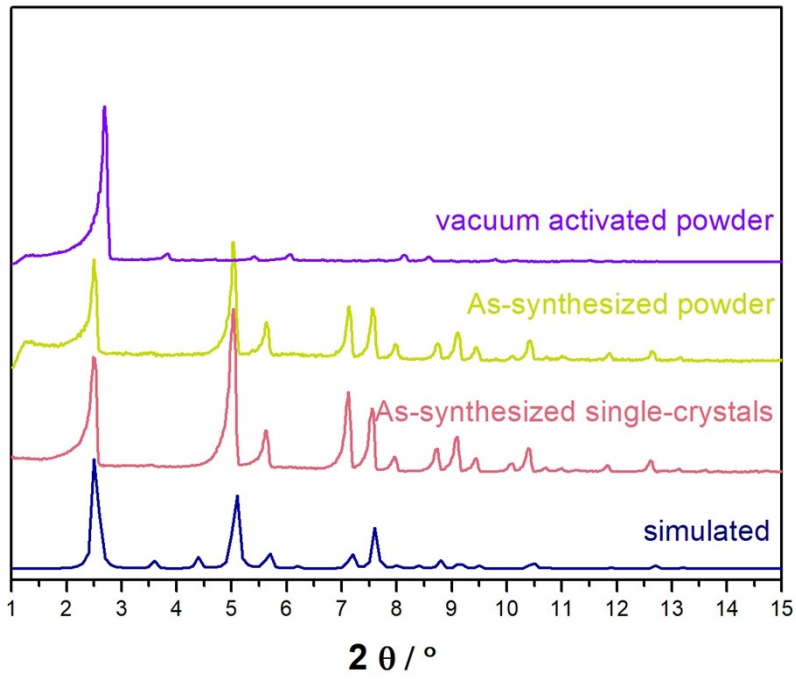


Figure S13. PXRD patterns of different versions of **NU-601**.

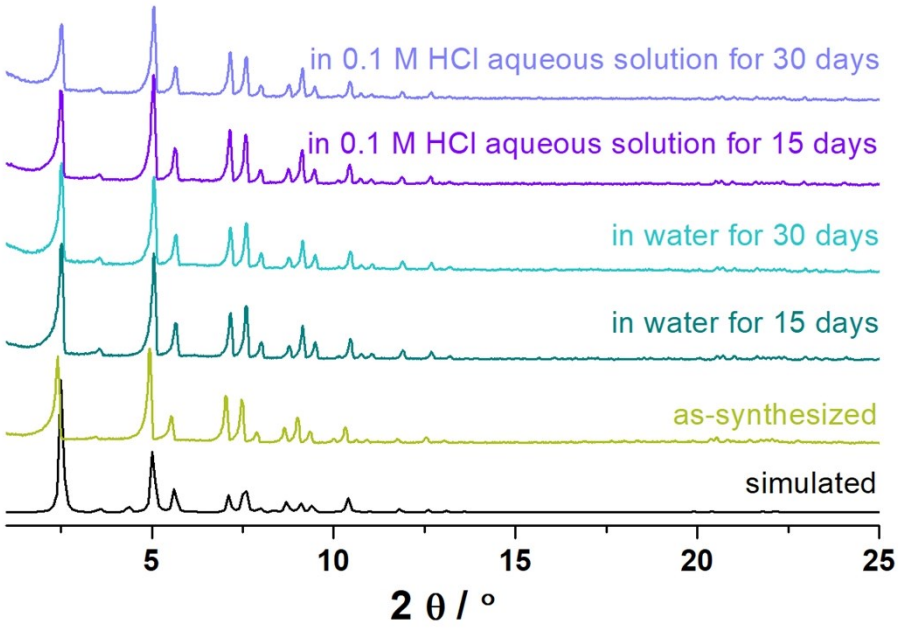


Figure S14. Water stability tests of **NU-601**.

SECTION S6. Thermal stability

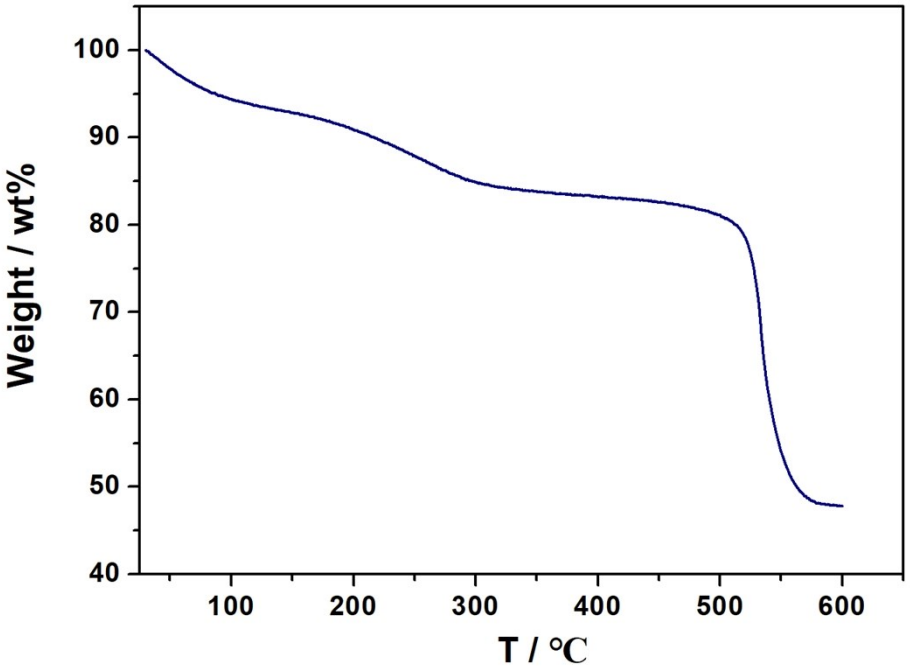


Figure S15. TG curve of **NU-601-p** after vacuum treatment.

SECTION S7. Catalytic activity of NU-601 for the hydrolysis of DMNP

Hydrolysis experiments were run at room temperature and the progress of the reaction was monitored by in situ ^{31}P NMR spectroscopy in water at pH 10.5 as fixed by added N-ethylmorpholine. A solid sample of **NU-601-p**, or **NU-1000** (6 mol%, 1.5 μmol Zr_6) was added to 0.4 M N-ethylmorpholine solution (1.05 mL; 0.05 mL N-ethylmorpholine, 0.9 mL deionized water and 0.1 mL D_2O) in a 1.5 dram vial. The resulting mixture was sonicated for 1 min to disperse the MOF powder homogeneously. DMNP (4.0 μL, 25 μmol) was added to the mixture and swirled for 15 sec. The pH was ~10.5. The reaction mixture was then transferred to an NMR tube and the spectrum was immediately measured; the first data point was collected 120 sec after the start of the reaction. The progress of the reaction was monitored in 1 min increments for 1 h or until 100% conversion – whichever occurred first (number of scans = 16, delay time = 28 sec). Background

reactivity was evaluated under identical conditions by *in situ* ^{31}P NMR, w/o catalyst.

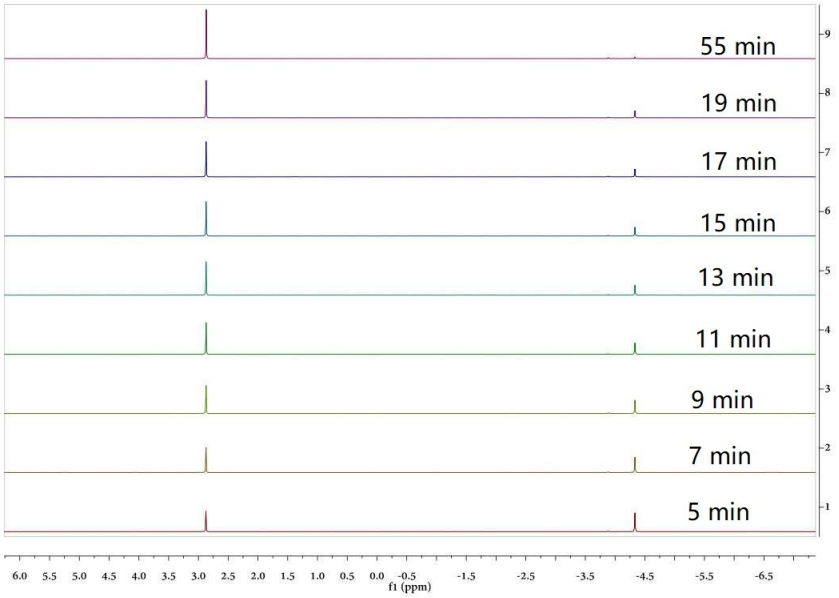


Figure S16. *In situ* ^{31}P NMR spectra indicating the progress of hydrolysis of DMNP (-4.3 ppm) to dimethoxy phosphate anion (2.9 ppm) in the presence of 1.5 μmol of **NU-601-5*μ*m** at room temperature.

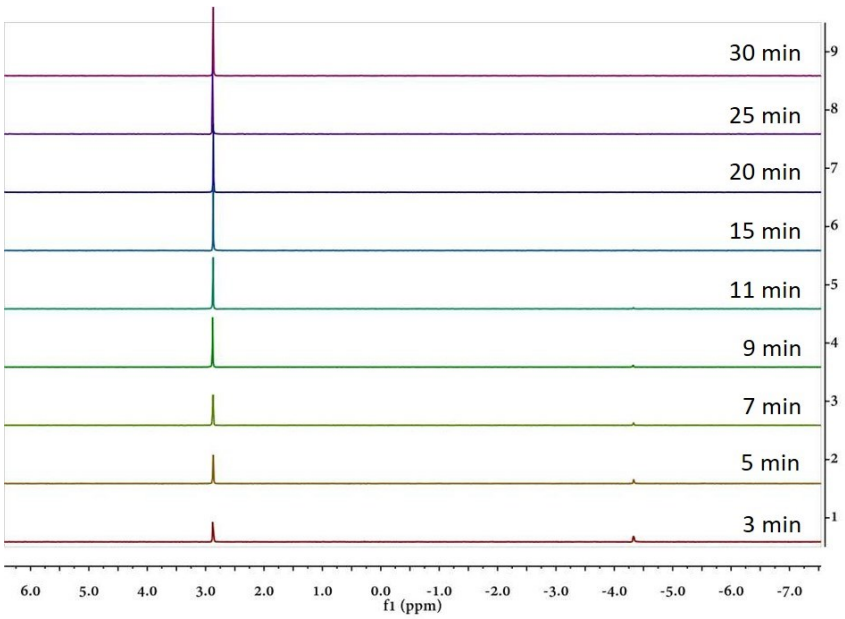


Figure S17. *In situ* ^{31}P NMR spectra indicating the progress of hydrolysis of DMNP (-4.3 ppm) to dimethoxy phosphate anion (2.9 ppm) in the presence of 1.5 μmol of **NU-601-1*μ*m** at room temperature.

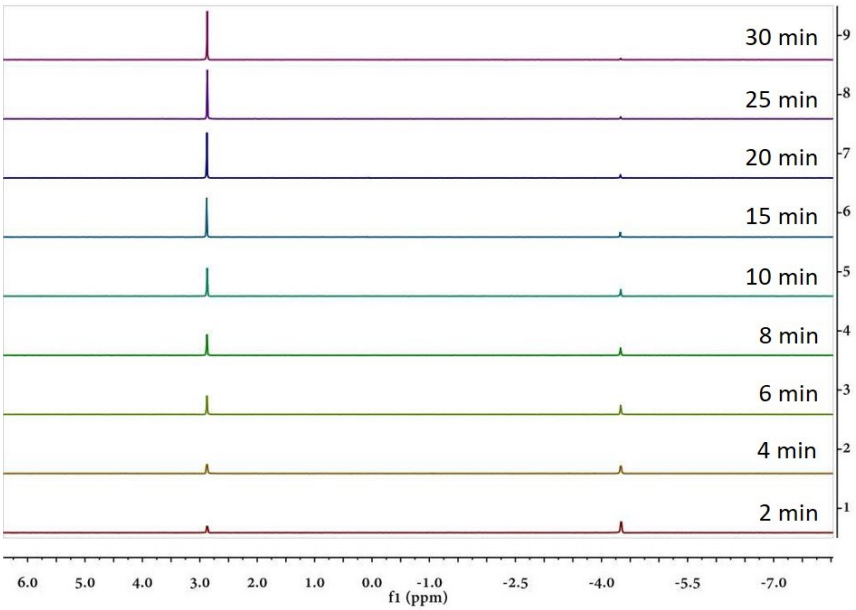


Figure S18. *In situ* ^{31}P NMR spectra indicating the progress of hydrolysis of DMNP (-4.3 ppm) to dimethoxy phosphate anion (2.9 ppm) in the presence of 0.7 μmol of **NU-601-1*μ*m** at room temperature.

Table S3. Comparison of the hydrolysis rate ($t_{1/2}$) of DMNP with various MOFs as well as TOFs for hydrolysis

MOF	Amount of Catalyst / umol	$t_{1/2}$ / min	TOF[a] / s^{-1}
NU-1000	1.5	11	0.013
NU-601-5 μm	1.5	5	0.028
NU-601-1 μm	1.5	<2	>0.07
NU-601-1 μm	0.7	3.5	0.085

SECTION S7. Comparison between NU-601 and NU-1000 for hydrolysis of DMNP

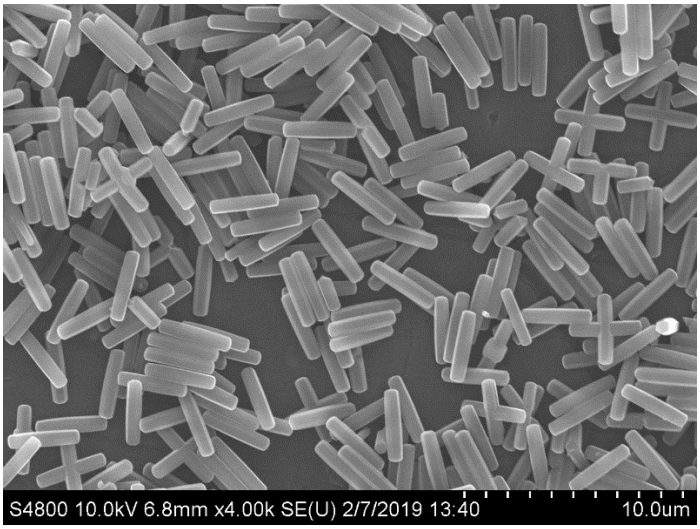


Figure 19. SEM image of **NU-1000** with particle length of 3~4 μm

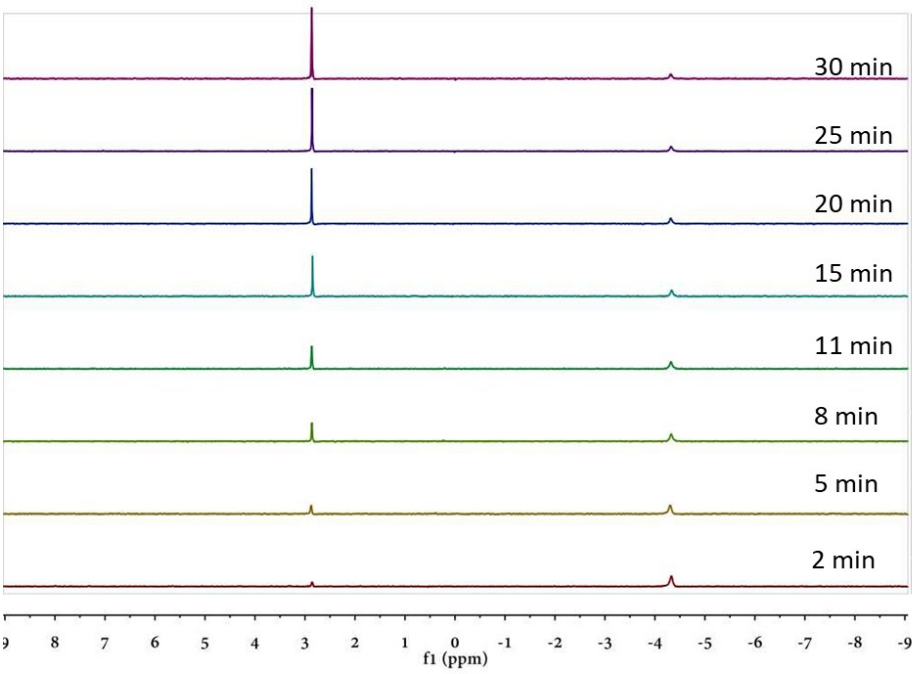


Figure S20. *In situ* ^{31}P NMR spectra indicating the progress of hydrolysis of DMNP (-4.3 ppm) to dimethoxy phosphate anion (2.9 ppm) in the presence of 1.5 μmol of **NU-1000** at room temperature.

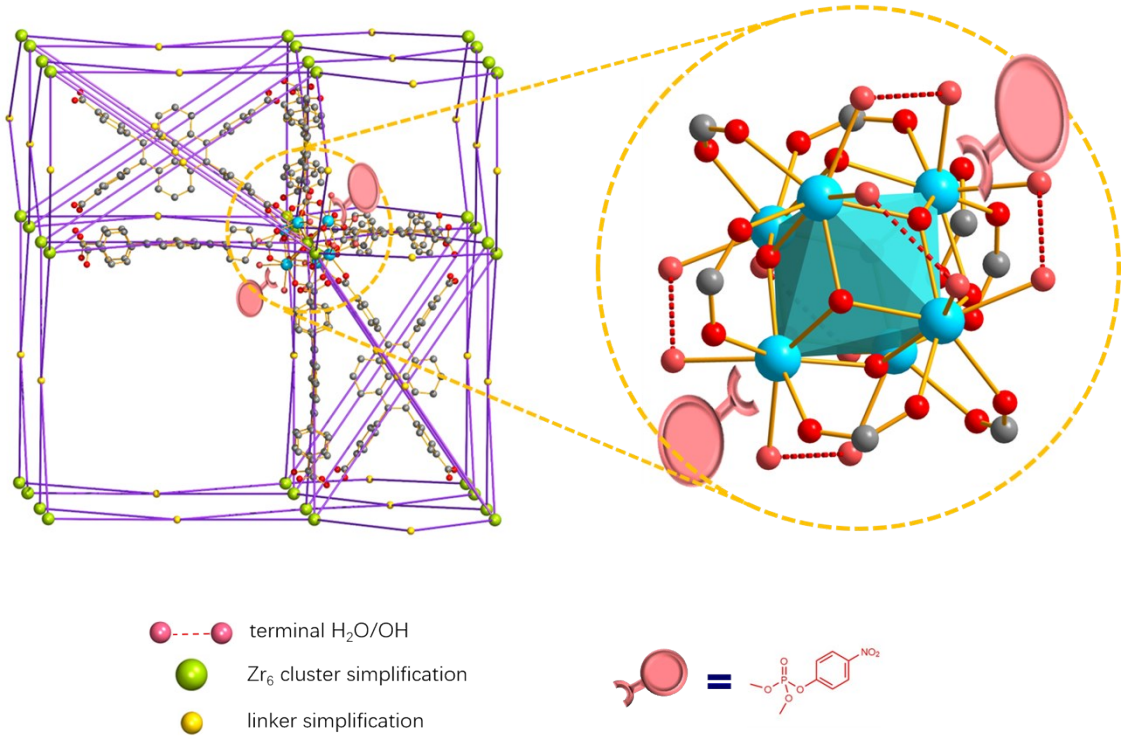


Figure S21. The accessibility of Zr_6 node in **NU-601**

SECTION S8. Catalyst Cycle Stability

Paralleling the protocol described by Z. Lu and et al. [6]

2.904 mg (6 mol%, 1.5 μmol Zr_6) **NU-601-1*μ*m** was added to 0.4 M N-ethylmorpholine solution (1.05 mL; 0.05 mL N-ethylmorpholine, 0.9 mL deionized water and 0.1 mL D_2O) in a 1.5 dram vial. The resulting mixture was sonicated for 1 min to disperse the MOF powder uniformly. DMNP (4.0 μL, 25 μmol) was added to the mixture and swirled for 10 sec. The reaction mixture was then transferred to an NMR tube and the spectrum was immediately measured; the first data point was collected 120 sec after the start of each cycle of reaction. The progress of the reaction was monitored in 1 min increments for 1 h. Between each cycle, the catalyst was washed with water for six times and soak in water overnight. It is clear that after the first cycle, reaction rates have slowed, but in the second cycle 100% conversion of substrate can be achieved within one hour, and in the third cycle

97% can be achieved after one hour. We attribute the slowing to partial product-inhibition, a topic we are addressing in detail elsewhere. We further characterized the catalyst after 3 cycles, by PXRD and SEM. From the accompanying figures the catalyst remains crystalline and that the crystallite morphology is unchanged.

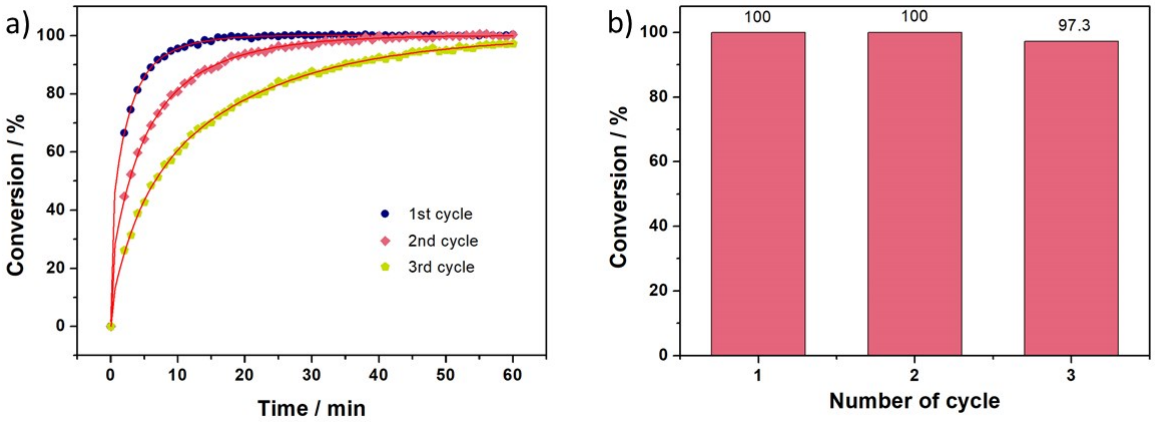


Figure S22. a) The kinetics of hydrolysis of DMNP in the presence of 1.5 μmol of **NU-601-1*μ*m** at room temperature for three cycles; b) The conversion of DMNP after one hour in the presence of 1.5 μmol of **NU-601-1*μ*m** at room temperature for three cycles.

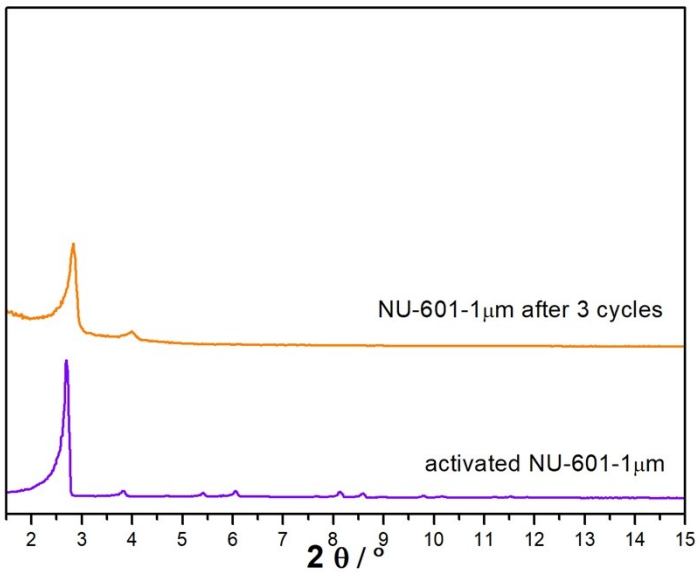


Figure S23. Comparison of PXRD patterns of **NU-601-1*μ*m** and **NU-601-1*μ*m** after 3 cycles of hydrolysis.

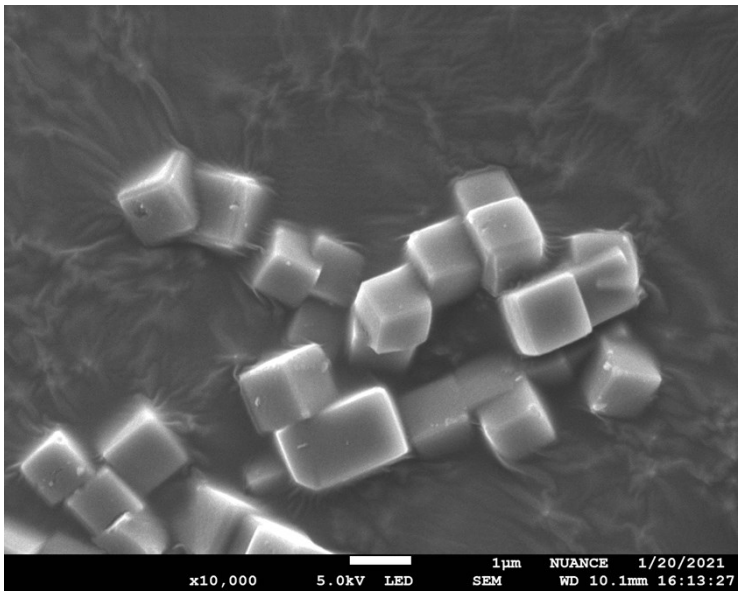


Figure S24. SEM image of **NU-601-1*µ*m** after 3 cycles of hydrolysis.

References

(1) Mondloch, J. E.; Bury, W.; Fairen-Jimenez, D.; Kwon, S.; DeMarco, E. J.; Weston, M. H.; Sarjeant, A. A.; Nguyen, S. T.; Stair, P. C.; Snurr, R. Q.et al. Vapor-phase metalation by atomic layer deposition in a metal-organic framework. *J Am Chem Soc* **2013,** *135* (28), 10294.

(2) Zhang, Q.; Su, J.; Feng, D.; Wei, Z.; Zou, X.; Zhou, H. C. Piezofluorochromic Metal-Organic Framework: A Microscissor Lift. *J Am Chem Soc* **2015,** *137* (32), 10064.

(3) Pang, J.; Yuan, S.; Qin, J.; Liu, C.; Lollar, C.; Wu, M.; Yuan, D.; Zhou, H. C.; Hong, M. Control the Structure of Zr-Tetracarboxylate Frameworks through Steric Tuning. *J Am Chem Soc* **2017,** *139* (46), 16939.

(4) Lyu, J.; Zhang, X.; Otake, K. I.; Wang, X.; Li, P.; Li, Z.; Chen, Z.; Zhang, Y.; Wasson, M. C.; Yang, Y.et al. Topology and porosity control of metal-organic frameworks through linker functionalization. *Chem Sci* **2019,** *10* (4), 1186.

(5) Pang, J.; Di, Z.; Qin, J. S.; Yuan, S.; Lollar, C. T.; Li, J.; Zhang, P.; Wu, M.; Yuan, D.; Hong, M.et al. Precisely Embedding Active Sites into a Mesoporous Zr-Framework through Linker Installation for High-Efficiency Photocatalysis. *J Am Chem Soc* **2020,** *142* (35), 15020.

(6) Lu, Z.; Liu, J.; Zhang, X.; Liao, Y.; Wang, R.; Zhang, K.; Lyu, J.; Farha, O. K.; Hupp, J. T. Node-Accessible Zirconium MOFs. *J Am Chem Soc* **2020,** *142* (50), 21110.