

## Supporting Information

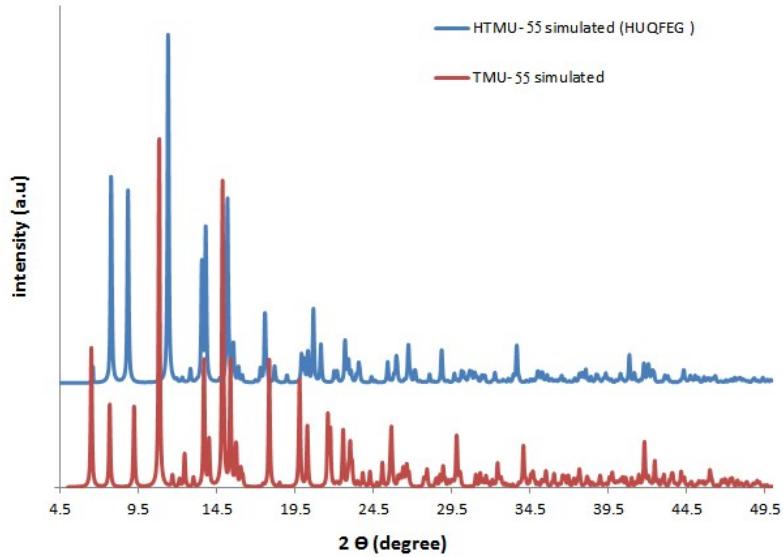
# Water-Stable Fluorinated Metal–Organic Frameworks (F-MOFs) with Hydrophobic Properties as Efficient and Highly Active Heterogeneous Catalysts in Aqueous Solution

**Table S1.** Crystal data and structural refinement for TMU-55.

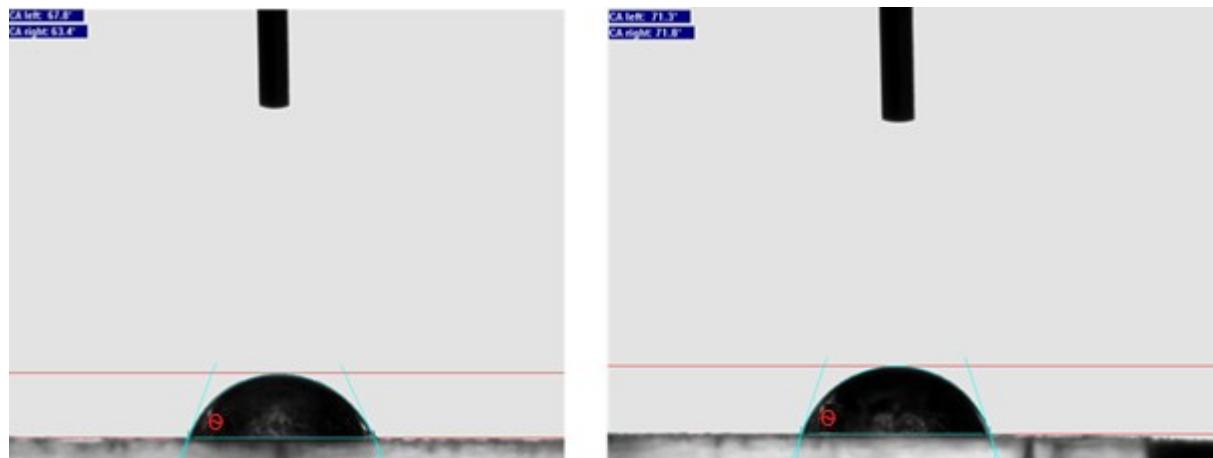
formula	C <sub>51</sub> H <sub>37</sub> F <sub>12</sub> N <sub>5</sub> O <sub>9</sub> Zn <sub>2</sub>
fw	1222.59
λ/Å	0.71073
T/K	150 (2)
crystal system	monoclinic
space group	C2/c
a/Å	27.5380(19)
b/Å	7.8870(6)
c/Å	23.3280(16)
α/°	90
β/°	99.2400(10)
γ/°	90
V/Å <sup>3</sup>	5000.9(6)
D <sub>calc</sub> /Mg.m <sup>-3</sup>	1.624
Z	4
μ (mm <sup>-1</sup> )	1.067
F(000)	2472
2θ (°)	63.57
R (int)	0.0927
GOOF	1.033
R <sub>1</sub> <sup>a</sup> (I>2σ(I))	0.0568
wR <sub>2</sub> <sup>b</sup> (I>2σ(I))	0.1279
CCDC No.	1852195

**Table S2.** Selected bond lengths (Å) and angles (°) for TMU-55.

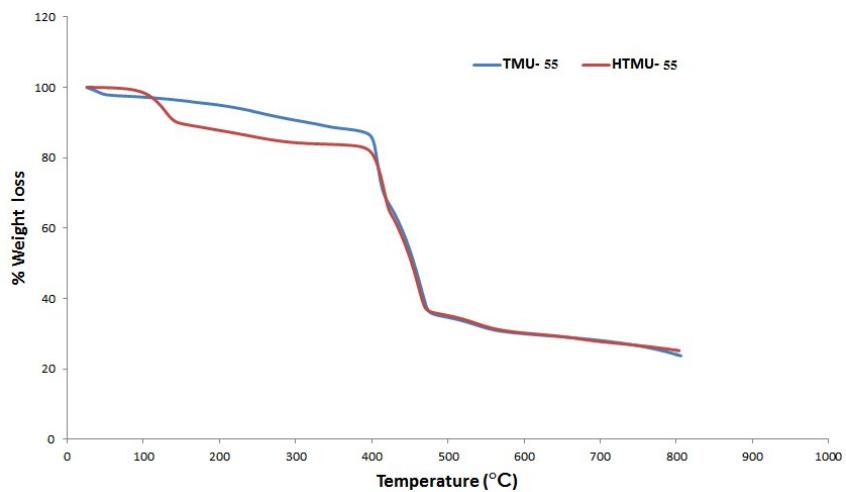
<b>Zn1-Zn1</b>	<b>2.9568(6)</b>	<b>O4-Zn1-N1</b>	<b>99.46(9)</b>	<b>O4- Zn1-O3</b>	<b>159.52(9)</b>
<b>Zn1-O1</b>	<b>2.048(2)</b>	<b>O4 -Zn1-O2</b>	<b>88.60(10)</b>	<b>N1-Zn1-O3</b>	<b>100.92(9)</b>
<b>Zn1-O2</b>	<b>2.044(2)</b>	<b>N1 -Zn1-O2</b>	<b>103.58(10)</b>	<b>O2-Zn1-O3</b>	<b>88.54(9)</b>
<b>Zn1-O3</b>	<b>2.044(2)</b>	<b>O4 -Zn1-O1</b>	<b>88.26(10)</b>	<b>O1-Zn1-O3</b>	<b>87.31(10)</b>
<b>Zn1-O4</b>	<b>2.043(2)</b>	<b>N1 -Zn1-O1</b>	<b>97.05(10)</b>	<b>C1-O3-Zn1</b>	<b>126.65(19)</b>
<b>Zn1-N1</b>	<b>2.026(2)</b>	<b>O2- Zn1-O1</b>	<b>159.37(10)</b>	<b>C1-O4-Zn1</b>	<b>128.06(19)</b>



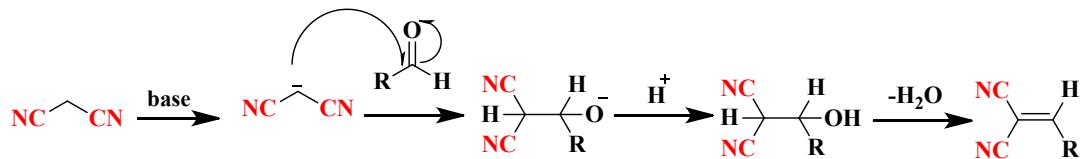
**Fig S1.** PXRD pattern calculated from the single crystal X-ray data of TMU-55 and HTMU-55 (HUQFEG).



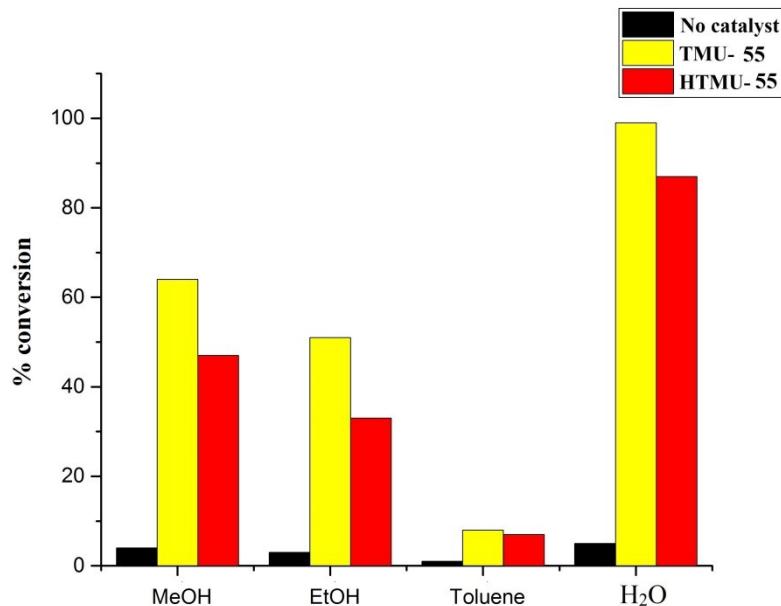
**Fig S2.** Contact angle analyses of TMU-55 (left) and HTMU-55 (right). The angle between this line and solid is  $\Theta$ .



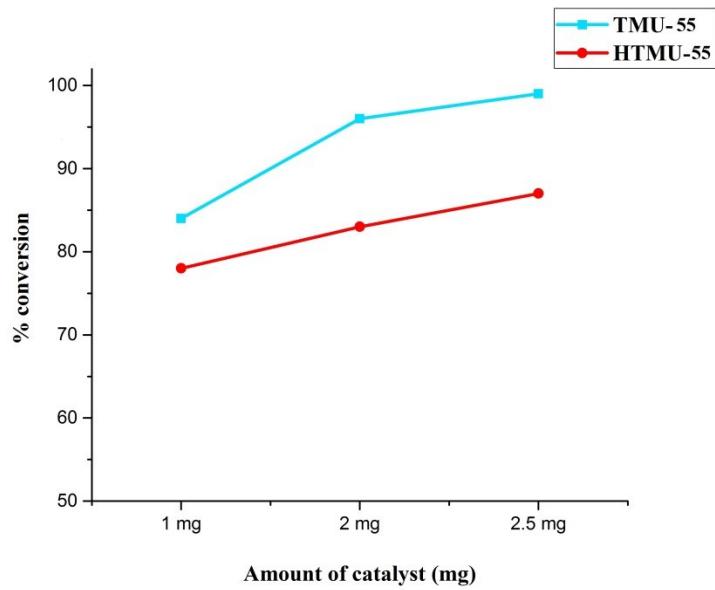
**Fig S3.** Thermogravimetric analysis of TMU-55 and HTMU-55.



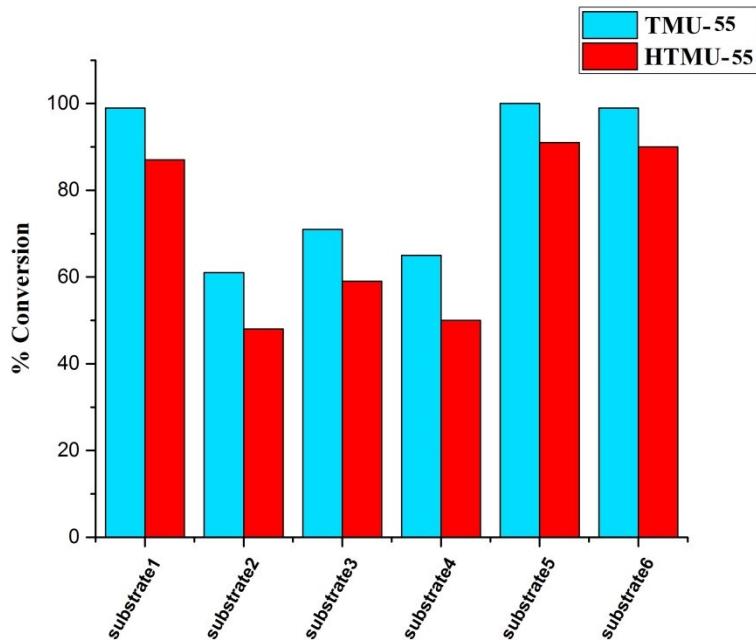
**Scheme S1.** Reaction mechanism for the Knoevenagel condensation reaction.



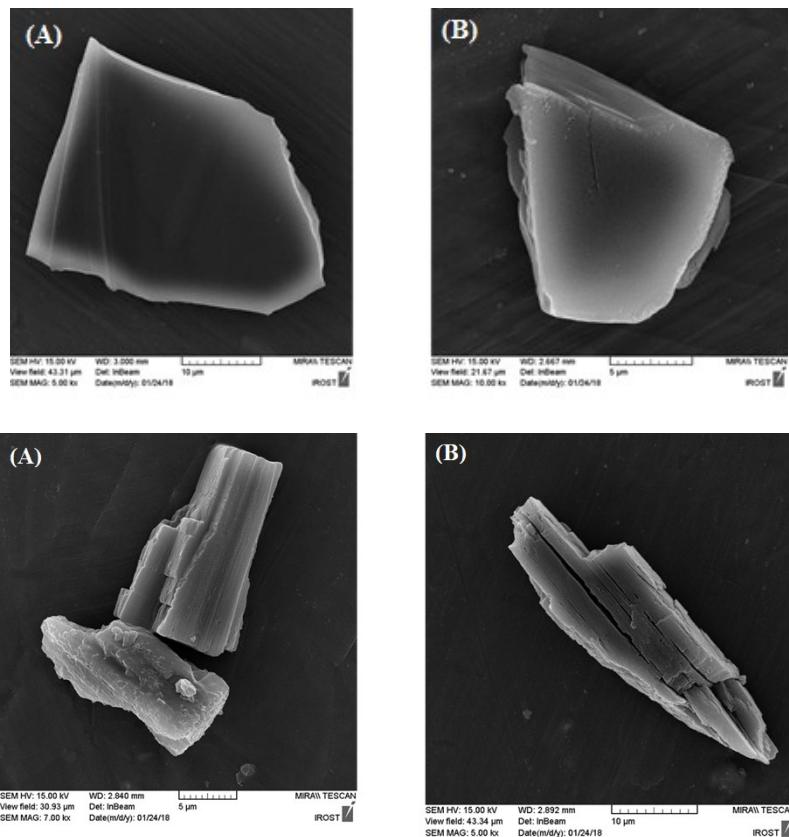
**Fig S4.** Reaction of benzaldehyde with malononitrile in the presence of TMU-55 and HTMU-55 in different solvents. Reaction conditions: benzaldehyde (0.2 mmol), malononitrile (0.5 mmol), 2.5 mg catalyst, solvent (3ml), r.t, 5 min.



**Fig S5.** Reaction of benzaldehyde with malononitrile in the presence of TMU-55 and HTMU-55 in different amount of catalysts. Reaction conditions: benzaldehyde (0.2 mmol), malononitrile (0.5 mmol), solvent ( $\text{H}_2\text{O}$ ): (3ml), r.t, 5 min.



**Fig S6.** The Knoevenagel condensation reaction catalyzed by two isoreticular F-MOFs catalysts (TMU-55 and HTMU-55) in the presence of aromatic aldehydes and ketone (The same as in Table 2). Reaction conditions: substrates (0.2 mmol), malononitrile (0.5 mmol), 2.5 mg catalyst, solvent:  $\text{H}_2\text{O}$  (3ml), r.t, 5 min.



**Fig S7.** SEM images of as-synthesized TMU-55 (up) and HTMU-55 (down) before (A) and after (B) catalysis reaction.