Supporting Information

Water-StableFluorinated 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	$C_{51}\ H_{37}\ F_{12}\ N_5\ O_9\ Zn_2$
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^3	5000.9(6)
D_{calc}/Mg.m^{-3}	1.624
Z	4
μ (mm^{-1})	1.067
F(000)	2472
2θ (˚)	63.57
R (int)	0.0927
GOOF	1.033
$R_1{}^a$(I>2σ(I))	0.0568
$wR_2{}^b$(I>2σ(I))	0.1279
CCDC No.	1852195

Table S2. Selected bond lengths (ºA) and angles (º) for TMU-55.

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

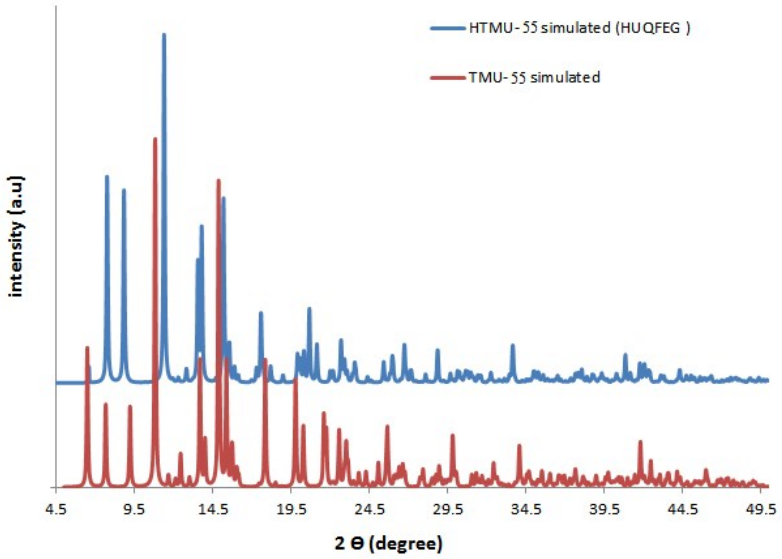


Fig S1. PXRD pattern calculated from the single crystal X-ray data of TMU-55 and HTMU-55 (HUQFEG).

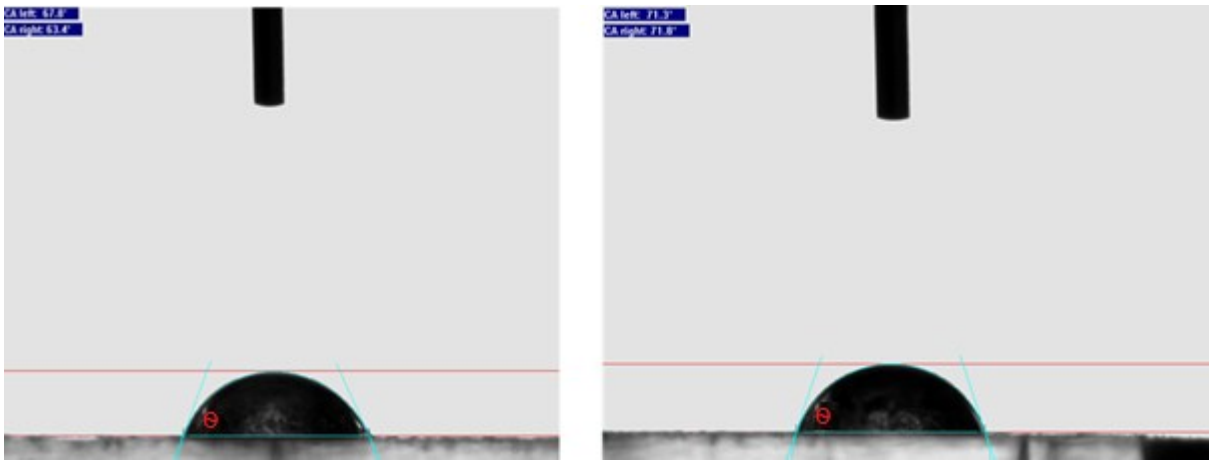


Fig S2.Contact angle analyses of TMU- 55 (left) and HTMU-55 (right). The angle between this line and solid is Θ.

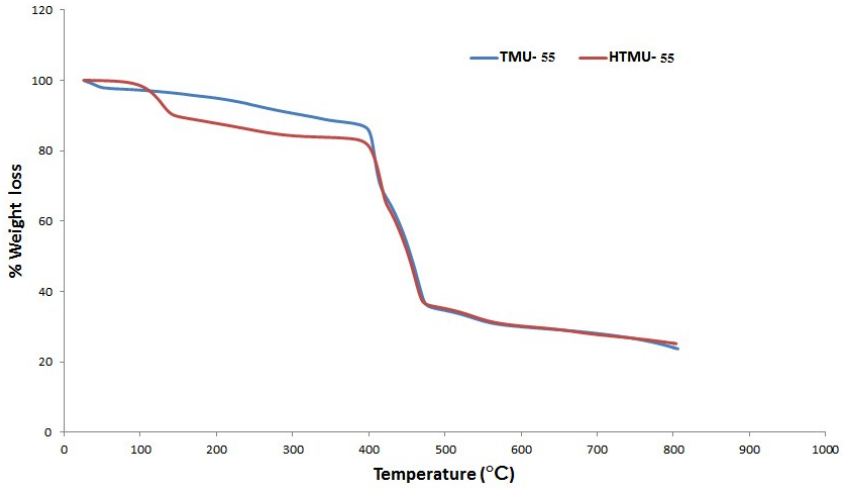
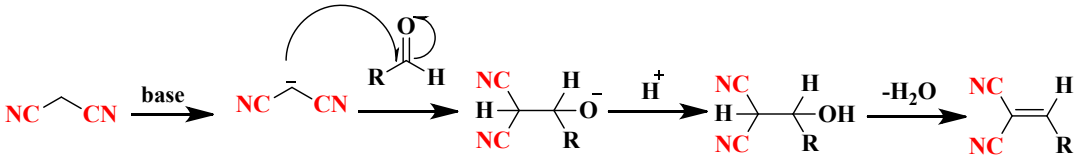


Fig S3. Thermogravimetric analysis of TMU-55 and HTMU-55**.**



Scheme S1. Reaction mechanism for the Knoevenagel condensation reaction.

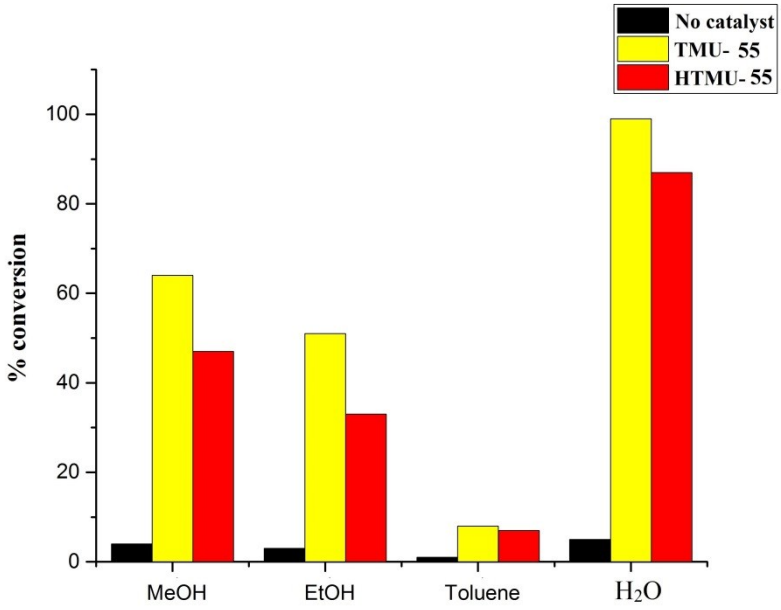


Fig S4. Reaction of benzaldehyde with malononitrile in the presence of TMU-55 and HTMU-55 in different solvents. Reaction conditions: benzaldehyde (0.2 mmol), malononitrile (0.5 mmol), 2.5 mg catalyst, solvent (3ml), r.t, 5 min.

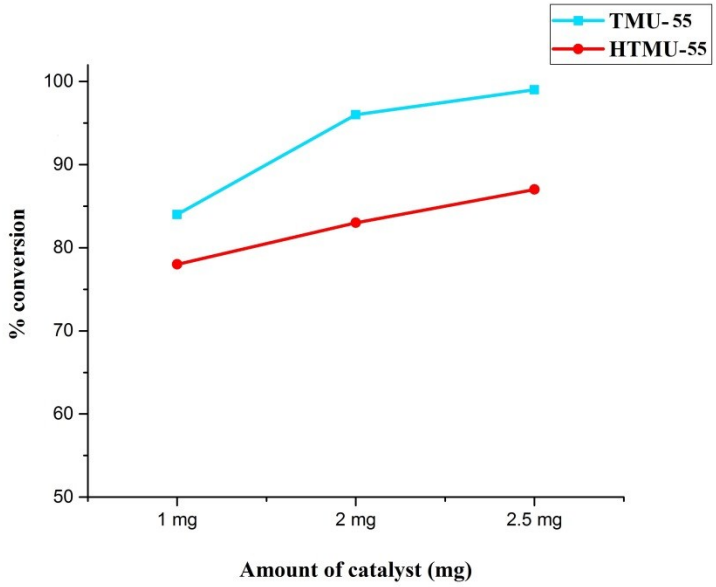


Fig S5. Reaction of benzaldehyde with malononitrile in the presence of TMU-55 and HTMU-55 in different amount of catalysts. Reaction conditions: benzaldehyde (0.2 mmol), malononitrile (0.5 mmol), solvent (H_2O): (3ml), r.t, 5 min.

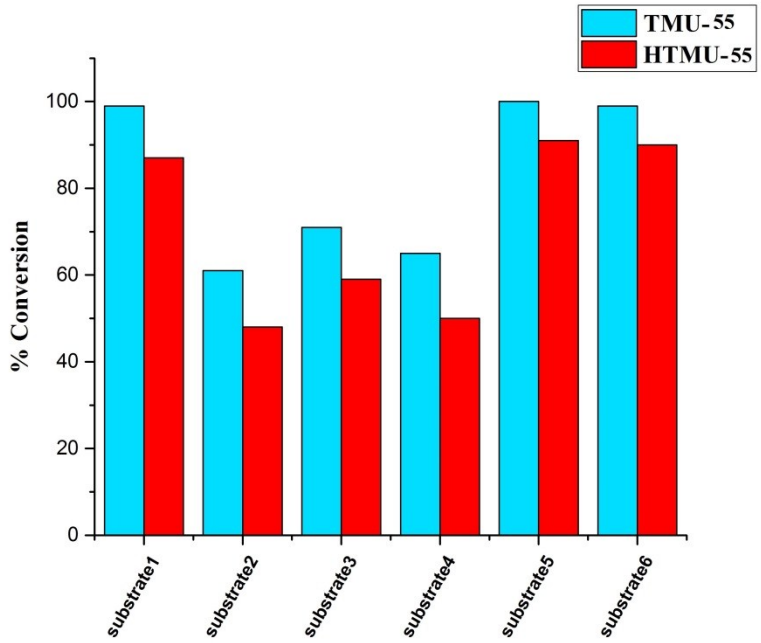


Fig S6. The Knoevenagel condensation reaction catalyzed by two isoreticular F-MOFs catalysts (TMU-55 and HTMU-55) in the presence of aromatic aldehydes and ketone (The same as in Table 2). Reaction conditions: substrates (0.2 mmol), malononitrile (0.5 mmol), 2.5 mg catalyst, solvent: H_2O (3ml), r.t, 5 min.

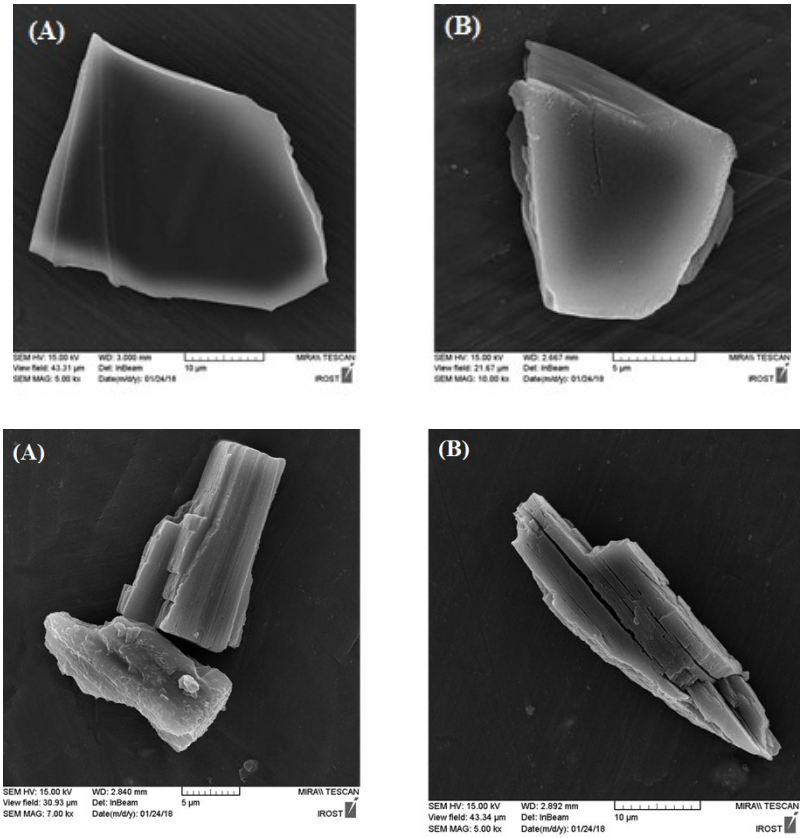


Fig S7. SEM images of as-synthesized TMU-55 (up) and HTMU-55 (down) before (A) and after (B) catalysis reaction.