Supporting information for

Ultrafast Post-Synthetic Modification of a Pillared Cobalt(II)-Based Metal-Organic Framework via Sulfurization of Their Pores for High-Performance Supercapacitors

Reza Abazari,[a] Soheila Sanati,[a] Ali Morsali,[a,*] Alexandra M. Z. Slawin,[b] Cameron L. Carpenter-Warren,[b] Wei Chen,[c,d] and Anmin Zheng[c,e]

[a] *Department of Chemistry, Faculty of Basic Sciences, Tarbiat Modares University, Tehran, Iran, 14115–175*

[b] *School of Chemistry, University of St Andrews, St Andrews, Fife, UK, KY16 9ST*

[c] *State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, the Chinese Academy of Sciences, Wuhan 430071, P. R. China*

[d] *University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

[e] *Wuhan-Oxford Joint Catalysis Laboratory, Wuhan 430071, P. R. China*

General experimental procedures

Materials and physical techniques

All starting materials for the synthesis were purchased from commercial providers and used without further purification (Sigma-Aldrich, Merck and the others). The N,N'-bis-(4-pyridylformamide)-1,4-benzenediamine) (bpfb) ligand was prepared by following the synthesis steps reported in the work of Sheykhan et al.[1] IR spectra were recorded using a Nicolet Fourier Transform IR, Nicolet 100 spectrometer in the range 400-4000 cm^{-1} using the KBr disk technique. The thermal behavior of the samples was analyzed by a PL-STA 1500 apparatus working under a nitrogen atmosphere and at the thermal rate of 10 ℃ min^{-1}. X-ray powder diffraction (PXRD) measurements were performed using a Philips X'pert diffractometer with monochromated Cu-Kα (λ=1.54056 A) radiation. The N_2 adsorption/desorption isotherm was measured at 77 K using a Micromeritics ASAP 2020 analyzer. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The inductively coupled plasma (ICP) analysss was performed on a Varian ICP-OES VISTA-PRO CCD instrument. A CHNS Thermo Scientific Flash 2000 elemental analyzer was used to analyze elemental contributions to the samples. Finally, melting points were measured on an Electrothermal 9100 apparatus.

Collection and reduction of X-ray data

X-ray diffraction data was collected at 125 K using a Rigaku SCXmini CCD diffractometer with a SHINE monochromator [Mo Kα radiation (λ = 0.71075 Å)].

Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. A multiscan absorption correction was applied by using CrysAlisPro[2] Structures were solved by

dual space methods (SHELXT) and refined by full-matrix least-squares against F^2 (SHELXL-2013).[3] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model, with the exception of the N-H's, which were refined freely. All calculations were performed using Olex 2.[4] The occupancy of the second DMF molecule was set to 0.5, in order to obtain consistent thermal parameters - the formula reflects this. Selected crystallographic data are presented in Table S1 to S3.

Activation method

TMU-61 was heated for 48 h at 140 ℃ in a vacuum oven. The framework of TMU-61 conserved its structure after elimination of the guest solvent molecules.

Stability of TMU-61

*Thermostability***:** To test the thermal stability of TMU-61, 70 mg of it was heated from 200 to 400 ℃ using a 50 ℃ gradient.

Stability in some solvents: Chemical stability of TMU-61 was assessed by immersing 70 mg of it in absolute ethanol, water, CH_2Cl_2, *n*-hexane, and acetonitrile for 48 h at 25 ℃.

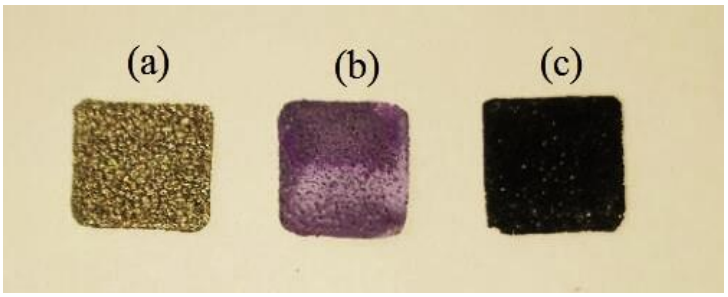

Figure S1. Bare of Ni foam (a), TMU-61 coated on Ni foam substrate (b), and S-TMU-61 coated on Ni foam substrate (c).

Figure S2. Light microscope image of solvated bulk TMU-61 crystals.

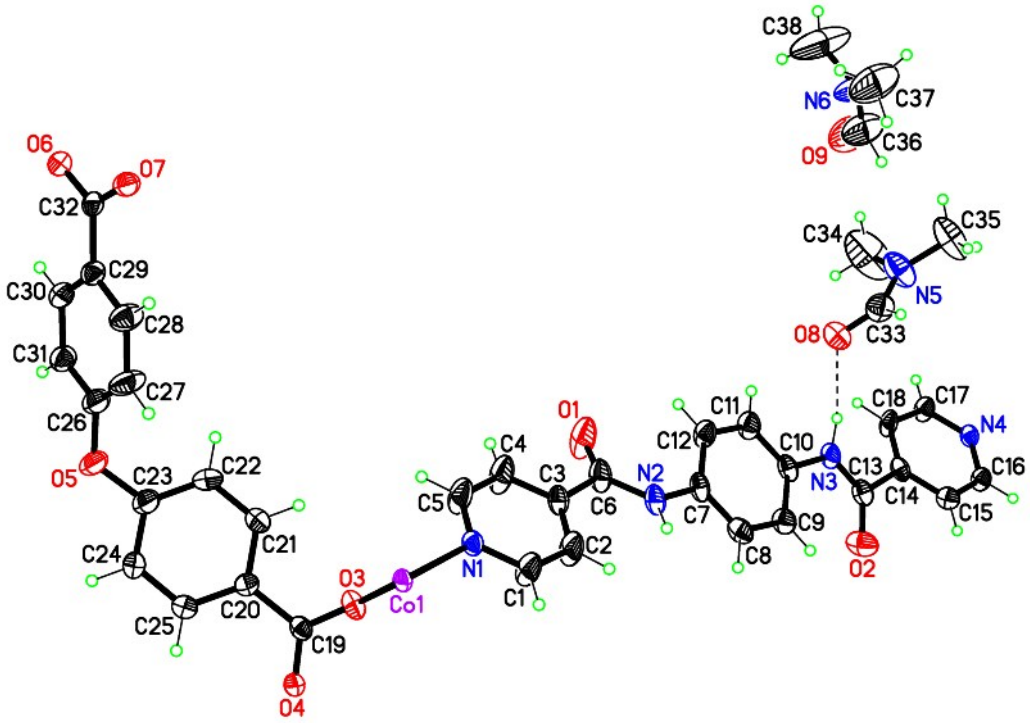

Figure S3. The asymmetric unit of TMU-61 with the thermal ellipsoids of non-hydrogen atoms shown at 50% probability and hydrogen atoms drawn as spheres of arbitrary radii.

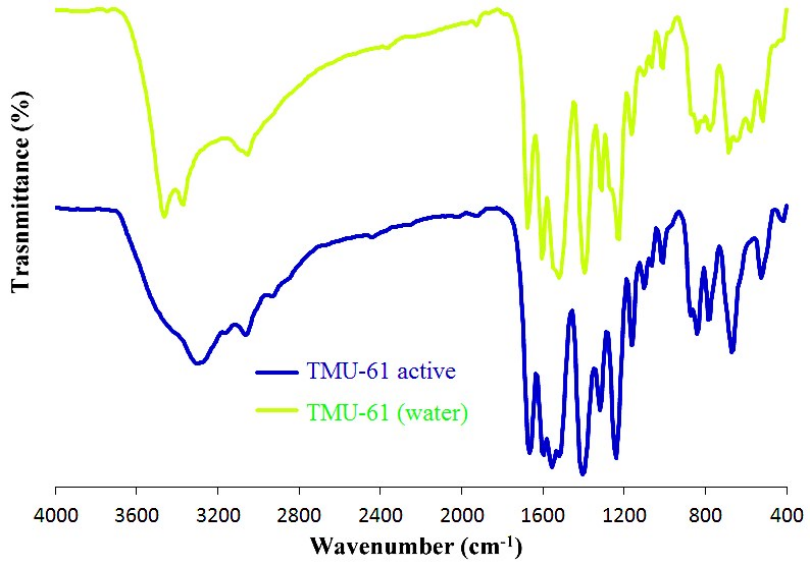

Figure S4. The FT-IR spectra of activated TMU-61 before (blue curve) and after 72 h (green curve) immersion into the aqueous solution.

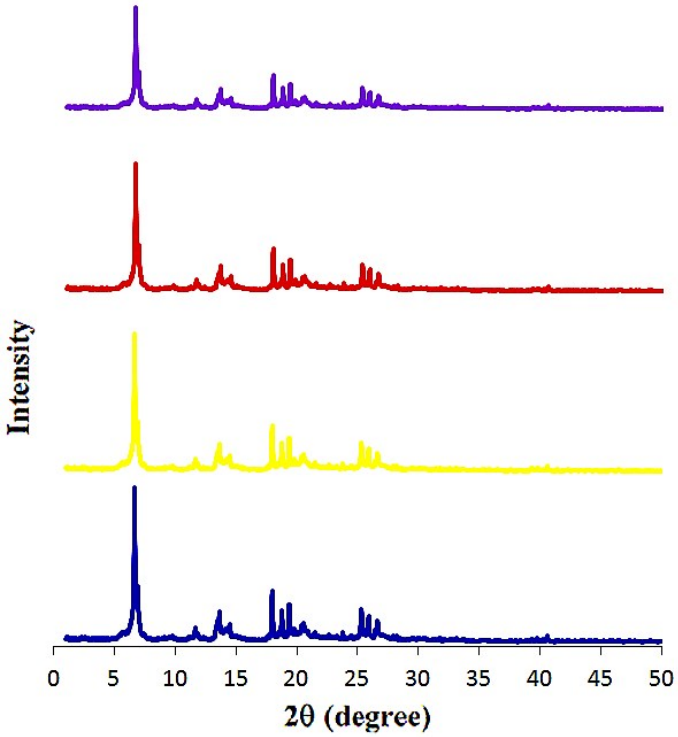

Figure S5. The PXRD patterns of the (a) as-synthesized TMU-61 (blue line) and the TMU-61 calcined in air at (b) 200 ℃ (yellow line), (c) 250 ℃ (brown line), and (d) 350 ℃ (purple line).

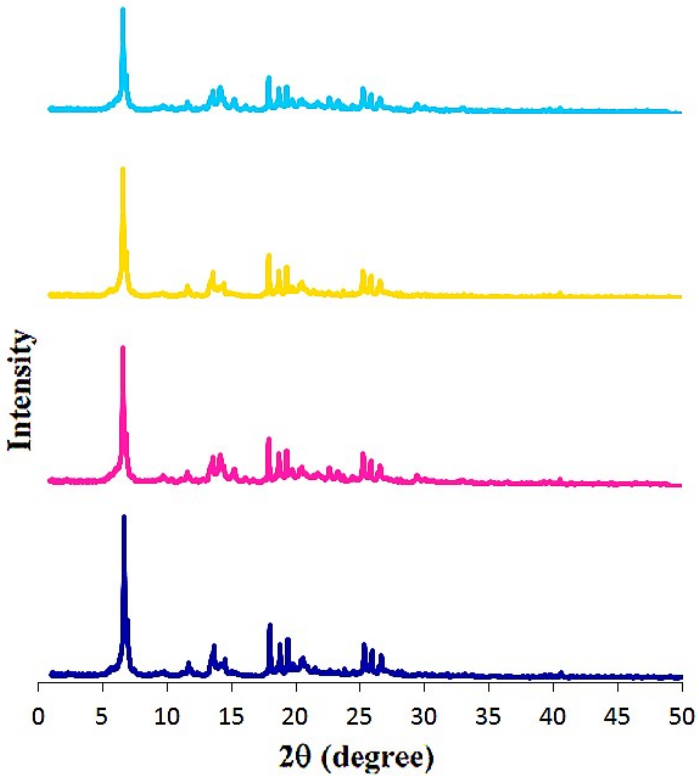

Figure S6. The PXRD patterns of the (a) as-synthesized TMU-61 (blue line) and the TMU-61 immersed in (b) absolute ethanol (pink line), (c) acetonitrile (orange line), and (d) water (cyan line).

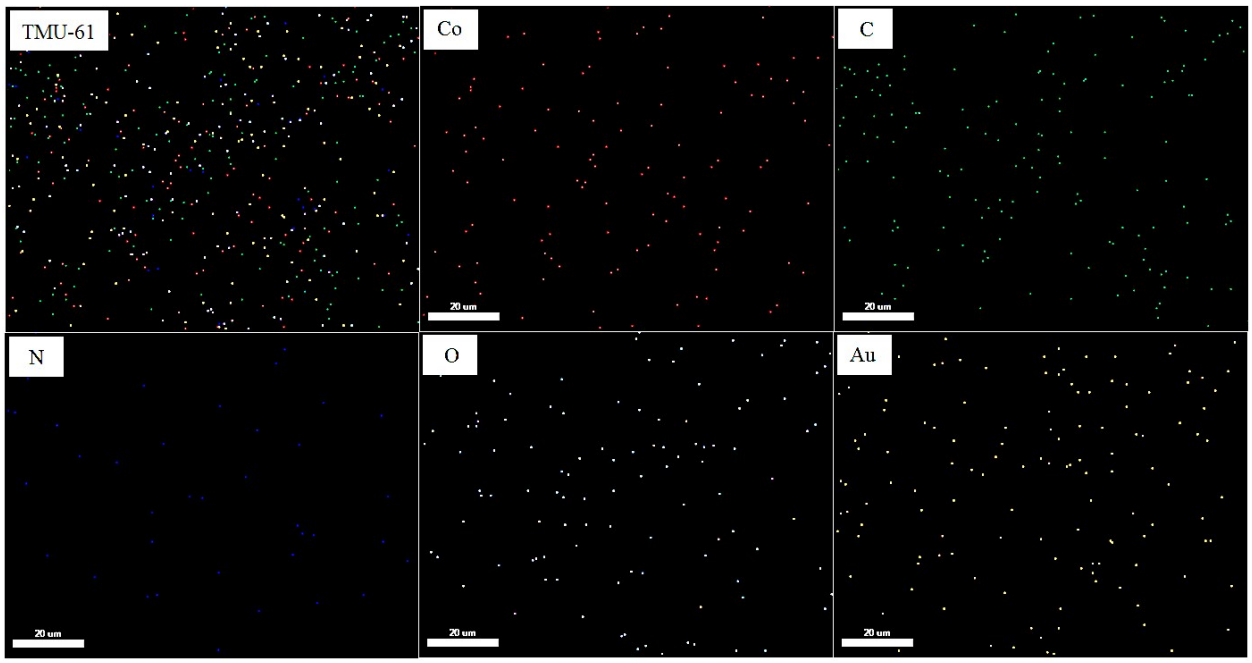

Figure S7. The elemental mapping of the TMU-61.

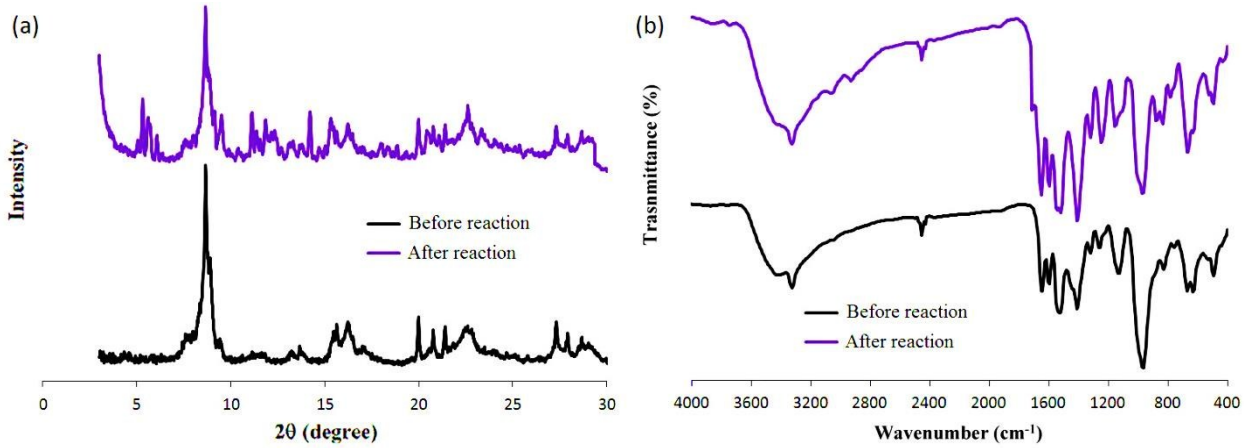

Figure S8. The XRD patterns (a) and FT-IR spectra (b) of the S-TMU-61 before and after 6000 cycles.

Table S1. Crystal data and structure refinement for TMU-61.

Identification code	TMU-61
Empirical formula	$C_{73}H_{65}Co_2N_{11}O_{17}$
Formula weight	1486.22
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.8591(11)
b/Å	14.9188(15)
c/Å	15.0675(13)
α/°	112.424(9)
β/°	99.484(8)
γ/°	106.304(9)
Volume/Å^3	1871.7(4)
Z	1
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	0.517
F(000)	770.0
Crystal size/mm^3	0.2 × 0.14 × 0.06
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.278 to 63.716
Index ranges	$-13 \leq h \leq 14$, $-20 \leq k \leq 21$, $-22 \leq l \leq 22$
Reflections collected	23590
Independent reflections	11685 [R_{int} = 0.0722, R_{sigma} = 0.1427]
Data/restraints/parameters	11685/26/499
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0906, wR_2 = 0.2020
Final R indexes [all data]	R_1 = 0.1750, wR_2 = 0.2382
Largest diff. peak/hole / e Å^{-3}	0.92/-0.55

Table S2. Bond Lengths for TMU-61.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	O3	2.007(3)	C7	C12	1.382(6)
Co1	O4[1]	2.053(3)	C8	C9	1.383(6)
Co1	O6[2]	2.257(3)	C9	C10	1.397(6)
Co1	O7[2]	2.133(3)	C10	C11	1.385(7)
Co1	N1	2.174(3)	C11	C12	1.392(6)
Co1	N4[3]	2.168(3)	C13	C14	1.506(6)
O1	C6	1.222(6)	C14	C15	1.383(6)
O2	C13	1.232(6)	C14	C18	1.388(6)
O3	C19	1.271(5)	C15	C16	1.376(6)
O4	Co1[1]	2.053(3)	C17	C18	1.390(6)
O4	C19	1.252(5)	C19	C20	1.486(6)
O5	C23	1.390(6)	C20	C21	1.386(6)
O5	C26	1.386(6)	C20	C25	1.385(6)
O6	Co1[2]	2.257(3)	C21	C22	1.390(7)
O6	C32	1.284(5)	C22	C23	1.379(7)
O7	Co1[2]	2.133(3)	C23	C24	1.370(7)
O7	C32	1.271(5)	C24	C25	1.387(7)
N1	C1	1.317(6)	C26	C27	1.379(7)
N1	C5	1.321(6)	C26	C31	1.376(7)
N2	C6	1.341(6)	C27	C28	1.396(7)
N2	C7	1.424(5)	C28	C29	1.396(6)
N3	C10	1.419(5)	C29	C30	1.383(6)
N3	C13	1.351(6)	C29	C32	1.481(6)
N4	Co1[4]	2.168(3)	C30	C31	1.397(6)
N4	C16	1.340(6)	O9	C36	1.151(17)
N4	C17	1.337(5)	N6	C36	1.293(18)
C1	C2	1.380(6)	N6	C37	1.385(18)
C2	C3	1.354(7)	N6	C38	1.451(18)
C3	C4	1.375(7)	O8	C33	1.232(6)
C3	C6	1.500(6)	N5	C33	1.311(7)
C4	C5	1.388(7)	N5	C34	1.459(9)
C7	C8	1.383(7)	N5	C35	1.444(8)

[1]-X,2-Y,2-Z; [2]-X,2-Y,1-Z; [3]-1+X,1+Y,+Z; [4]1+X,-1+Y,+Z

Table S3. Selected bond angles (°) for TMU-61.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	Co1	O4[1]	108.67(13)	C10	C11	C12	121.2(4)
O3	Co1	O6[2]	157.89(12)	C7	C12	C11	119.7(4)
O3	Co1	O7[2]	97.59(13)	O2	C13	N3	123.8(4)
O3	Co1	N1	85.35(13)	O2	C13	C14	119.3(4)
O3	Co1	N4[3]	92.69(13)	N3	C13	C14	116.9(4)
O4[1]	Co1	O6[2]	92.84(12)	C15	C14	C13	117.5(4)
O4[1]	Co1	O7[2]	152.85(12)	C15	C14	C18	118.0(4)
O4[1]	Co1	N1	87.55(12)	C18	C14	C13	124.5(4)
O4[1]	Co1	N4[3]	95.62(13)	C16	C15	C14	119.4(4)
O7[2]	Co1	O6[2]	60.49(11)	N4	C16	C15	123.7(4)
O7[2]	Co1	N1	87.80(13)	N4	C17	C18	123.9(4)
O7[2]	Co1	N4[3]	89.81(13)	C14	C18	C17	118.5(4)
N1	Co1	O6[2]	90.63(12)	O3	C19	C20	117.6(4)
N4[3]	Co1	O6[2]	90.19(12)	O4	C19	O3	122.9(4)
N4[3]	Co1	N1	176.69(14)	O4	C19	C20	119.6(4)
C19	O3	Co1	141.5(3)	C21	C20	C19	119.6(4)
C19	O4	Co1[1]	125.2(3)	C25	C20	C19	121.2(4)
C26	O5	C23	119.2(4)	C25	C20	C21	119.1(4)
C32	O6	Co1[2]	86.7(2)	C20	C21	C22	120.1(4)
C32	O7	Co1[2]	92.6(2)	C23	C22	C21	119.9(4)
C1	N1	Co1	121.6(3)	C22	C23	O5	122.9(4)
C1	N1	C5	115.7(4)	C24	C23	O5	116.7(4)
C5	N1	Co1	122.7(3)	C24	C23	C22	120.3(4)
C6	N2	C7	127.1(4)	C23	C24	C25	119.9(5)
C13	N3	C10	127.2(4)	C20	C25	C24	120.6(4)
C16	N4	Co1[4]	123.4(3)	C27	C26	O5	122.9(4)
C17	N4	Co1[4]	120.1(3)	C31	C26	O5	116.3(4)
C17	N4	C16	116.5(4)	C31	C26	C27	120.6(4)
N1	C1	C2	124.3(5)	C26	C27	C28	119.1(5)
C3	C2	C1	120.4(5)	C29	C28	C27	121.1(5)
C2	C3	C4	116.0(4)	C28	C29	C32	119.0(4)
C2	C3	C6	124.4(4)	C30	C29	C28	118.8(4)
C4	C3	C6	119.6(4)	C30	C29	C32	122.2(4)
C3	C4	C5	120.2(5)	C29	C30	C31	120.2(4)
N1	C5	C4	123.4(5)	C26	C31	C30	120.2(4)
O1	C6	N2	124.2(4)	O6	C32	C29	120.8(4)
O1	C6	C3	120.1(4)	O7	C32	O6	120.0(4)
N2	C6	C3	115.7(4)	O7	C32	C29	119.2(4)
C8	C7	N2	117.7(4)	C36	N6	C37	132.1(12)

C12	C7	N2	122.8(4)	C36	N6	C38	111.0(13)
C12	C7	C8	119.4(4)	C37	N6	C38	115.9(12)
C7	C8	C9	121.1(4)	O9	C36	N6	133.5(15)
C8	C9	C10	119.9(4)	C33	N5	C34	120.8(6)
C9	C10	N3	123.1(4)	C33	N5	C35	123.4(5)
C11	C10	N3	118.2(4)	C35	N5	C34	115.7(6)
C11	C10	C9	118.7(4)	O8	C33	N5	125.6(5)

[1]-X,2-Y,2-Z; [2]-X,2-Y,1-Z; [3]-1+X,1+Y,+Z; [4]1+X,-1+Y,+Z

Table S4. Hydrogen bonding information for TMU-61.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	H2	O6[1]	0.91(4)	2.11(4)	3.003(5)	167(5)
N3	H3	O8	0.94(4)	1.98(4)	2.888(6)	164(6)

[1]1+X,+Y,1+Z

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