Supplementary Information

Mechanosynthesis of new azine-functionalized Zn(II) Metalorganic frameworks for improved catalytic performance

Mohammad Yaser Masoomi^a, Saeideh Beheshti^a and Ali Morsali^{*a}

^a Department of Chemistry, Faculty of Sciences, TarbiatModares University, P.O. Box 14115-175, Tehran, Islamic Republic of Iran

Email: Morsali_a@modares.ac.ir, Morsali_a@yahoo.com

Experimental Section

Materials and Physical Techniques

Zinc(II) nitrate hexahydrate, zinc(II) acetate dihydrate and 4,4'-oxybis(benzoic acid) (H₂oba) were purchased from Aldrich and Merck Company and used as received. The ligands 1,4bis(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb), 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (4-bpdh) and N^1,N^4 -bis((pyridin-4-yl)methylene)benzene-1,4-diamine (4-bpmb) were synthesized according to previously reported methods.¹ Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded using Thermo Nicolet IR 100 FT-IR. The thermal behaviour was measured with a PL-STA 1500 apparatus with the rate of 10 °C.min⁻¹ in a static atmosphere of argon. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromated Cu-K_a radiation.

Data collection for **TMU-6** was performed on a Bruker SMART APEX2 CCD area detector X-ray diffractometer with graphite-monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by refinement of F² against all reflections. Structure solution and refinement were accomplished using SIR97, SHELXL97 and WinGX.² GC runs were performed on an Echrom GC A90 gas chromatograph.

$[Zn_2(oba)_2(4-bpdb)]_n.(DMF)_x$ (TMU-4) and $[Zn(oba)(4-bpdh)_{0.5}]_n.(DMF)_y$ (TMU-5), were synthesized according previously paper (where x and y vary depending on the synthetic methodology used; for mechanosynthesis: x = y = 0; for conventional heating: x =2 and y = 1.5).³

In the mechanochemical synthesis, the products were heated at 100 °C for 8 h before and after washing with DMF.

Water stability test of TMU-4 and TMU-5

The as synthesized **TMU-4** and **TMU-5** were soaked in water for 45 days to see whether they are stable in water or not. A new crystalline phase was formed as confirmed by PXRD (Fig. S5). Single crystal X-ray diffraction experiments were not successful due to the poor quality of the crystals after being exposed in H_2O .³

Synthesis of $[Zn(oba)(4-bpmb)_{0.5}]_n.(DMF)_z$ (TMU-6; where z varies depending on the synthetic methodology used; for mechanosynthesis: z = 0; for conventional heating: z = 1.5) Solvothermal reaction: Brown crystals of TMU-6 were obtained using the same reaction conditions used for the isolation of TMU-4 but using 4-bpmb instead of 4-bpdb $(Zn(NO_3)_2.6H_2O \ (0.297 \text{ g}, 1 \text{ mmol}), H_2\text{oba} \ (0.258 \text{ g}, 1 \text{ mmol}) 4-bpmb \ (0.143 \text{ g}, 0.5 \text{ mmol}),.$ Yield: 0.373 g (65% based on oba). IR data (KBr pellet, v/cm⁻¹):selected bands: 654(m), 773(m), 878(m), 1016(m), 1089(m), 1159(s), 1233(vs), 1404(vs), 1499(m), 1609(vs), 1675(s) and 3421(w-br). Elemental analysis (%) calculated for

[Zn(C₁₄O₅H₈)(C₁₈H₁₄N₄)_{0.5}]·(C₃NOH₇)_{1.5}: C: 57.6, H: 4.6, N: 8.5; Found: C: 57.1, H: 4.2, N: 8.9.

Mechanochemical synthesis:

TMU-6 was synthesized by grinding $Zn(OAc)_2 \cdot 2H_2O$ (1 mmol), H_2oba (1 mmol) and 4-bpmb (0.5 mmol) by hand for 15 minutes. The resulting powder was washed with small amounts of DMF in order to remove any unreacted starting material. The product was heated at 100 °C for 8 h before and after washing with DMF (yield: 90%). Elemental analysis (%) calculated for $[Zn(C_{14}O_5H_8)(C_{18}H_{14}N_4)_{0.5}]$: C: 59.5, H: 3.2, N: 6.0; Found: C: 58.9, H: 3.5, N: 6.2.

Water stability test of TMU-6

The as synthesized **TMU-6** was soaked in water for 20 days to see whether **TMU-6** is stable in water or not. The XRD patterns are consistent confirming that the structure has a high water-stability (Fig. S5).

Knoevenagel condensation

To a mixture of malononitrile (1.1 mmol) and benzaldehyde (1 mmol), was added 2 mol% of catalyst in different solvents. The resulting mixture was stirred at room temperature for 30 minutes. The course of the reaction was followed by GC analysis. Reaction mixture diluted with 5 mL of CH₂Cl₂. On completion of the reaction, the catalyst was recovered by centrifugation and the supernatant liquid was collected and evaporated to dryness. Pure product was obtained by recrystallization from EtOH. The catalyst was washed repeatedly with EtOAc, dried and reused when required.

Identification code	TMU-6
Empirical formula	$C_{27.50}H_{25.50}N_{3.50}O_{6.50}Zn$
Formula weight	574.38
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 14.900(4) Å
	b = 24.324(6) Å
	c = 16.253(6) Å
	$\alpha = 90.00^{\circ}$
	$\beta = 113.233(4)^{\circ}$
	$\gamma = 90.00^{\circ}$
Cell volume, Å ³	5413(3)
Z value	8
Density (calc.) (g.cm ⁻³)	1.410
Absorption coefficient	0.957 mm ⁻¹
F(000)	2376
Crystal size	$0.19\times0.16\times0.04\ mm^3$
θ range for data collection	1.67 to 29.00°
Index ranges	-20≤h≤20
	-33≤k≤33
	-22≤1≤22
Reflections collected/unique	41525/7129 [R(int) = 0.0940]
Completeness to theta = 29.00°	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.962 and 0.873
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	7129/4/341
Goodness-of-fit on F ²	1.161
Final R indices (for 4966 rfln with I> $2.00\sigma(I)$)	R1 = 0.0780, wR2 = 0.2189
R indices (all data)	R1 = 0.1083, wR2 = 0.2387
Extinction coefficient	0.0032(5)
Largest diff. Peak, hole	0.897 and -0.883 e.Å ⁻³

 Table S1. Crystal data and structure refinement of TMU-6.

Zn(1)-O(5)#1	1.965(3)	O(5)#1-Zn(1)-O(4)#2	103.67(13)
Zn(1)-O(4)#2	1.999(3)	O(5)#1-Zn(1)-O(2)	136.17(14)
Zn(1)-O(2)	2.010(3)	O(4)#2-Zn(1)-O(2)	98.51(12)
Zn(1)-N(1)	2.043(4)	O(5)#1-Zn(1)-N(1)	106.49(14)
Zn(1)-O(3)	2.297(3)	O(4)#2-Zn(1)-N(1)	98.30(13)
Zn(1)-C(7)	2.493(4)	O(2)-Zn(1)-N(1)	107.08(14)
		O(5)#1-Zn(1)-O(3)	89.77(12)
		O(4)#2-Zn(1)-O(3)	158.84(12)
		O(2)-Zn(1)-O(3)	61.01(11)
		N(1)-Zn(1)-O(3)	93.33(13)
		C(4)-O(1)-C(8)	115.4(3)

Table S2. Selected bond lengths /Å and angles /° for TMU-6.

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,-z+3/2 #2 x+1/2,y+1/2,z #3 x-1/2,y-1/2,z #4 -x+1/2,y-1/2,-z+3/2 #5 -x,-y,-z #6 -x+1,y,-z+5/2 #7 -x,y,-z+3/2

Entry	Catalyst	Yield (%)
1	Zn(OAc) ₂	27
2	4-bpdb	32
3	4-bpdh	36
4	4-bpmb	8

Table S3. Knoevenagel condensation reaction with the synthetic precursors of TMU-4, TMU-**5** and TMU-6 as a catalyst.^a

^a Reaction conditions: H₂O as solvent, 2 mol% catalyst, r.t, 30 minutes.

Table S4. Catalytic performance of **TMU-4**, **TMU-5** and **TMU-6**, obtained by mechanochemical synthesis and by conventional heating in H_2O as solvent.

	Mechanosynthesis	Conventional heating
TMU-4	45	46
TMU-5	100	100
TMU-6	38	38



Fig. S1 Perspective views of the a) TMU-4, b) TMU-5 and c) TMU-6 structural units.



Fig. S2. Thermogravimetric profiles of (a) TMU-4, (b) TMU-5 and (c) TMU-6 isolated by either solvothermal reaction or mechanosynthesis. The TGA curve of TMU-4 (solvothermal reaction) shows a plateau in the range of 30 to 100 °C followed by a continuous loss of 16.5% (expected: 14.6%) up to 315 °C, which can be ascribed to removal of the guest DMF molecules. Similarly, the TGA profile of TMU-5 also shows a plateau in the range of 30 to 100 °C and a loss of DMF molecules of 18% (expected: 19.9%) in the temperature range of 100 to 190 °C. TMU-5 is thermally stable up to 290 °C, above which point it begins to decompose. Also TMU-6 shows a plateau in the range of 30 to 100 °C and a loss of DMF molecules of 16% (expected: 19%) in the temperature range of 100 to 380 °C. The TGA profiles of the mechanosynthesized TMU-4, TMU-5 and TMU-6 before washing with DMF show plateaus in the range of 30 to 315 °C, 30 to 290 °C and 30 to 380 °C, respectively, reveal that the first weight loss correctly attributed to loss of DMF guest molecules.



Fig. S3. Comparison of XRPD patterns for **TMU-6**: simulated; solvothermal synthesis; mechanosynthesized before and after washing with DMF in order to remove any unreacted metal salt or ligands.



Fig. S4. Comparison of XRPD patterns for TMU-4, TMU-5 and TMU-6 before and after 4 successive runs.



Fig. S5. Comparison of XRPD patterns for TMU-4, TMU-5 and TMU-6 before and after immersing in H_2O for 20 days.



Fig. S6. Comparison of XRPD patterns for testing stability of **TMU-4** in MeOH, EtOH, n-Hexane, CH₃CN, CH₂Cl₂ and Toluene.



Fig. S7. Comparison of XRPD patterns for testing stability of TMU-5 in MeOH, EtOH, n-Hexane, CH_3CN , CH_2Cl_2 and Toluene.



Fig. S8. Comparison of XRPD patterns for testing stability of **TMU-6** in MeOH, EtOH, n-Hexane, CH₃CN, CH₂Cl₂ and Toluene.



Fig. S9. Leaching test for TMU-4, TMU-5 and TMU-6 in H₂O as solvent.



Fig. S10. Leaching test for TMU-4, TMU-5 and TMU-6 in EtOH as solvent.



Fig. S11. Leaching test for TMU-4, TMU-5 and TMU-6 in MeOH as solvent.



Fig. S12. IR spectra for TMU-4 before and after 4 successive runs.



Fig. S13. IR spectra for TMU-5 before and after 4 successive runs.



Fig. S14. IR spectra for TMU-6 before and after 4 successive runs.

References

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