Supporting Information

Solvent/additive-free synthesis of porous/zeolitic metal azolate frameworks from metal oxide/hydroxide

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Experiment Section

Materials and Methods. Hmim (99%, Alfa Aesar) and other commercially available reagents were used as received without further purification. Hmdpt (3-(3-methyl-2-pyridyl)-5-(4-pyridyl)-1,2,4-triazole) was prepared according to a reported method.[1] Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer (Cu-Kα). Gas sorption isotherms were measured on a volumetric adsorption apparatus (ASAP 2020M for N_2, Bel-max for CO_2). Before the measurement, the samples were all activated under a dynamic vacuum up to 10^{-2} Pa at 180 ^{o}C for 5 hrs. All compounds synthesized by different methods were measured with the same equilibrium criterion.

Syntheses of MAF-4: A mixture of ZnO (200 mg, 2.5 mmol) and Hmim (410 mg, 5.0 mmol) was grinded uniformly and then sealed in a 15-mL Teflon-lined autoclave and heated at 180^{o}C for 12 hrs to give white powders (yield: 567 mg, ~100%). When the same vessel was naturally filled by a mixture of ZnO (2.44 g, 30 mmol) and Hmim (4.93 g, 60 mmol), a shaped material with an apparent density 0.46 g cm^{-3} was obtained.

Solvothermal synthesis of MAF-27: A mixture of $MgCl_2{\cdot}6H_2O$ (100 mg, 0.50 mmol), Hmdpt (240 mg, 1.0 mmol), ethanol (10 mL) and Et_3N (0.50 mL) was stirred continuously for 1 hr and then sealed in a 15-mL Teflon-lined autoclaves and heated at 160^{o}C for 3 days, and then cooled by 5^{o}C/hr to room temperature to give colorless crystals of MAF-27 (yield: 61 mg, 25 %), which was sometimes contaminated by some crystals of $[Mg(mdpt)_2(H_2O)_2]{\cdot}2H_2O$.

Solvothermal synthesis of MAF-28: A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (80 mg, 0.25 mmol), Hmdpt (120 mg, 0.50 mmol), ethanol (4.0 mL) and DMF (0.20 mL) was sealed in a 15-mL Teflon-lined autoclaves and heated at 160^{o}C for 3 days, and then cooled by 5^{o}C/hr to room temperature to give colorless crystals (yield: 88 mg, 65 %).

Synthesis of MAF-27 and MAF-28 by OSFR: A mixture of $Mg(OH)_2$ (15 mg, 0.25 mmol) or $Zn(OH)_2$ (25 mg, 0.25 mmol) and Hmdpt (119 mg, 0.50 mmol) was grinded uniformly and then sealed in a glass tube and heated at 300^{o}C for 16 hrs to give white powders (yield: 124 and 134 mg for MAF-27 and MAF-28, respectively, ~100%).

Single-crystal of $[Mg(mdpt)_2(H_2O)_2]{\cdot}2H_2O$ can be also obtained by dissolving MAF-27 in 95% ethanol and then slowly evaporated in air for several weeks.

Crystal Structure Determination. Intensity data were collected on a Bruker Apex CCD area-detector diffractometer (Mo-Kα). Absorption corrections were applied by using the multi-scan program SADABS.[2] The structures were solved with direct method and refined with a full-matrix least-squares technique with the SHELXTL program package.[3] Anisotropic thermal parameters were applied to all non-hydrogen atoms except the guest molecules. The organic hydrogen atoms were generated geometrically. The solvent molecules in the MAF-27 and MAF-28 are highly disordered and cannot be modeled, thus the SQUEEZE routine[4] was applied to remove the contributions to the scattering from the solvent molecules.

1 E. J. Browne, *Aust. J. Chem.* 1975, **28**, 2543.
2 G. M. Sheldrick, University Göttingen: Göttingen, Germany 2002.
3 Bruker Analytical Instrumentation: Madison, WI 2000.
4 A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7.

Table S1. Crystallographic data.

Complex	MAF-27	MAF-28	$[Mg(mdpt)_2(H_2O)_2]\cdot 2H_2O$
Formula	$C_{26}H_{20}MgN_{10}$	$C_{26}H_{20}N_{10}Zn$	$C_{26}H_{28}MgN_{10}O_4$
Formula weight	496.83	537.89	568.89
Crystal system	Hexagonal	Hexagonal	Monoclinic
Space group	$R\bar{3}$	$R\bar{3}$	$P2_1/c$
a/Å	27.085(6)	27.214(9)	7.9467(5)
b/Å	27.085(6)	27.214(9)	11.6001(8)
c/Å	10.329(6)	10.206(6)	29.750(2)
β/°	120	120	92.9390(10)
V/Å^3	6562(4)	6546(5)	2738.8(3)
Z	9	9	4
D_c /g cm^{-3}	1.132	1.228	1.380
μ/mm^{-1}	0.092	0.875	0.118
reflns coll.	8142	5258	15692
unique reflns	2572	2521	5373
R_{int}	0.1481	0.0656	0.0517
R_1 [$I > 2\sigma$][a]	0.0751	0.0680	0.0633
wR_2 [$I > 2\sigma$][b]	0.1265	0.1181	0.1619
R_1 (all data)	0.2207	0.1204	0.1010
wR_2 (all data)	0.1444	0.1300	0.1958
GOF	1.000	1.008	1.002
$\Delta\rho_{min/max}$/e/Å^3	0.260/-0.266	0.836/-0.578	0.567/-0.518

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

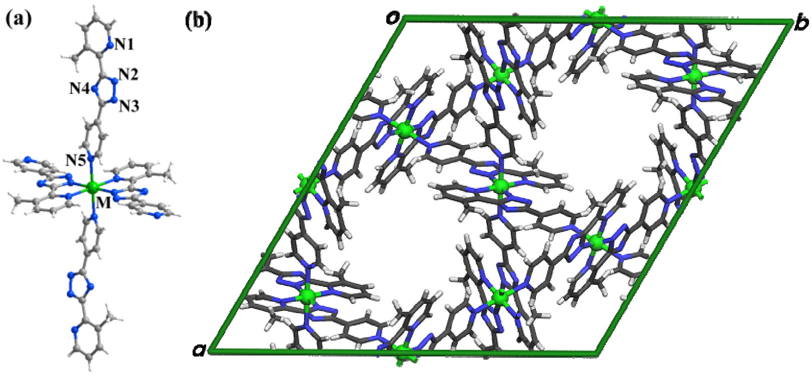

Fig. S1 (a) Coordination environment of the M^{II} ion, and (b) the framework structure viewed along the *c*-axis of MAF-27/28.

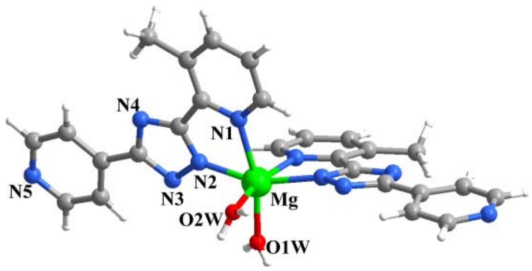

Fig. S2 Molecular structure of $[Mg(mdpt)_2(H_2O)_2]\cdot 2H_2O$.

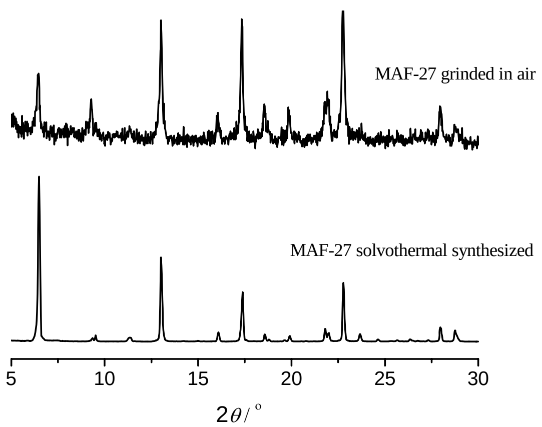

Fig. S3 PXRD patterns of the solvothermally synthesized MAF-27 before and after grinded in air (crystallinity lowered).

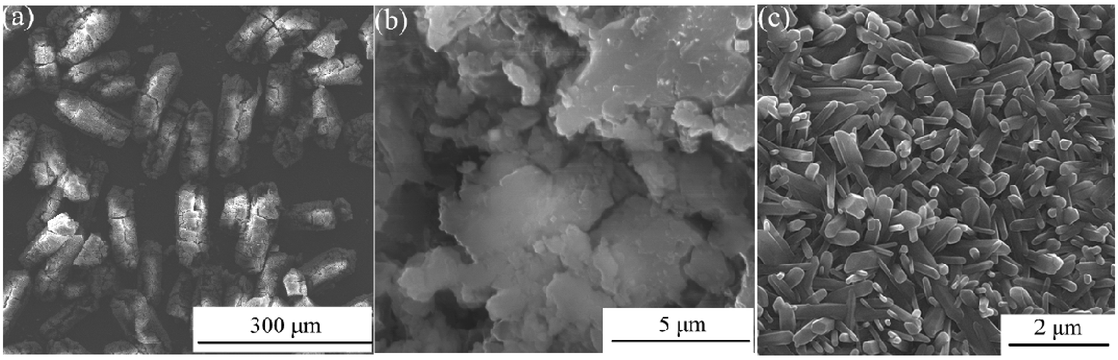

Fig. S4 SEM images of MAF-27 obtained by solvothermal method: (a) before and (b) after grinding, and (c) by OSFR.

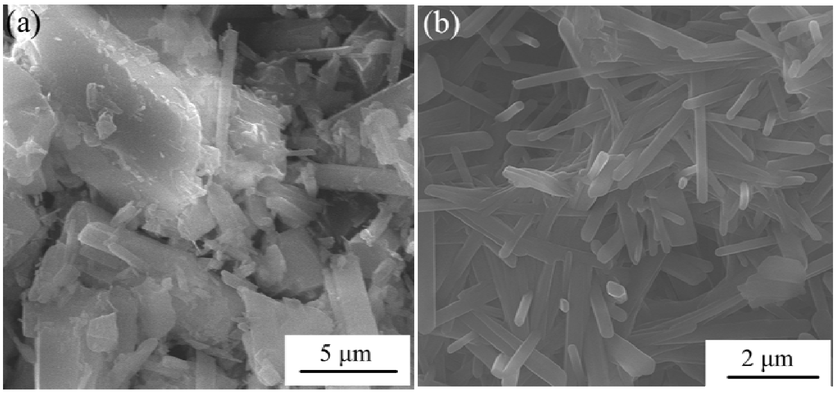

Fig. S5 SEM images of MAF-27 obtained by (a) solvothermal method, and (b) by OSFR.

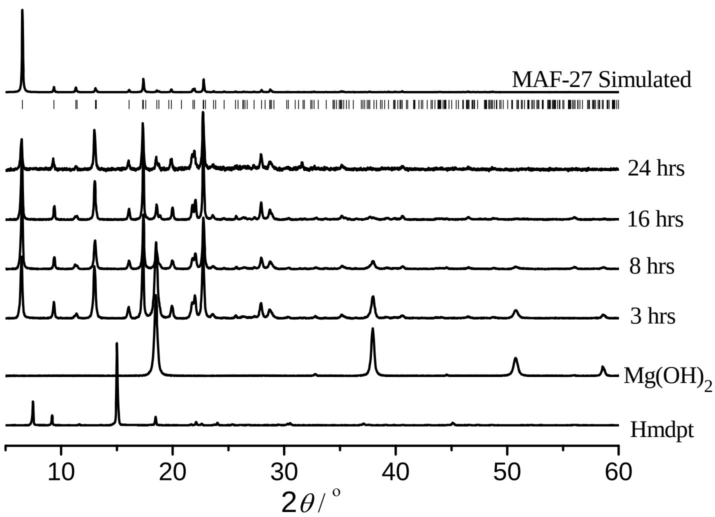

Fig. S6 PXRD patterns of Hmdpt, $Mg(OH)_2$, the mixture of Hmdpt and $Mg(OH)_2$ after heated at 300 ^{o}C for different time, and simulated MAF-27.

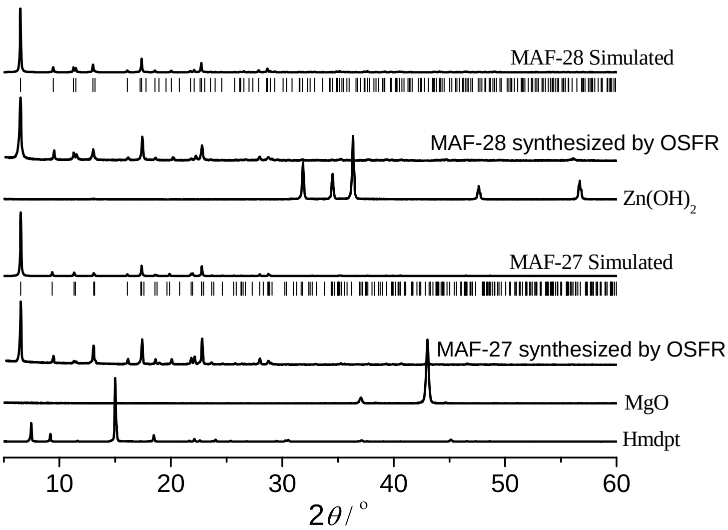

Fig. S7 PXRD patterns of Hmdpt, MgO, MAF-27 synthesized by OSFR, simulated MAF-27, $Zn(OH)_2$, MAF-28 synthesized by OSFR, and simulated MAF-28.

Table S2. Indexing and refinement results of PXRD patterns of MAF-4, MAF-27 and 28 obtained by OSFR.

Complex	MAF-4	MAF-27	MAF-28
Space group	$I\bar{4}3m$	$R\bar{3}$	$R\bar{3}$
a/Å	16.909(4)	27.124(15)	26.082(12)
b/Å	16.909(4)	27.124(15)	26.082(12)
c/Å	16.909(4)	10.231(6)	9.705(4)
R_{wp}	6.27%	6.34%	7.08%
R_p	4.59%	4.67%	5.09%

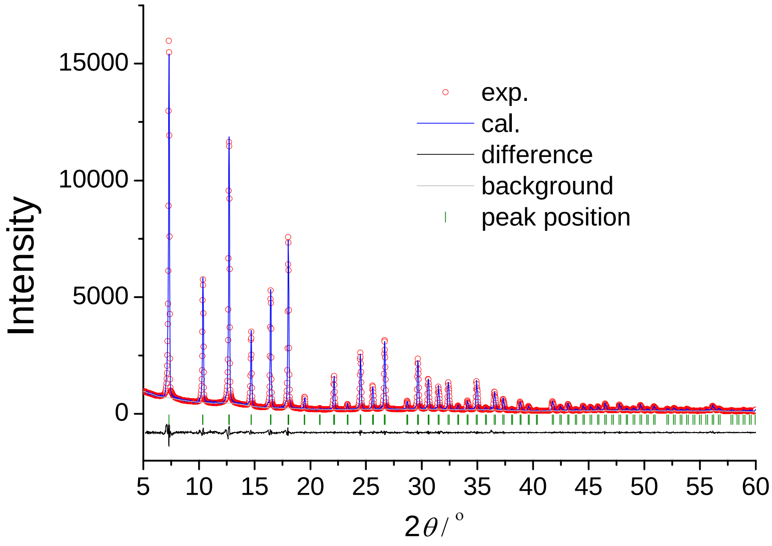

Fig. S8 Pawley fitting of PXRD pattern of MAF-4 obtained by OSFR.

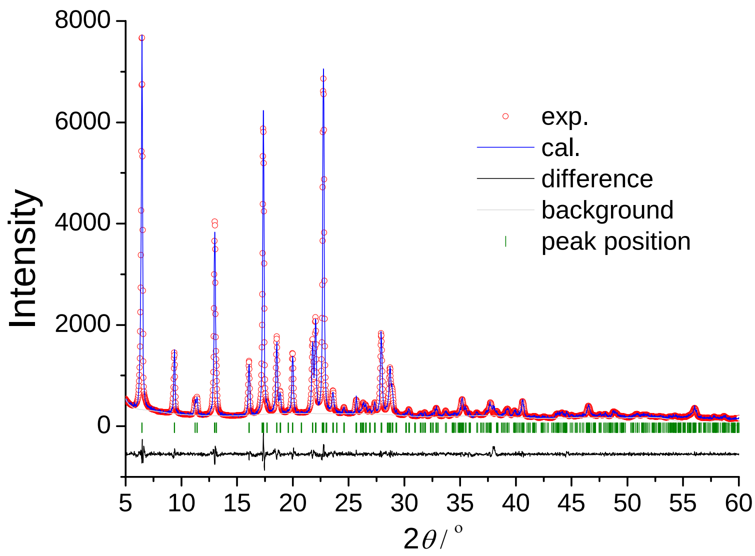

Fig. S9 Pawley fitting of PXRD pattern of MAF-27 obtained by OSFR.

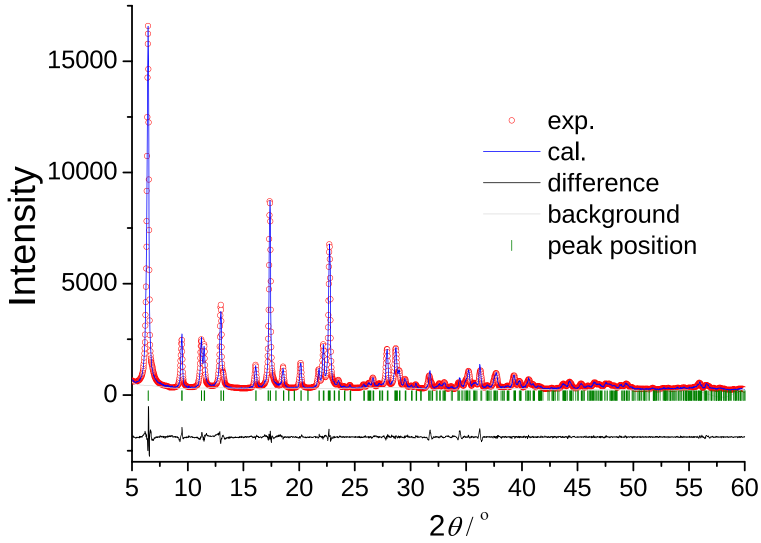

Fig. S10 Pawley fitting of PXRD pattern of MAF-28 obtained by OSFR.