Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Single-crystal X-ray diffraction and Raman spectroscopy studies of isobaric N_2 adsorption in SOD-type metal-organic zeolites

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Experimental details

Single crystals of MAF-4 and MAF-7 were synthesized according to the literature.[2b, 5] The intensity data were collected on a Bruker Apex CCD area-detector diffractometer (Mo-Kα). All diffraction data sets of a given compound were collected continuously from a single specimen. The single-crystal specimen was mounted on the top of a glass fiber with minimum amount of glue to allow free gas diffusion into the crystal. The measurement temperatures were controlled by an open-flow dry N_2 cryostat (Rigaku GN2), and corrected by a thermocouple at the position of the crystal. Each data set was measured after the specimen was stayed at the targeted temperature after 5 min and no further change of the unit-cell parameters. Only for special purpose, the single crystal was further coated with a very thin layer of Vaseline to slow down the gas diffusion rate.

Absorption corrections were applied by using multi-scan program SADABS. The structures were solved with the direct method and refined with a full-matrix least-squares technique with the SHELXTL program package. The organic hydrogen atoms were generated geometrically and refined in a riding model. Anisotropic thermal parameters were applied to all non-hydrogen atoms except some guest molecules.

Table S1. Crystallographic data and refinement parameters of MAF-4·xN$_2$.

Compound	MAF-4·0.2N$_2$	MAF-4·3.50N$_2$	MAF-4·3.82N$_2$	MAF-4·4.33N$_2$	MAF-4·4.33N$_2$
Formula	$C_8H_{10}N_{4.40}Zn$	$C_8H_{10}N_{11.00}Zn$	$C_8H_{10}N_{11.64}Zn$	$C_8H_{10}N_{12.67}Zn$	$C_8H_{10}N_{12.67}Zn$
FW	233.17	325.64	342.45	348.99	348.99
Space group	*I*-43*m*	*I*-43*m*	*I*-43*m*	*I*-43*m*	*I*-43*m*
T / K	293(2)	113(2)	111(2)	109(2)	100(2)
a / Å	17.039(3)	17.086(2)	17.120(2)	17.1236(19)	17.133(2)
V / Å^3	4946.6(13)	4987.7(11)	5018.1(12)	5020.9(10)	5029.3(12)
Z	12	12	12	12	12
D_c / g cm^{-3}	0.939	1.301	1.329	1.385	1.383
μ / mm^{-1}	1.466	1.485	1.479	1.483	1.481
R_{int}	0.0628	0.0561	0.1309	0.0501	0.0667
R_{sig}	0.0320	0.0271	0.0686	0.0265	0.0326
Completeness	0.994	0.998	0.996	0.998	0.998
R_1/wR_2 ($I > 2\sigma$)	0.0415/0.0802	0.0362/0.0916	0.0629/0.1586	0.0295/0.0752	0.0333/0.0822
R_1/wR_2 (all data)	0.0499/0.0847	0.0378/0.0932	0.0648/0.1599	0.0300/0.0754	0.0342/0.0826
GOF	1.087	1.056	1.075	1.024	1.049
Restraints	0	0	0	0	0
Parameters	37	53	64	58	58
Residue	0.198/-0.500	0.495/-0.762	0.652/-0628	0.944/-0.487	1.373/-0.597
Flack	0.01(3)	0.02(3)	0.04(6)	0.00(2)	-0.04(2)

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

Table S2. Crystallographic data and refinement parameters of MAF-7·xN$_2$.

	MAF-7·0.2N$_2$	MAF-7·3.50N$_2$	MAF-7·4.33N$_2$	MAF-7·3.50N$_2$	MAF-7·3.95N$_2$	MAF-7·4.33N$_2$
Formula	$C_6H_8N_{6.40}Zn$	$C_6H_8N_{13.00}Zn$	$C_6H_8N_{14.67}Zn$	$C_6H_8N_{13.00}Zn$	$C_6H_8N_{13.91}Zn$	$C_6H_8N_{14.67}Zn$
FW	235.16	327.62	350.97	327.62	340.43	350.97
Space group	*I*-43*m*	*I*-43*m*	*I*-43*m*	*I*-43*m*	*I*-43*m*	*I*-43*m*
T / K	293(2)	118(2)	115(2)	100(2)	100(2)	100(2)
a / Å	17.019(3)	17.0641(19)	17.082(2)	17.0550(8)	17.0659(12)	17.0797(19)
V / Å^3	4929.2(13)	4968.8(10)	4984.5(10)	4960.8(4)	4970.4(6)	4982.4(10)
Z	12	12	12	12	12	12
D_c / g cm^{-3}	0.951	1.314	1.403	1.316	1.365	1.404
μ / mm^{-1}	1.475	1.495	1.498	1.497	1.498	1.498
R_{int}	0.0431	0.0357	0.0554	0.0807	0.0845	0.0441
R_{sig}	0.0242	0.0196	0.0310	0.0302	0.0595	0.0230
Flack	0.02(3)	-0.02(3)	0.02(4)	-0.00(4)	0.06(6)	0.00(2)
R_1/wR_2 ($I > 2\sigma$)	0.0369/0.0753	0.0341/0.0878	0.0423/0.1106	0.0422/0.1209	0.0629/0.1679	0.0302/0.0750
R_1/wR_2 (all data)	0.0470/0.0798	0.0347/0.0896	0.0426/0.1109	0.0422/0.1209	0.0632/0.1683	0.0306/0.0754
GOF	1.034	1.040	1.040	1.078	1.123	1.053
Restraints	0	1	0	1	0	0
Parameters	37	50	62	50	53	62
Residue	0.192/-0.542	0.497/-0.577	0.496/-0.552	0.860/-0.347	0.933/-0.893	0.588/-0.564
Flack	0.02(3)	-0.02(3)	0.02(4)	0.00(4)	0.06(6)	0.00(2)

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

Table S3. Adsorption sites and occupancies in MAF-4

T / K	Site	**I**	**II**	**III**	**IV**	**V**	Sum[d]
	PS[a]	-42*m*	*m*	3*m*	*mm*	-43*m*	
	NP[b]	6	24	8	12	2	26
293	SOF[c]	0	0	~0	~0	0	~0
113		0	1	1	1	1	21
111		0.37	1	1	1	1	23
109		1	1	1	1	1	26
100		1	1	1	1	1	26

[a] Point symmetry.

[b] Number of equivalent positions per unit cell.

[c] Site occupancy factor.

[d] Sum = ΣSOF×NP/2 (sum of adsorbed molecules per β-cage).

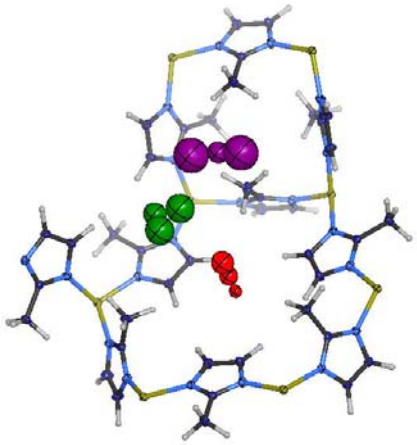

Fig. S1. Ortep plots of MAF-4·3.50N_2 measured at 113 K (30% probability).

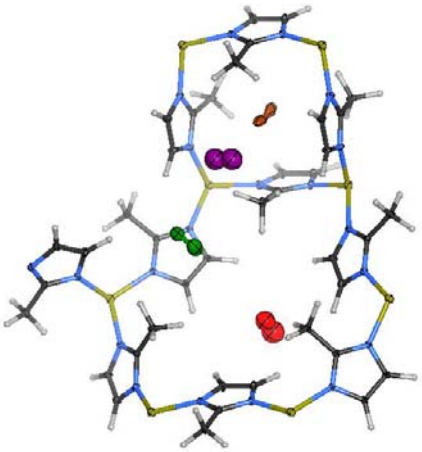

Fig. S2. Ortep plots of MAF-4·4.33N_2 measured at 109 K (30% probability).