

Supporting Information

Remarkable Pressure Responses of Metal–Organic Frameworks: Proton Transfer and Linker Coiling in Zinc Alkyl Gates

Aurélie U. Ortiz, Anne Boutin, Kevin J. Gagnon,*

Abraham Clearfield, François-Xavier Coudert*

Table S1. Cell parameters of ZAG-4 and ZAG-6, comparing experiments and DFT calculations.

Table S2. Elastic stiffness matrix for ZAG-4.

Table S3. Summary of the elastic properties of ZAG-4 and ZAG-6.

Table S4. Crystallographic data for ZAG-6.

Table S5. Elastic stiffness matrix for ZAG-6.

Figure S1. Linear compressibility of ZAG-4 and ZAG-6.

Figure S2. Visualization of ZAG-4 at 4 GPa.

Structure	Space group	a (Å)	b (Å)	c (Å)	β (deg.)	Volume (Å ³)
ZAG-4 (exp, $P = 0$)	$C2/c$	18.515(4)	8.291(2)	8.265(2)	113.837(2)	1160.5(5)
ZAG-4 (DFT, $P = 0$)	$C2/c$	18.764	8.440	8.173	112.63	1194.7
ZAG-4 (exp, $P = 7.32$ GPa)	$C2/c$	17.023(2)	8.066(3)	7.4078(8)	123.227(8)	850.9(3)
ZAG-6 (exp, $P = 0$)	$C2/c$	23.180(5)	8.2859(16)	8.2008(16)	120.3870(19)	1358.7(4)
ZAG-6 (DFT, $P = 0$)	$C2/c$	23.753	8.371	8.180	117.18	1447.0
ZAG-6 (exp, $P = 6.9$ GPa)	$C2/c$	19.782(4)	8.430(3)	7.7146(12)	128.672(12)	1004.4(4)
ZAG-6 (DFT, $P = 7$ GPa)	$C2/c$	19.891	8.495	7.712	128.40	1021.4

Table S1. Cell parameters of ZAG-4 and ZAG-6, obtained experimentally and from DFT calculations.

79.1	16.7	6.4	0	-25.0	0
*	20.6	11.5	0	-5.7	0
*	*	24.1	0	-3.6	0
0	0	0	11.5	0	-5.8
*	*	*	0	11.4	0
0	0	0	*	0	7.9

Table S2. Elastic stiffness matrix for ZAG-4, in GPa.

Asterisks indicate nonzero elements constrained by the symmetric nature of the tensor.

	E_{\min} (GPa)	E_{\max} (GPa)	A_E	G_{\min} (GPa)	G_{\max} (GPa)	A_G	β_{\min} (TPa ⁻¹)	β_{\max} (TPa ⁻¹)	ν_{\min}	ν_{\max}
ZAG-4	6.18	74.12	12.0	3.19	18.03	5.7	-18.4	89.7	0.14	1.33
ZAG-6	4.26	83.51	19.6	2.62	15.50	5.9	-18.7	136.3	-0.30	1.64

Table S3. Summary of the elastic properties of ZAG-4 and ZAG-6, from tensorial analysis of the elastic stiffness tensor obtained by quantum chemical calculations.

Sample	Ambient	6.9 GPa
Chemical formula	ZnP ₂ O ₈ C ₆ H ₁₈	ZnP ₂ O ₈ C ₆ H ₁₈
Formula mass (g/mol)	345.51	345.51
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
λ (Å)	0.6048	0.6702
a (Å)	23.180(5)	19.782(4)
b (Å)	8.2859(16)	8.430(3)
c (Å)	8.2008(16)	7.7146(12)
β (deg.)	120.3870(19)	128.672(12)
Z	4	4
V (Å ³)	1358.7(4)	1004.4(4)
Temperature (K)	296(2)	296(2)
Density (g/cm ³)	1.689	2.285
Measured reflections	9639	4317
Unique reflections	2697	587
Parameters	78	78
Restraints	0	0
R_{int}	0.0715	0.0931
θ range (deg.)	4.989 – 28.213	3.458 – 25.412
R_1, wR_2 all data	0.0464, 0.1280	0.0606, 0.1517
S (GooF) all data	0.993	1.114
Max/min res. Dens. (e/Å ³)	0.381/-0.473	1.054/-0.861

All unit cells are reported as unconventional representations utilizing the transformation matrix $1\ 0\ 2\ 0\ -1\ 0\ 0\ 0\ -1$. This was done to maintain the same orientation as in the ZAG-4 structure previously published.

Table S4. Crystallographic data for ZAG-6.

97.3	14.3	1.5	0	-21.5	0
*	15.3	7.8	0	-4.1	0
*	*	15.2	0	-3.3	0
0	0	0	9.0	0	-5.1
*	*	*	0	8.0	0
0	0	0	*	0	5.8

Table S5. Elastic stiffness matrix for ZAG-6, in GPa. Asterisks indicate nonzero elements constrained by the symmetric nature of the tensor.

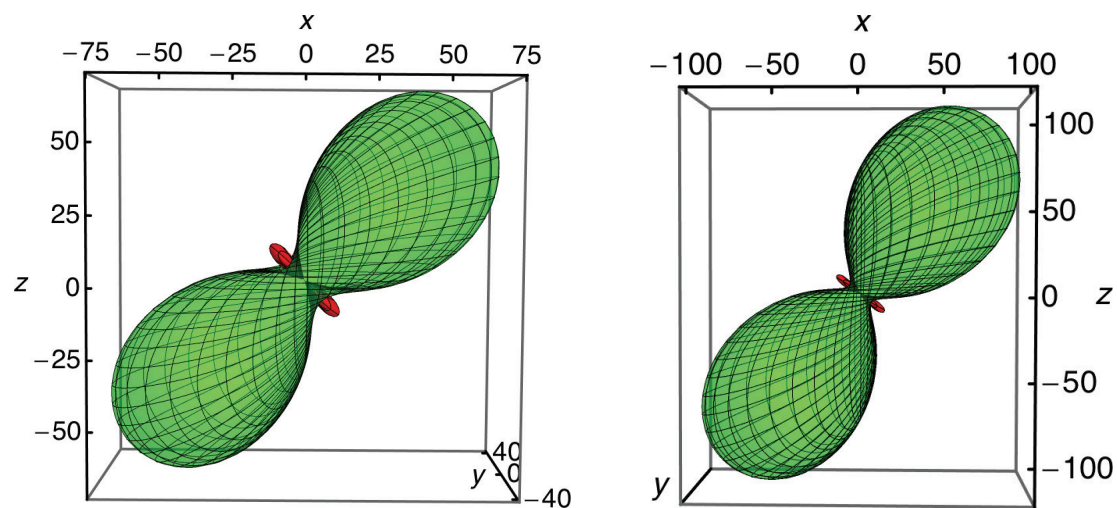


Figure S1. Linear compressibility of ZAG-4 (left) and ZAG-6 (right) as a function of direction, represented as a 3D surface (in units of TPa^{-1}).

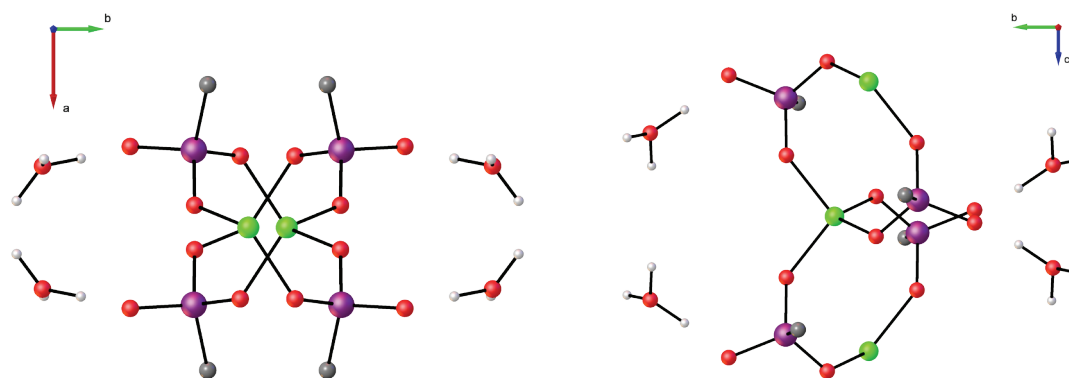


Figure S2. Visualization of part of the structure of ZAG-4 at 4 GPa, with the protonated water molecule and the nearby oxygen atom whose proton it abstracted. Left: view along the hinge of the wine rack (b axis); right: view in the perpendicular plane, with the phosphate-linked Zn chain clearly visible. In both cases, non-water hydrogen atoms were hidden for clarity's sake.