Electronic Supplementary Information for Dalton Transactions

Supporting Information For

A Cubic Coordination Framework Constructed from Benzobistriazolate Ligands and Zinc Ions Having Selective Gas Sorption Properties

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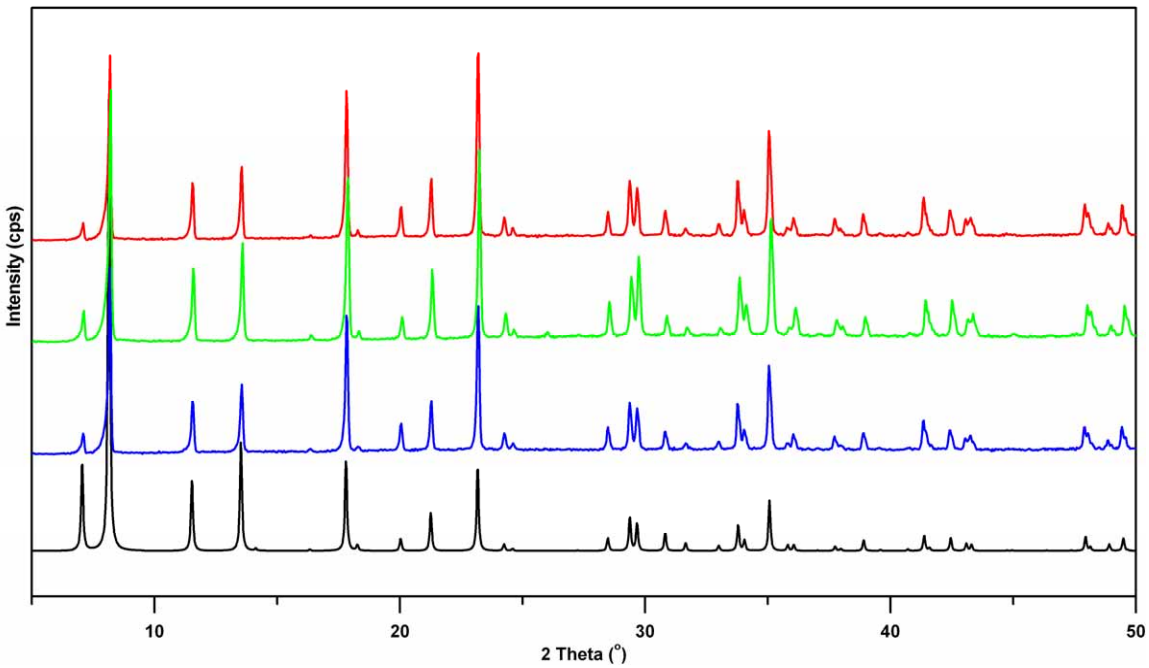

Fig. S1 Theoretical XRPD pattern (black) and experimental XRPD patterns of compound **1** synthesized by solvothermal method (batch 1, blue; batch 2, green) and by microwave assisted method (red).

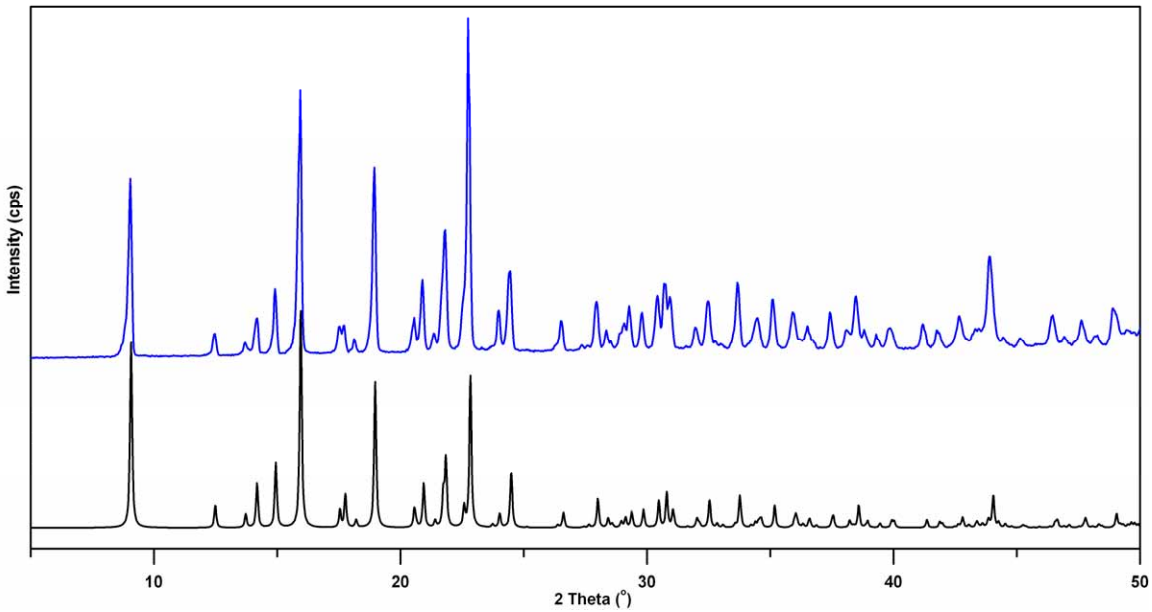

Fig. S2 Theoretical (black) and experimental (blue) XRPD patterns of compound **2**.

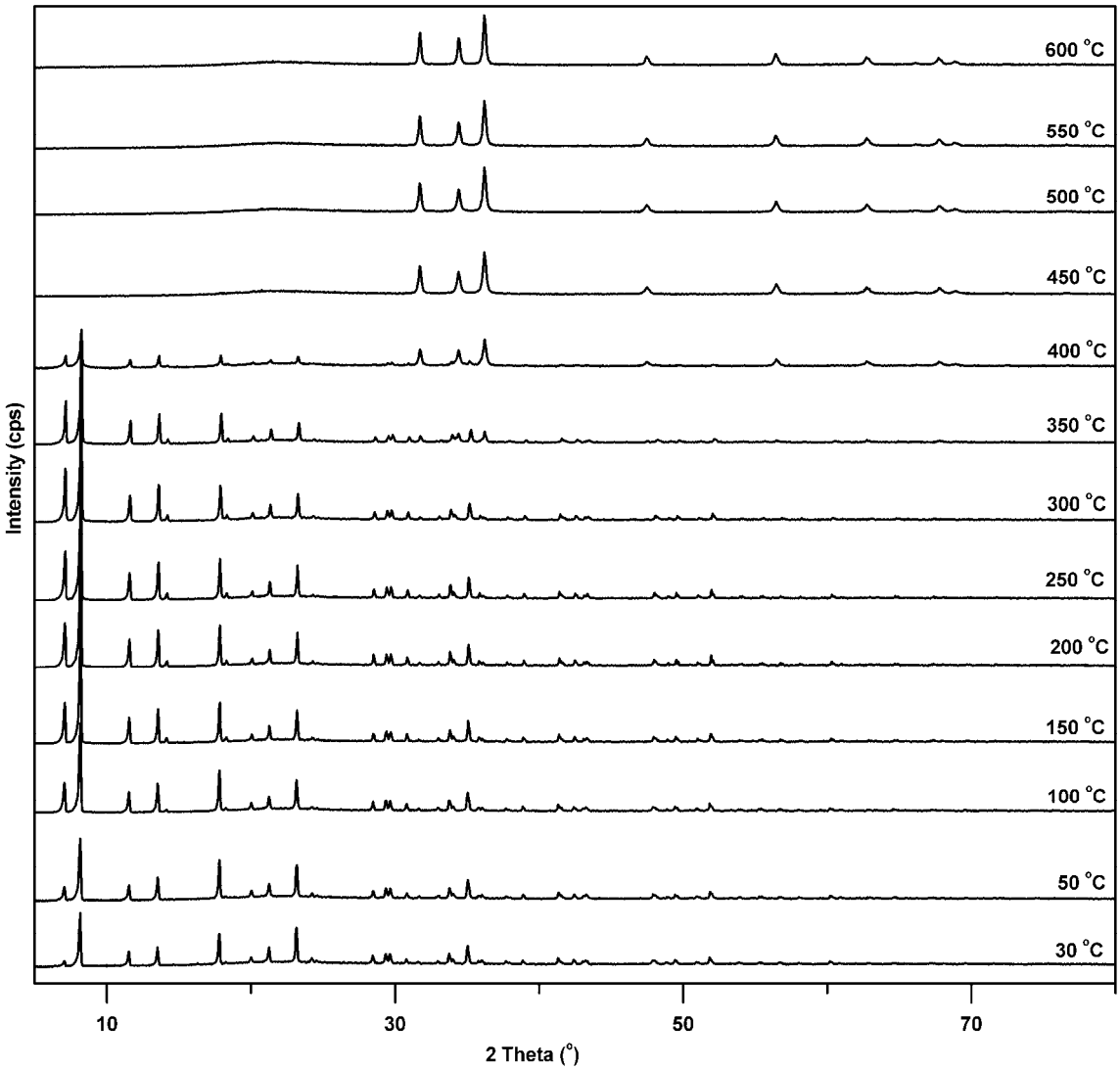

Fig. S3 Detailed VTXRPD plots of compound **1** in the range 30-600 °C.

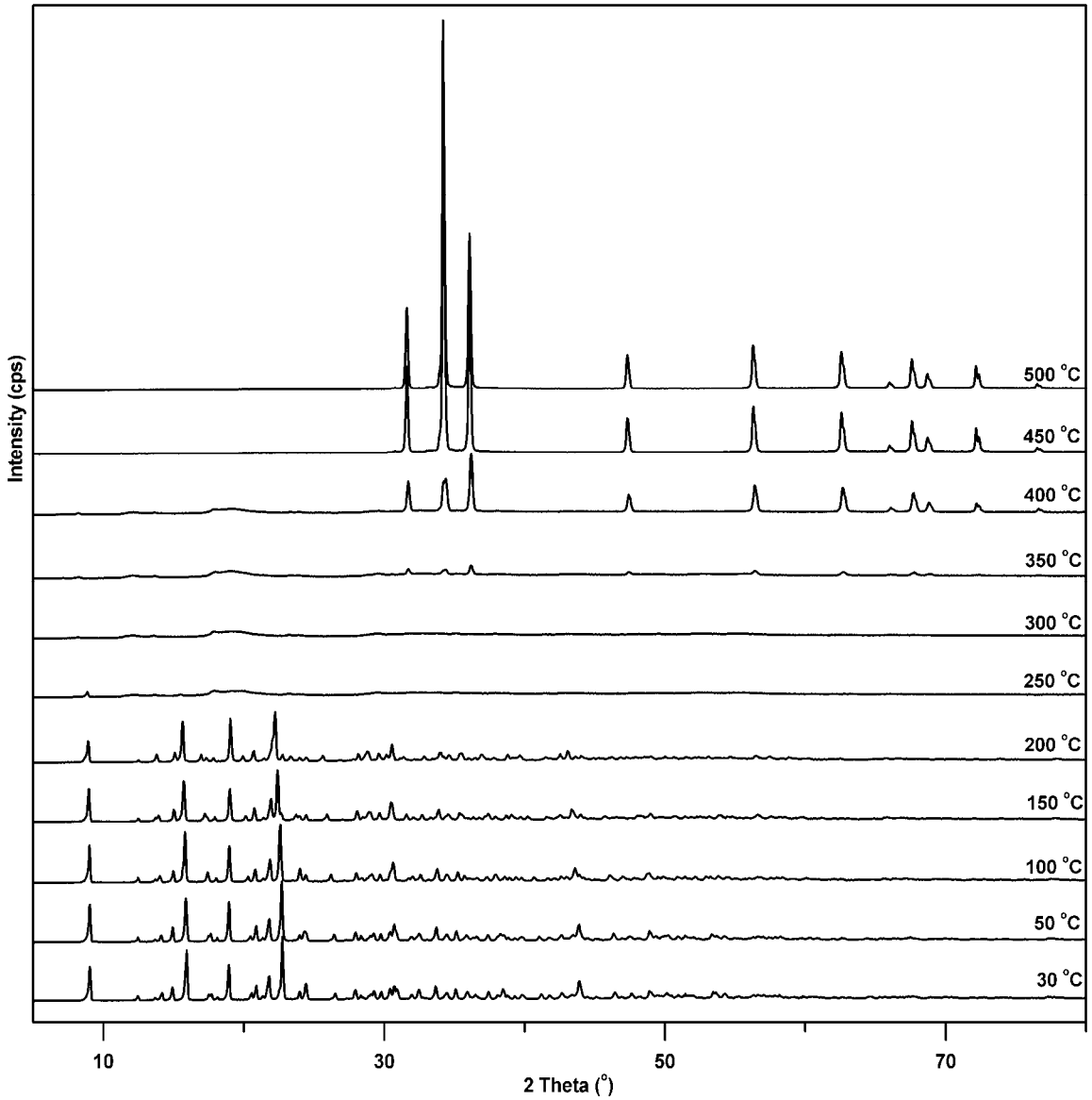

Fig. S4 Detailed VTXRPD plots of compound **2** in the range 30-500 °C.

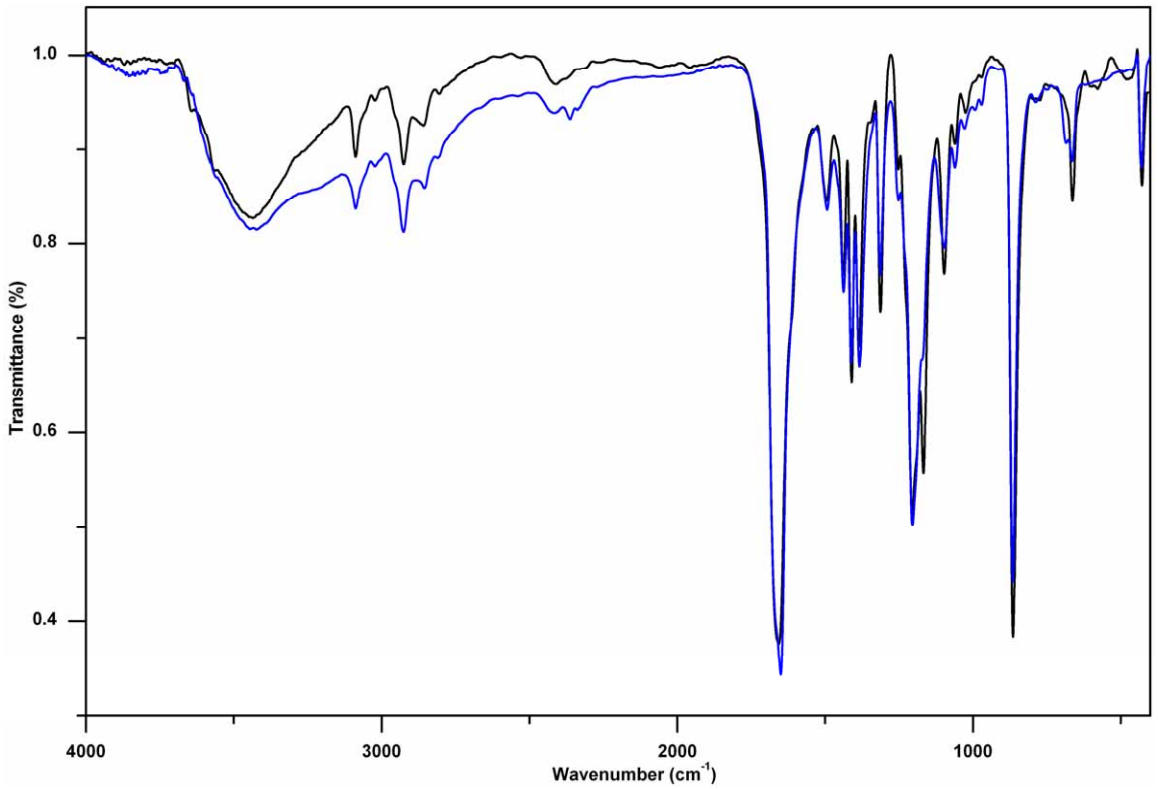

Fig. S5 FT-IR spectra of compound **1** synthesized by solvothermal method (black) and by microwave assisted method (blue).

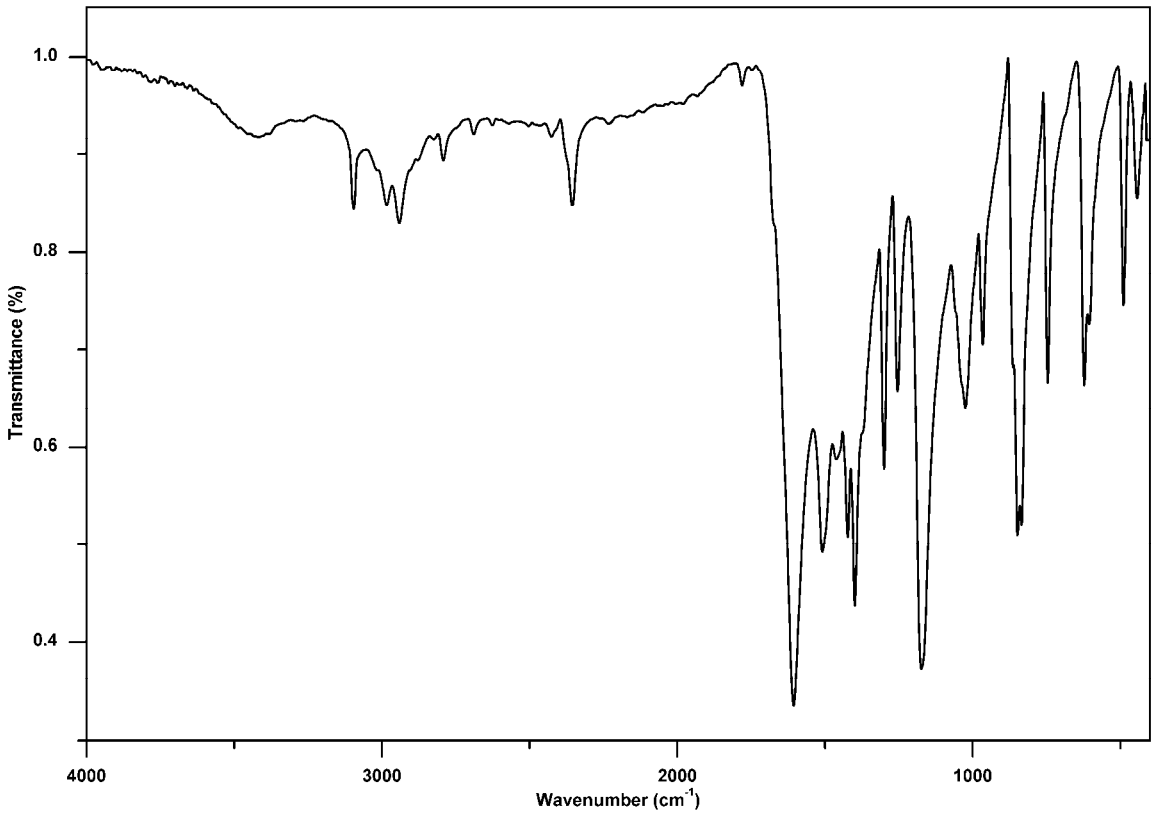

Fig. S6 FT-IR spectrum of compound **2**.

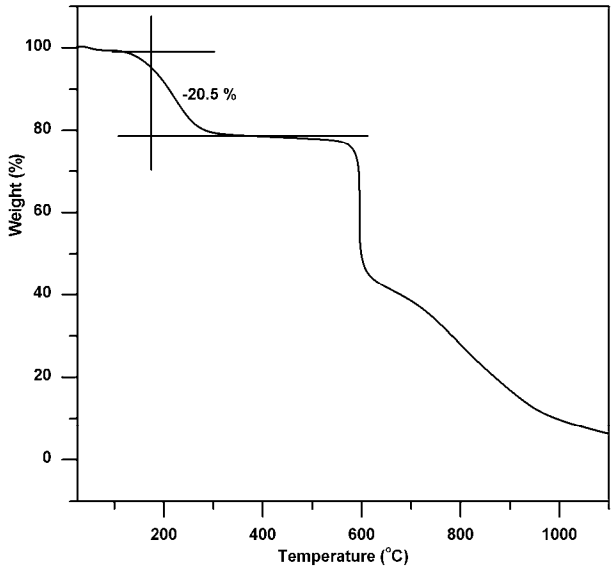

Fig. S7 TG analysis under N_2 atmosphere of compound **1** synthesized by microwave irradiation method.

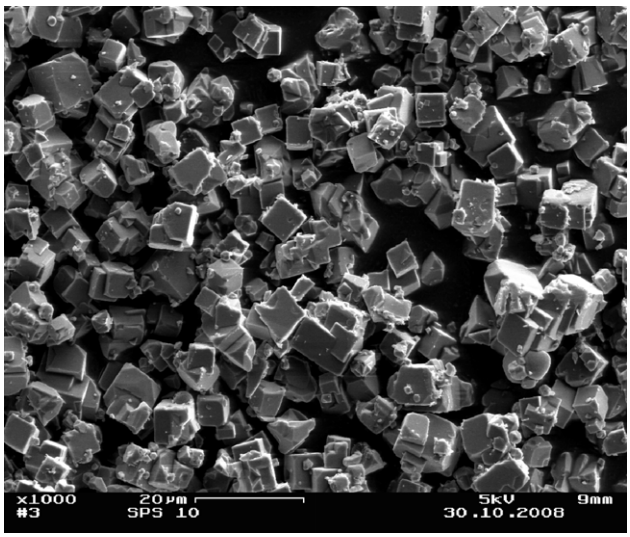

Fig. S8 SEM image of as-synthesized compound **1** by microwave irradiation method.

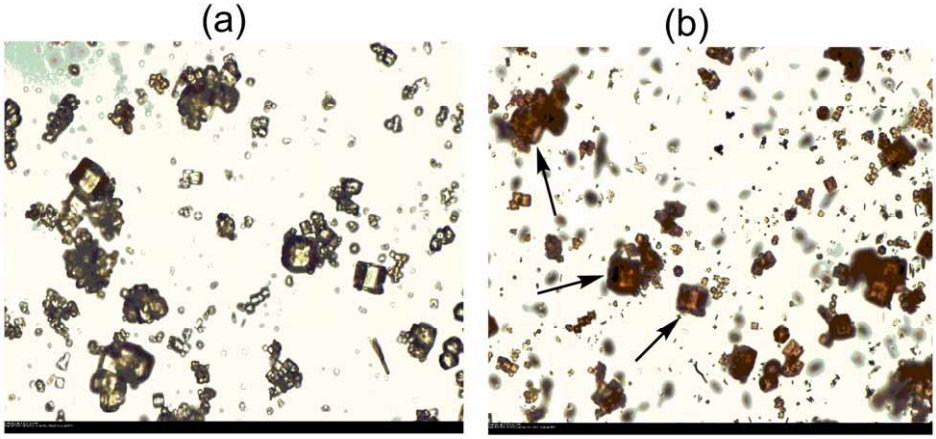

Fig. S9 Heating stage micrographs of compound **1**: (a) before heating, (b) after heating at 450 °C for 15 min. Black arrows point towards cubic crystals of **1** which have changed color but maintained crystallinity after heating.

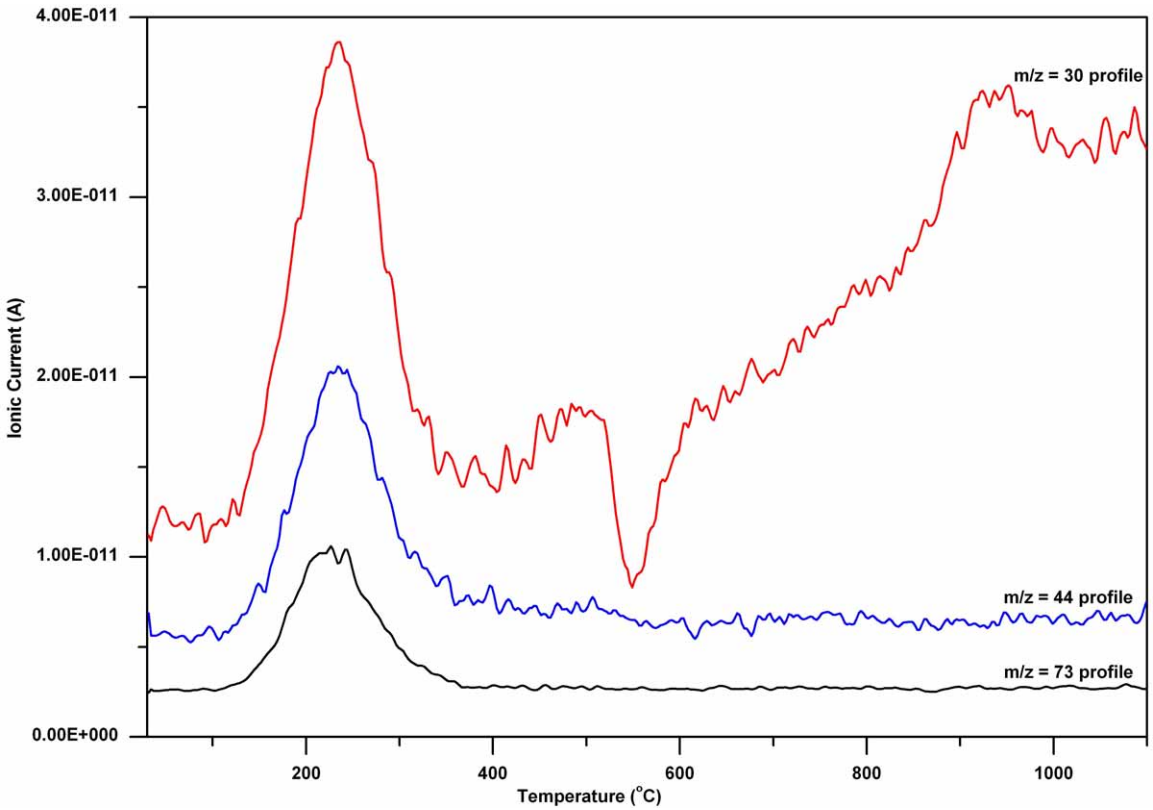

Fig. S10 Ion-chromatograms of gases released by heating compound **1** under Ar atmosphere (m/z = 73 profile, black; m/z = 44 profile, blue; m/z = 30 profile, red).

Table S1 Crystal data and structure refinement parameters of **1** from Rietveld refinement using powder data at 350 °C.

Formula	$C_{18}Cl_4N_{18}Zn_5$
Formula mass/g mol^{-1}	937.03
Calculated density/g cm^{-3}	1.2303
Crystal system	Cubic
Space group	Fm-3m, No. 225
a/Å	21.6265(9)
V/Å^3	10114.9(4)
Z	8
T/K	623(2)
Figures of merit	M_{21}= 19.52; F_{21}= 33.60
2θ Range/°	5-80
Number of observations	3748
R_p	9.03
R_{wp}	13.67
R_{obs}	10.62
R_{wobs}	8.81

Table S2 Change of lattice parameters of **1** obtained from VTXRPD data.

Measurement Temperature (°C)	a = b= c (Å)	V (Å^3)	M_{20}	F_{20}
30	21.739(1)	10273(2)	92.68	128.58
100	21.7295(8)	10260(1)	53.51	79.67
200	21.689(2)	10203(3)	58.84	79.31
300	21.644(4)	10139(6)	23.44	33.58
350	21.6265(9)	10114.9(4)	19.52	33.60

Table S3 Principal bond lengths (Å) of **1** from single crystal data.

Zn(1)-N(1)#1	2.046(6)	Zn(2)-N(2)#4	2.212(7)
Zn(1)-N(1)	2.046(6)	N(1)-N(2)	1.312(7)
Zn(1)-N(1)#2	2.046(6)	N(1)-C(1)#1	1.372(8)
Zn(1)-Cl(1)	2.106(5)	N(2)-N(1)#1	1.312(7)
Zn(2)-N(2)#3	2.212(7)	C(1)-N(1)#1	1.372(8)
Zn(2)-N(2)#3	2.212(7)	C(1)-C(1)#1	1.390(12)
Zn(2)-N(2)	2.212(7)	C(1)-C(2)	1.422(8)
Zn(2)-N(2)#4	2.212(7)	C(2)-C(1)#5	1.422(8)
Zn(2)-N(2)#4	2.212(7)		

Symmetry transformations used to generate equivalent atoms:
#1 –z+1/2,x,-y+1/2 #2 y,-z+1/2,-x+1/2
#3 y,z,x #4 -y+1/2,z,-x+1/2
#5 -x+1,y,z

Table S4 Principal bond lengths (Å) of **2** from single crystal data.

Zn(1)-O(1)	1.961(5)	C(1)-C(3)	1.392(9)
Zn(1)-N(3)	1.992(6)	C(1)-C(2)#2	1.393(9)
Zn(1)-N(1)	1.995(5)	C(2)-C(3)#3	1.377(9)
Zn(1)-Cl(2)	2.207(3)	C(2)-C(1)#1	1.393(9)
N(1)-N(2)	1.330(8)	C(3)-C(2)#4	1.377(9)
N(1)-C(2)	1.390(8)	C(4)-N(4)	1.299(9)
N(2)-N(3)#1	1.320(7)	C(4)-C(6)	1.498(11)
N(3)-N(2)#2	1.320(7)	N(4)-C(7)	1.456(11)
N(3)-C(1)	1.388(8)	N(4)-C(5)	1.459(11)
O(1)-C(4)	1.265(9)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y-1/2,-z+1/2 #2 -x+1,y+1/2,-z+1/2
#3 x,-y+1/2,z+1/2 #4 x,-y+1/2,z-1/2

Table S5 Selected bond lengths (Å) of **1** from Rietveld refinement using powder data at 350 °C.

Zn(2)–Cl(1)	2.320(8)	N(1)–N(2)	1.292(8)
Zn(2)–N(1)	1.90(1)	N(1)–C(2)	1.45(2)
Zn(1)–N (2)	2.29(2)	C(1)–C(2)	1.39(2)