

## SUPPORTING INFORMATION

***In situ variable-temperature single crystal X-ray diffraction studies of the single-crystal-to-single crystal dehydration and rehydration of a mixed-ligand 2D zinc metal-organic framework using trimesate and 4,4-dipyridyl-N,N'-dioxide as ligands***

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**Table S1** Crystal data for **1** at 104 K, 298 K, 323 K, 373 K on the same crystal, whilst 298K after heated to 373 K and at 298 K after exposed to air for 1 day is on a different crystal

	104 K	298K	323K	373 K	298 K (after heated to 373 K)	298 K (1 day after heated to 373 K)
Empirical formula	$C_{57}H_{60}N_6O_{55}S_3Zn_9$	$C_{57}H_{54}N_6O_{52.2}S_3Zn_9$	$C_{57}H_{54}N_6O_{48.9}S_3Zn_9$	$C_{57}H_{42}N_6O_{42}S_3Zn_9$	$C_{57}H_{42}N_6O_{42}S_3Zn_9$	$C_{57}H_{42}N_6O_{50.95}S_3Zn_9$
Formula weight	2393.62	2326.82	2290.93	2167.47	2167.47	2310.67
Temperature/K	104	298	323	373(2)	298(2)	298
Crystal system	trigonal	trigonal	trigonal	trigonal	trigonal	trigonal
Space group	<i>R</i> 3	<i>R</i> 3	<i>R</i> 3	<i>R</i> 3	<i>R</i> 3	R 3
<i>a</i> /Å, $\alpha$ /°	18.816(4), 90	18.798(19), 90	18.795(18), 90	18.889(19), 90	18.723(5), 90	18.815(5), 90
<i>b</i> /Å, $\beta$ /°	18.816(4), 90	18.798(19), 90	18.795(18), 90	18.889(19), 90	18.723(5), 90	18.815(5), 90
<i>c</i> /Å, $\gamma$ /°	21.441(5), 120	21.57(2), 120	21.47(2), 120	21.67(2), 120	21.353(6), 120	21.425(6), 120
Volume/Å <sup>3</sup>	6574(3)	6602(15)	6568(14)	6695(15)	6483(4)	6568(4)
<i>Z</i>	3	3	3	3	3	3
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.814	1.756	1.738	1.613	1.666	1.753
$\mu$ /mm <sup>-1</sup>	2.598	2.581	2.591	2.532	2.615	2.594
F(000)	3606	3497	3443	3240.0	3240	3455
Crystal size/mm <sup>3</sup>	0.475 × 0.344 × 0.317	0.475 × 0.344 × 0.317	0.475 × 0.344 × 0.317	0.314 × 0.344 × 0.475	0.4 × 0.388 × 0.351	0.4 × 0.388 × 0.351
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
2 $\theta$ range for data collection/°	4.33 to 61.336	4.334 to 61.748	3.14 to 61.81	3.12 to 60.796	4.568 to 61.424	3.14 to 61.4
Index ranges	-25 ≤ <i>h</i> ≤ 25, -26 ≤ <i>k</i> ≤ 19, -29 ≤ <i>l</i> ≤ 30	-25 ≤ <i>h</i> ≤ 26, -26 ≤ <i>k</i> ≤ 20, -29 ≤ <i>l</i> ≤ 31	-25 ≤ <i>h</i> ≤ 26, -26 ≤ <i>k</i> ≤ 21, -29 ≤ <i>l</i> ≤ 31	-22 ≤ <i>h</i> ≤ 26, -24 ≤ <i>k</i> ≤ 25, -29 ≤ <i>l</i> ≤ 30	-26 ≤ <i>h</i> ≤ 25, -26 ≤ <i>k</i> ≤ 25, -25 ≤ <i>l</i> ≤ 30	-25 ≤ <i>h</i> ≤ 20, -25 ≤ <i>k</i> ≤ 26, -30 ≤ <i>l</i> ≤ 25

Reflections collected	19838	20095	20037	13265	10863	18950
Independent reflections	7900 [ $R_{\text{int}} = 0.0233$ , $R_{\text{sigma}} = 0.0529$ ]	7886 [ $R_{\text{int}} = 0.0301$ , $R_{\text{sigma}} = 0.0681$ ]	7879 [ $R_{\text{int}} = 0.0383$ , $R_{\text{sigma}} = 0.0661$ ]	7012 [ $R_{\text{int}} = 0.0476$ , $R_{\text{sigma}} = 0.1026$ ]	7156 [ $R_{\text{int}} = 0.0403$ , $R_{\text{sigma}} = 0.1511$ ]	12155 [ $R_{\text{int}} = 0.0306$ , $R_{\text{sigma}} = 0.0982$ ]
Data/restraints/parameters	7900/2/408	7886/1/390	7879/1/378	7012/1/354	7156/1/354	12155/1/384
Goodness-of-fit on $F^2$	1.071	1.081	1.066	1.024	0.911	1.099
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0383$ , $wR_2 = 0.1085$	$R_1 = 0.0519$ , $wR_2 = 0.1465$	$R_1 = 0.0482$ , $wR_2 = 0.1347$	$R_1 = 0.0508$ , $wR_2 = 0.1377$	$R_1 = 0.0556$ , $wR_2 = 0.1379$	$R_1 = 0.0610$ , $wR_2 = 0.1578$
Final R indexes [all data]	$R_1 = 0.0394$ , $wR_2 = 0.1090$	$R_1 = 0.0608$ , $wR_2 = 0.1524$	$R_1 = 0.0539$ , $wR_2 = 0.1372$	$R_1 = 0.0635$ , $wR_2 = 0.1473$	$R_1 = 0.0880$ , $wR_2 = 0.1590$	$R_1 = 0.0738$ , $wR_2 = 0.1654$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	2.49/-0.69	1.22/-0.67	1.00/-0.89	0.97/-0.51	0.92/-0.70	0.83/-0.85
Flack parameter	0.001(5)	0.057(6)	0.016(7)	-0.002(11)	0.001(19)	0.337(11)
Refined minor twin component fraction	0.180(2)	0.186(1)	0.185(3)	0.188(1)	0.206(4)	0.262(1)

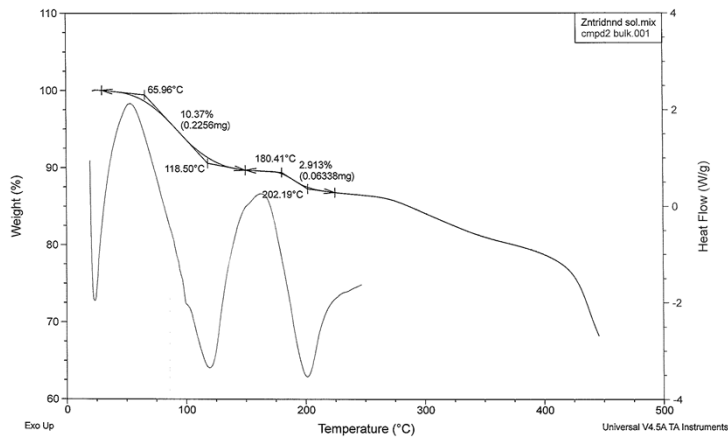
**Table S2** Bond lengths [ $\text{\AA}$ ] for **1** at 104 K, 298 K, 323 K, 373 K on the same crystal, whilst 298K after heated to 373 K and at 298 K after exposed to air for 1 day is on a different crystal

Bonded atoms		104 K	298 K	323 K	373 K	298 K (after heated to 373 K)	298K after 1 day exposure to air
Zn01	O9	2.065(4)	2.069(6)	2.077(5)	2.076(6)	2.050(6)	2.069(5)
Zn01	O3	2.134(4)	2.143(6)	2.152(5)	2.200(6)	2.171(7)	2.159(6)
Zn01	O2	2.037(4)	2.025(7)	2.027(6)	2.072(6)	2.059(7)	2.028(6)
Zn01	O7	2.097(4)	2.093(7)	2.089(5)	2.097(5)	2.075(6)	2.085(7)
Zn01	O1S	2.158(4)	2.141(7)	2.142(6)	2.162(6)	2.141(6)	2.164(7)
Zn01	O3W	2.093(4)	2.089(7)	2.097(6)	2.076(6)	2.053(6)	2.100(6)
Zn02	O1W	2.091(5)	2.115(8)	2.164(8)	-	-	2.154(8)
Zn02	O1	2.056(5)	2.037(7)	2.015(6)	1.948(7)	1.940(8)	2.032(7)
Zn02	O2W	2.104(5)	2.084(8)	2.079(7)	-	-	2.069(8)
Zn02	O3S	2.069(4)	2.072(7)	2.053(7)	2.013(8)	2.001(8)	2.089(7)
Zn02	O6	2.179(5)	2.166(8)	2.142(7)	1.979(7)	1.947(8)	2.158(8)
Zn03	O9	1.978(4)	1.968(5)	1.972(5)	1.995(6)	1.962(6)	1.964(6)
Zn03	O4	1.939(5)	1.942(7)	1.920(6)	1.937(7)	1.939(8)	1.937(7)
Zn03	O2S	1.990(5)	1.970(7)	1.965(7)	1.998(7)	1.979(7)	1.983(7)
Zn03	O5	1.940(6)	1.928(8)	1.909(7)	1.937(7)	1.899(7)	1.922(7)
S1	O4S	1.465(4)	1.457(7)	1.466(7)	1.448(7)	1.439(7)	1.454(8)
S1	O1S	1.473(4)	1.469(7)	1.471(7)	1.486(6)	1.469(6)	1.468(7)
S1	O3S	1.484(5)	1.468(7)	1.471(7)	1.479(9)	1.468(9)	1.464(7)
S1	O2S	1.487(5)	1.481(8)	1.483(7)	1.485(8)	1.473(9)	1.484(8)
O3	Zn01	2.134(4)	2.143(6)	2.152(5)	2.200(6)	2.171(7)	2.159(6)
O3	C8	1.253(7)	1.246(11)	1.254(9)	1.242(11)	1.224(12)	1.260(10)
O2	C7	1.246(7)	1.246(11)	1.240(10)	1.237(10)	1.242(12)	1.244(11)
O7	N1	1.335(6)	1.348(10)	1.350(9)	1.338(9)	1.325(9)	1.334(10)
O1	C7	1.261(7)	1.248(11)	1.243(10)	1.281(11)	1.244(12)	1.246(11)
O8	N2	1.325(6)	1.316(10)	1.311(10)	1.324(10)	1.297(9)	1.322(10)
O4	Zn03	1.939(5)	1.942(7)	1.920(6)	1.937(7)	1.939(8)	1.937(7)
O4	C8	1.275(7)	1.265(11)	1.265(11)	1.271(11)	1.257(11)	1.279(10)
O6	Zn02	2.179(5)	2.166(7)	2.166(7)	1.979(7)	1.947(8)	2.158(7)
O6	C9	1.231(8)	1.238(12)	1.238(12)	1.262(14)	1.261(15)	1.239(12)
N2	C17	1.357(8)	1.337(13)	1.337(13)	1.316(12)	1.332(12)	1.368(13)
N2	C18	1.352(8)	1.330(13)	1.330(13)	1.376(12)	1.354(12)	1.329(13)
N1	C10	1.360(8)	1.342(13)	1.342(13)	1.365(12)	1.349(12)	1.351(13)
N1	C14	1.352(8)	1.342(13)	1.342(13)	1.357(12)	1.336(12)	1.334(14)
C11	C10	1.381(8)	1.361(14)	1.361(14)	1.375(13)	1.366(13)	1.356(14)
C11	C12	1.406(8)	1.377(14)	1.377(14)	1.416(12)	1.397(13)	1.389(14)
C1	C2	1.394(8)	1.395(11)	1.395(11)	1.394(12)	1.381(13)	1.398(11)

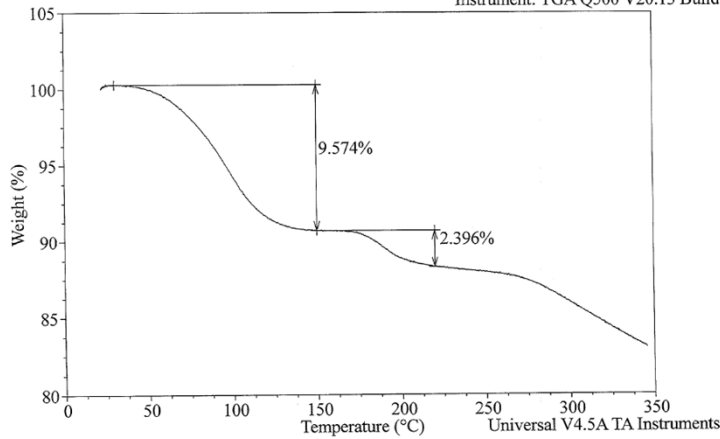
C1	C6	1.391(8)	1.387(11)	1.387(11)	1.384(11)	1.382(12)	1.394(11)
C1	C7	1.509(7)	1.496(11)	1.496(11)	1.520(11)	1.519(12)	1.504(11)
C16	C15	1.409(8)	1.385(13)	1.385(13)	1.392(12)	1.365(13)	1.394(13)
C16	C17	1.386(8)	1.390(14)	1.390(14)	1.389(13)	1.387(14)	1.372(14)
C3	C2	1.387(8)	1.384(11)	1.384(11)	1.389(11)	1.399(13)	1.400(11)
C3	C4	1.390(8)	1.395(11)	1.395(11)	1.416(11)	1.397(13)	1.395(11)
C3	C8	1.510(8)	1.499(11)	1.499(11)	1.518(12)	1.504(14)	1.479(11)
C15	C12	1.474(8)	1.478(12)	1.478(12)	1.490(11)	1.488(11)	1.496(13)
C15	C19	1.394(8)	1.387(15)	1.387(15)	1.384(13)	1.364(14)	1.391(14)
C6	C5	1.395(9)	1.375(12)	1.375(12)	1.396(13)	1.378(13)	1.366(12)
O5	Zn03	1.940(6)	1.928(7)	1.928(7)	1.937(7)	1.899(7)	1.922(7)
O5	C9	1.282(8)	1.271(13)	1.271(13)	1.291(12)	1.271(14)	1.283(12)
C12	C13	1.411(8)	1.399(13)	1.399(13)	1.407(12)	1.389(13)	1.395(14)
C13	C14	1.376(8)	1.378(14)	1.378(14)	1.366(13)	1.360(13)	1.376(14)
C4	C5	1.384(8)	1.368(12)	1.368(12)	1.394(13)	1.387(13)	1.383(12)
C19	C18	1.373(8)	1.367(14)	1.367(14)	1.382(13)	1.374(14)	1.360(14)
C5	C9	1.492(8)	1.498(12)	1.498(12)	1.510(11)	1.499(12)	1.496(12)
Zn02	O9	2.079(4)	2.067(6)	2.056(5)	1.989(6)	1.981(6)	2.061(6)
Zn02*	Zn03*	3.219(1)	3.219(1)	3.215(1)	3.137(4)	3.101(2)	3.219(2)

\* These are non-bonded distances

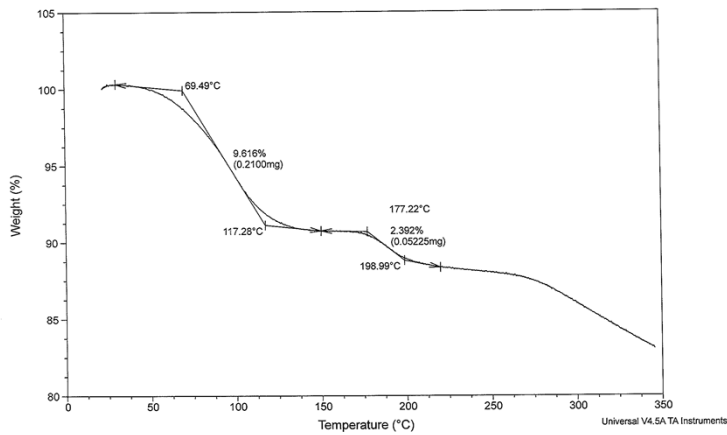
**Figure S1. DSC and TGA graphs of 1**



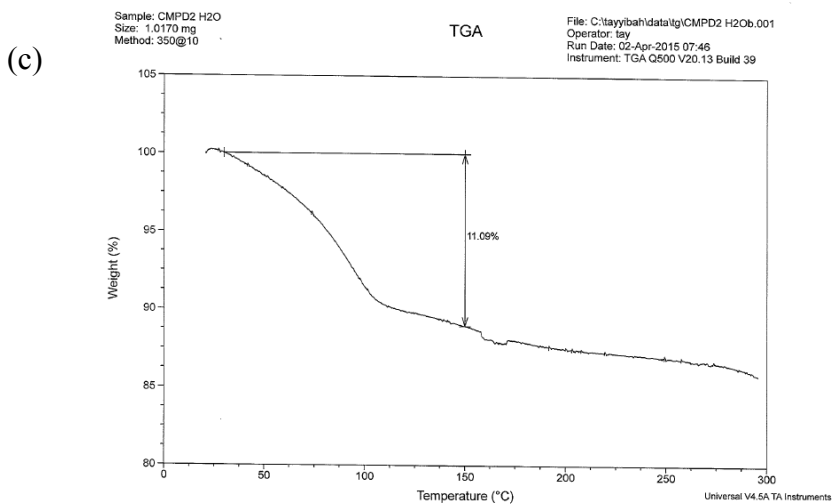
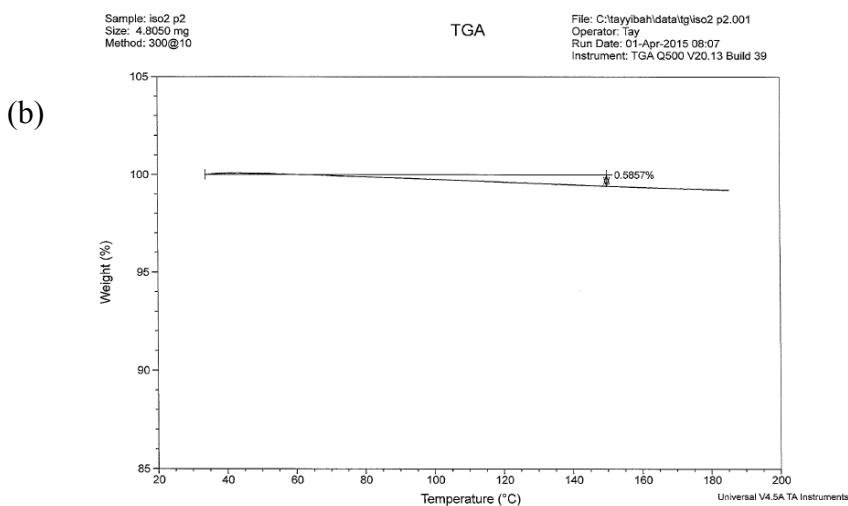
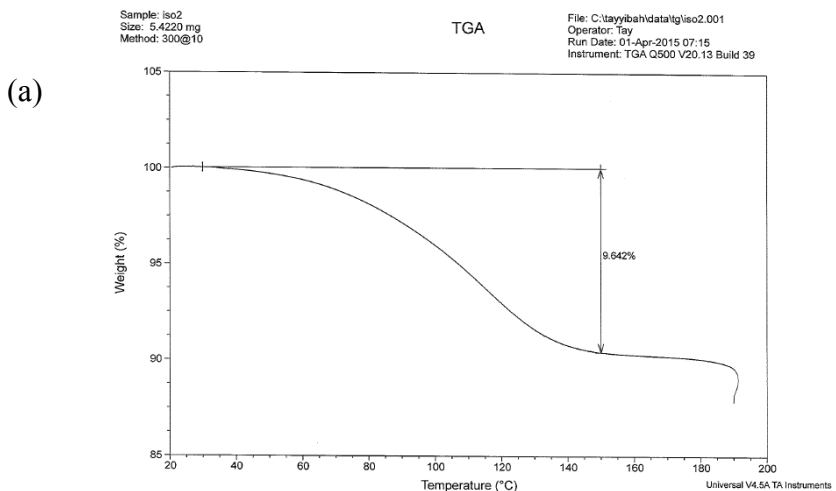
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 Instrument: TGA Q500 V20.13 Build



Sample: cmpd sol ex  
 Size: 2.1840 mg  
 Method: 400B/10  
 Comment: 80C vac overnight  
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 Instrument: TGA Q500 V20.13 Build 39

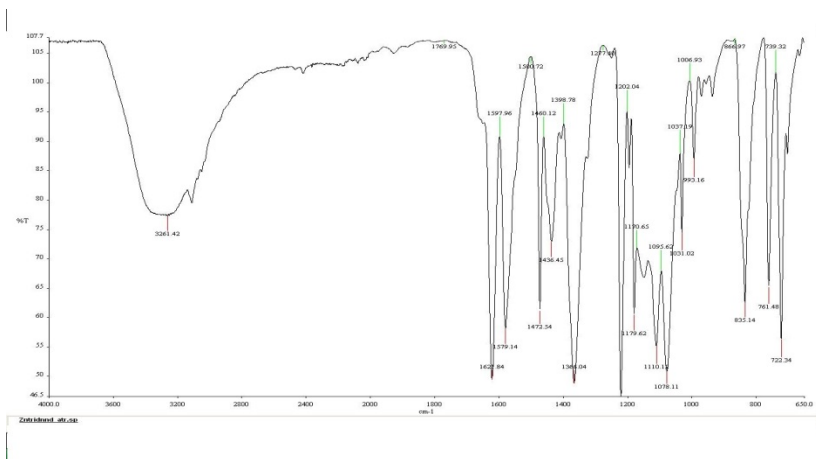


**Figure S2.** TGA graphs for rehydration experiment: (a) as-synthesized MOF (b) the immediate reheat and (c) after 24 hours of being exposed to a humid atmosphere

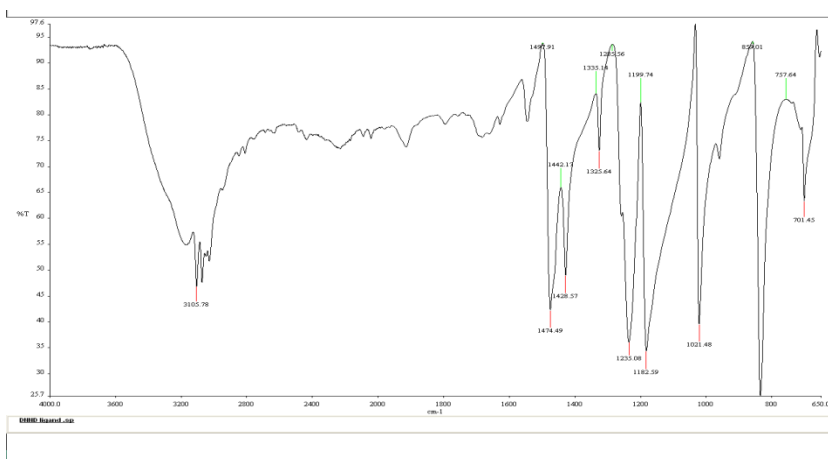


**Figure S3.** FT-IR spectra for the (a) 2D MOF (b) trimesic acid and (c) 4,4'-bipyridine-N,N'-dioxide

(a)



(b)



(c)

