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ARTICLE

The role of C-H····π interactions in modulating the breathing amplitude of a 2D square lattice net: Alcohol sorption studies

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A breathing 2D net **1** $\{[Zn(34pba)_2]\cdot DMF\}_n$ assembled from mononuclear zinc (II) centres and 3-(4-pyridyl) benzoate (34pba) ditopic linker is presented. **1** undergoes a displacive phase transition to give **1d**, $[Zn(34pba)_2]_n$ on evacuation of DMF. This is accompanied by a 37% decrease in solvent accessible void volume. Exposure of **1d** to alcohol vapours shows that the saturation uptake increases with an increase in number of carbon atoms in the alcohol. The enhanced uptake of *n*-butanol and *n*-propanol is attributed to the long alkyl chain which enhances C-H····π interactions with the hydrophobic pyridyl and phenyl rings of the network. These interactions trigger the breathing motion of the 2D network and allow for the entry of *n*-propanol and *n*-butanol into the channels. Methanol and ethanol are unable to initiate the dynamic motion of the framework which increases the channel volume. In consequence, these solvents are absorbed to a lesser extent. Vapour phase competition studies show that the activated material is able to absorb *n*-butanol in the presence of a high vapour pressure of methanol. The selectivity observed may be based on factors that allow the metal organic framework inclusion compound to assume the most relaxed conformation.

Supplementary Material

Table S1. Crystallographic data for compounds **1** and **1d**

Compound	**1**	**1d**
Molecular Formula	$(C_{24}H_{16}N_2O_4Zn).(C_3H_7NO)$	$C_{24}H_{16}N_2O_4Zn$
Molecular Mass	534.85	461.78
Crystal Size $(mm)^3$	0.21 x 0.22 x 0.25	0.23 x 0.28 x 0.26
Temp. Of collection / K	173(2)	173(2)
Crystal symmetry	tetragonal	tetragonal
Space group	P43212	P43212
a / Å	11.5361(3)	11.5806(3)
b / Å	11.5361(3)	11.5806(3)
c / Å	37.317(2)	34.904(2)
β /°	90	90
Z	8	8
Volume $Å^3$	4966.2(3)	4681.0(3)
Dc / g cm^{-3}	1.4306	1.310
2θ range	1.85 – 27.89	1.85-28.39
No. of reflections collected	24798	43511
No. Unique reflections	5934	5871
No. Reflections with I> 2σI	5045	5200
Data/ parameters refined	5934/329	5871/274
Goodness of fit, S	1.059	1.053
R (I> 2σI)	0.0429	0.0404
Final wR_2 (all data)	0.1029	0.1340
Min, Max e density / e	-0.29, 0.47	-0.39, 0.61

Table S2. Bond lengths of atoms coordinated to the zinc centre in compound **1**

Bond type	Bond length	Bond type	Bond length
Zn1 - O14A	2.268(2)	Zn - O15B	2.026(2)[a]
Zn1 - O14B	2.387(2)[a]	Zn1 - N1B	2.115(3)
Zn1 - O15A	2.081(2)	Zn1 - N1A	2.095(2)[b]

[a] via *x, y, 1-z*

[b] via *x-1, y, z*

Table S3. Bond angles around the Zinc metal centre in compound **1**

	Bond angle		Bond angle
O14A - Zn1 - O15A	60.03(11)	O15A - Zn1 - N1B	98.38(13)
O14A - Zn1 - N1B	94.24(13)	O15A - Zn1 - N1A	93.09(11)
O14A - Zn1 - N1A	152.67(12)	O15A - Zn1 - O14B	106.61(12)
O14A - Zn1 - O14B	89.26(12)	O15A - Zn1 - O15B	160.91(12)
N1B - Zn1 - O15B	52.84(12)	N1B - Zn1 - O15B	94.06(12)
O14A - Zn1 - O15B	104.80(13)	N1B - Zn1 - N1A	94.64(13)

Table S4. Bond lengths of atoms coordinated to the zinc centre in compound **1d**

Bond type	Bond length	Bond type	Bond length
Zn1 - O14A	2.367(2)	Zn - O15B	2.0414(2)
Zn1 - O14B	2.390(2)	Zn1 - N1B	2.077(2)[a]
Zn1 - O15A	2.031(2)	Zn1 - N1A	2.090(2)[b]

[a] via *x, y-1, z*

[b] via *1+x, y, z*

Table S5. Bond angles around the zinc centre in compound **1d**

	Bond angle		Bond angle
O14A - Zn1 - O14B	86.46(10)	O14A - Zn1 - N1A	158.85(9
O14A - Zn1 - O15A	59.39(8)	O14B - Zn1 - O15A	92.04(9)
O14A - Zn1 - O15B	96.24(9)	O14B - Zn1 - O15B	59.11(8)
O14A - Zn1 - N1B	93.66(9)	O14B - Zn1 - N1B	158.84(9)
O14B - Zn1 - N1A	92.64(10)	O15A - Zn1 - O15B	144.75(9)

Table S6. Hydrogen bonding interactions in compound **1**

Donor --- H....Acceptor	D - H	H...A	D...A	D - H...A
C6A --H6A ..O15A[a]	0.95	2.57	3.121(8)	119
C6A --H6A ..O15A[b]	0.95	2.45	3.173(8)	135
C6B --H6B ..O14A[c]	0.95	2.42	3.218(6)	144
C12A --H12A ..O14B[d]	0.95	2.65	3.473(4)	145
C12A –H12A ..O1C1[b]	0.95	3.04	3.555(8)	116
C8B --H8B ..O1C1[c]	0.95	2.56	3.490(11)	174

[a] via *1+x, y, z*
[b] via *1+y, x, -z*
[c] via *x-0.5, 0.5-y, 0.25-z*
[d] via *y, x, -z*

Table S7. Hydrogen bonding interactions in compound **1d**

Donor --- H....Acceptor	D - H	H...A	D...A	D - H...A
C6A --H6A ..O15A[a]	0.95	2.33	3.059(3)	133
C6A --H6A ..O15A[b]	0.95	2.92	3.343(3)	109
C6B --H6B ..O14A[c]	0.95	2.44	3.334(4)	157
C12A--H12A ..O15B[d]	0.95	2.48	3.319(4)	147

[a] via *y-1, x, -z*
[b] via *x-1, y, z*
[c] via *0.5+x, 2.5-y, 0.25-z*
[d] via *x-0.5, 1.5-y, 0.25-z*

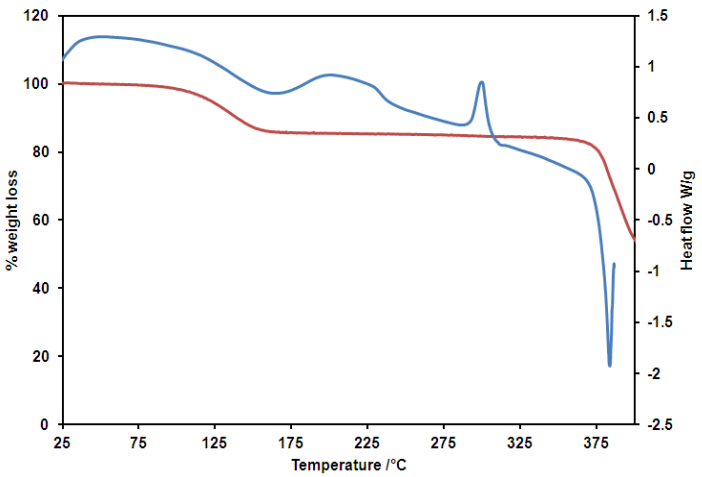

Fig.S1.TGA (red) and DSC (blue) profiles of compound **1**

Table S8. Crystallographic parameters of **1d-propanol** and **1d-butanol**

Compound	**1d-propanol**	**1d-butanol**
Molecular Formula	$(C_{24}H_{16}N_2O_4Zn).(C_3H_8O)$	$(C_{24}H_{16}N_2O_4Zn).(C_4H_{10}O)$
Molecular Mass	503.85	539.91
Crystal Size $(mm)^3$	0.13 x 0.16 x 0.20	0.06 x 0.25 x 0.25
Temp. Of collection / K	173(2)	173(2)
Crystal symmetry	Tetragonal	Tetragonal
Space group	P43212	P43212
a / Å	11.6638(4)	11.728 (1)
c / Å	36.790(3)	36.977(4)
Z	8	8
Volume $Å^3$	5005.0(5)	5086(2)
Dc / g cm^{-3}	1.385	1.3995
2θ range	1.83 – 27.10	2.06 – 26.53
No. of reflections collected	28248	32238
No. Unique reflections	5524	5164
No. Reflections with I> 2σI	4271	4646
Data/ parameters refined	5524/297	5164/78
Goodness of fit, S	1.043	2.141
R (I> 2σI)	0.0917	0.1880
Final wR_2 (all data)	0.2739	0.4585
Min, Max e density / e	-0.46, 0.88	-1.23, 3.75

Table S9. Selected bond lengths in 1d-propanol

Bond type	Bond length	Bond type	Bond length
Zn1 - O14A	1.948(7)	Zn1 - N1A[a]	2.092(10)
Zn1 - O14B	1.991(8)	Zn1 - N1B[b]	2.070(9)
Zn1 - O15A	2.459(10)		
(Zn1 - O15B) non-bonded	2.683(7)		

[a] via *x-1, y, z*
[b] via *x, 1+y, z*

Table S10. Bond angles around Zinc in compound **1d-propanol**

	Angle		Angle
O14A - Zn1 - O14B	143.5(3)	O14B - Zn1 - O15A	97.2(3)
O14A - Zn1 - O15A	57.2(2)	O14B - Zn1 - O15B	53.6(2)
O14A - Zn1 - O15B	94.7(3)	O14B - Zn1 - N1A	103.0(3)
O14B - Zn1 - O15B	53.6(2)	O14B - Zn1 - N1B	100.6(3)
O14A - Zn1 - N1A	99.0(3)	O15A - Zn1 - O15B	83.5(3)
O14A - Zn1 - N1B	105.9(3)	O15A - Zn1 - N1A	156.1(2)
N1A - Zn1 - N1B	95.5(3)	O15A - Zn1 - N1B	93.1(3)
O15B - Zn1 - N1B	152.9(3)	O15B - Zn1 - N1A	98.4(4)

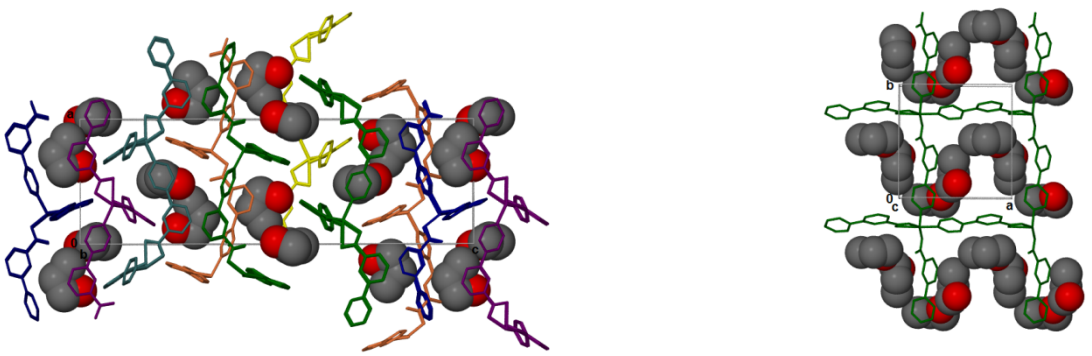

Figure S2. Packing diagrams of **1d-propanol**, (a) viewed along [010], (b) viewed along [001]

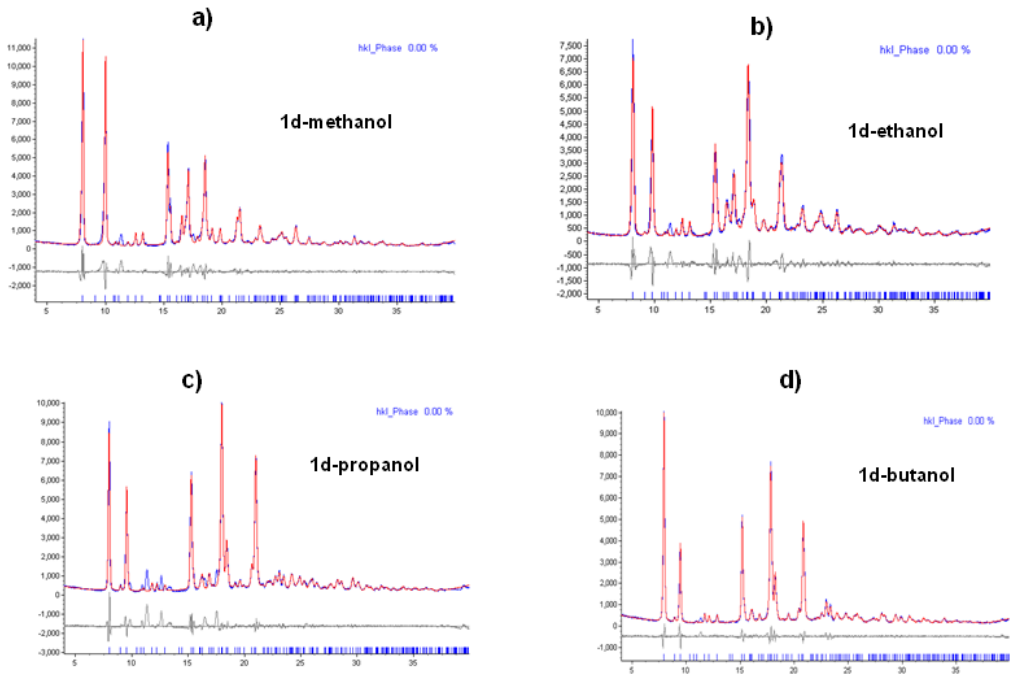

Fig.S3. Whole powder pattern decomposition of the alcohol inclusion compounds. The blue trace corresponds to the experimental PXRD trace, the red is the calculated. The difference between the calculated and the observed is displayed in grey colour.

Table S11. Unit cell parameters of the alcohol inclusion compounds

	1(with DMF) (sc)	**1d** (sc)	**1d-MeOH** (pf)	**1d-EtOH** (pf)	**1d-propanol** (pf)	**1d-propanol** (sc)	**1d-butanol** (pf)	**1d-butanol** (sc)
a (Å)	11.536	11.581	11.572	11.520	11.606	11.664	11.677	11.728
c (Å)	37.317	34.904	35.482	36.122	37.052	36.790	37.500	36.977
V (Å^3)	4966.2	4681.0	4751.5	4793.7	4990.9	5005.0	5113.1	5086.1

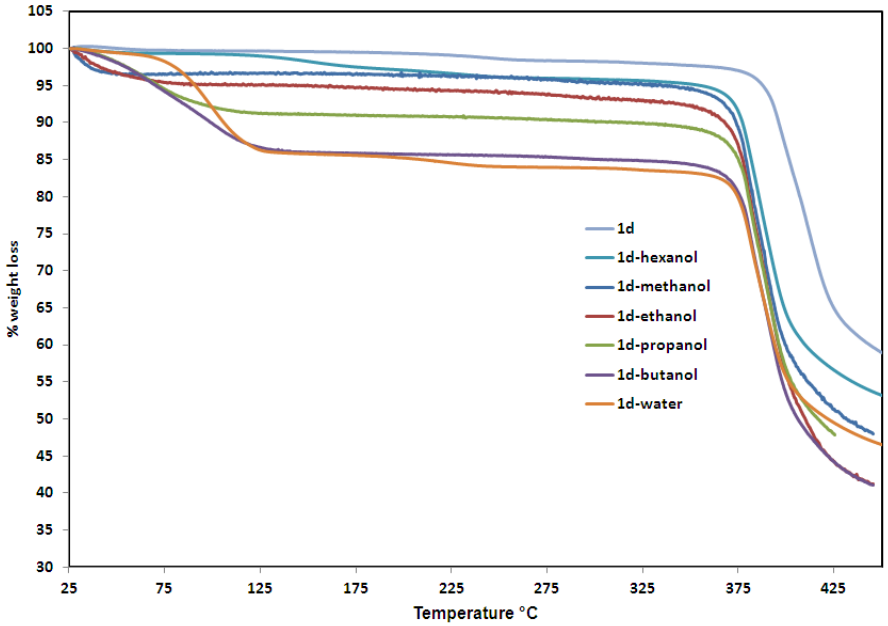

Fig.S4.Thermogravimetric measurements of **1d**-inclusion compounds

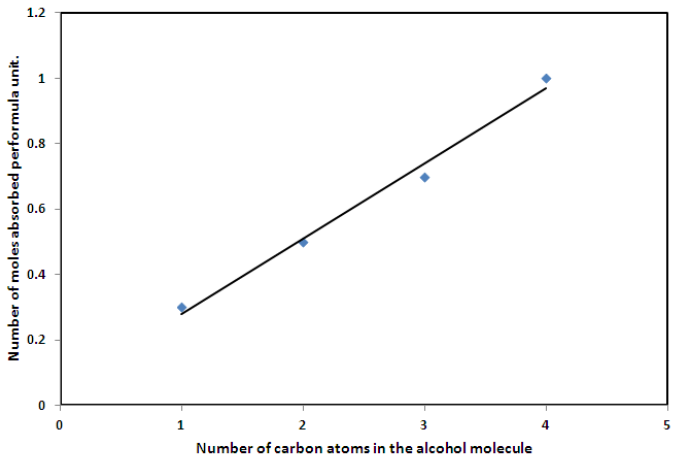

Fig.S5. A linear relationship between the number of carbon atoms and the number of moles absorbed per formula unit.

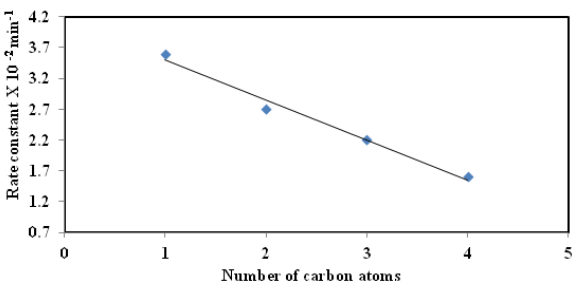

Fig.S6. Plot of number of carbon atoms in the alcohol vs the rate constant.

