MJ Rosseinsky
'Flexible sorption and transformation behavior in a microporous metal-organic framework'
Supplementary Information

Manuscript Number JA0262737

Supplementary Figure Captions

Figure S1 The disordered methanol guests in a single large pore as determined by single crystal X-ray diffraction a) viewed along [100] and b) along [001]. c) and d) show the positions of methanol guests determined by Monte Carlo docking calculations after reducing the symmetry of the (fixed) framework to P1. The C, H and O atoms of the guest molecules are shown as green, white and yellow space filling spheres respectively. Framework Ni, C, H, N and O atoms are shown as small cyan, gray, white, blue and red spheres respectively. Only framework atoms which lie within 7 Å of a guest atom are shown.

Figure S2 The phase purity of the sample was confirmed by powder X-ray diffraction. The pattern calculated from the structure determined by single crystal X-ray diffraction (a) shows excellent agreement with the observed data (b).

Figure S3 The variation of mass of **A** as a function of temperature. Guest methanol molecules were lost whilst handling the sample at room temperature before the thermogravimetric analysis began.

Figure S4 *In-situ* variable temperature X-ray powder diffraction from **A** at room temperature and 175 $^{o}$C. Both patterns can be fully indexed using the structure determined by single crystal X-ray diffraction.

Figure S5 The variation in the lattice parameters and cell volume of **A** as a function of temperature. These parameters were determined by refinement against powder X-ray diffraction data collected *in-situ* from **A** contained in a glass capillary.

Figure S7 X-ray powder diffraction data collected from i) a sample of pristine **A**.2$CH_3OH$ and ii) **A**.1.2toluene. Both patterns can be fully indexed using a unit cell of similar dimensions to those observed in the single crystal diffraction experiments. These give unit cells parameters of i) $a$ = 11.292(4) Å, $b$ = 20.598(9) Å, $c$ = 34.462(16) Å, V = 8015.4(97) Å$^3$ and ii) $a$ = 11.285(5) Å, $b$ = 20.632(11) Å, $c$ = 34.447(18) Å, V = 8020.7(58) Å$^3$.

Figure S8 The variation of mass of **A** in response to exposure to a) 1,3,5 triethylbenzene (TB) vapour, b) 2ethyl butan-1-ol (EB) vapour and c) benzyl alcohol (BA) vapour. The mass change to the plateau value in a) corresponds to an uptake of 0.13TB per $Ni_2bip_3(NO_3)_4$ formula unit whilst the maximum uptake in b) gives 0.08 EB molecules per formula unit and c) gives 0.06 BA molecules per formula unit. Dashed black lines indicate the switching of the He flow between dry and saturated with toluene vapour.

Figure S9 Gas chromatographs obtained for a) a standard mixture of toluene (1.85 min) and 2ethyl butan-1-ol (2.38 min) in benzyl alcohol, b) a mixture of ethyl butan-1-ol (2.38 min) and benzyl alcohol (5.58 min) before addition of toluene loaded sample **A** and c) the same mixture of ethyl butan-1-ol in benzyl alcohol 1 hour after addition of toluene-loaded sample **A**.

Figure S9 The rate of reaction for the transformation **B** to **A**. The phase fractions were estimated by following the intensities (relative to the main peak at $2\theta = 9.2^{o}$) of Bragg reflections from each phase in angular regions of the powder diffraction pattern where no other Bragg peaks are observed. These peaks examined were at $2\theta = 11.8^{o}$ for methanol phase **A** and $2\theta = 18.9^{o}$ for the ethanol phase, **B**. The phase fraction of the two phases as a function of methanol exposure is shown . The peak intensities of **B** and **A** are indicated by white squares and triangles respectively. The phase fractions of **A** and **B** thus determined for phase pure MeOH templated material **A** are shown as a red square and triangle, demonstrating the precision of the phase fraction estimation.

Crystallographic Information follows the supplementary Figures

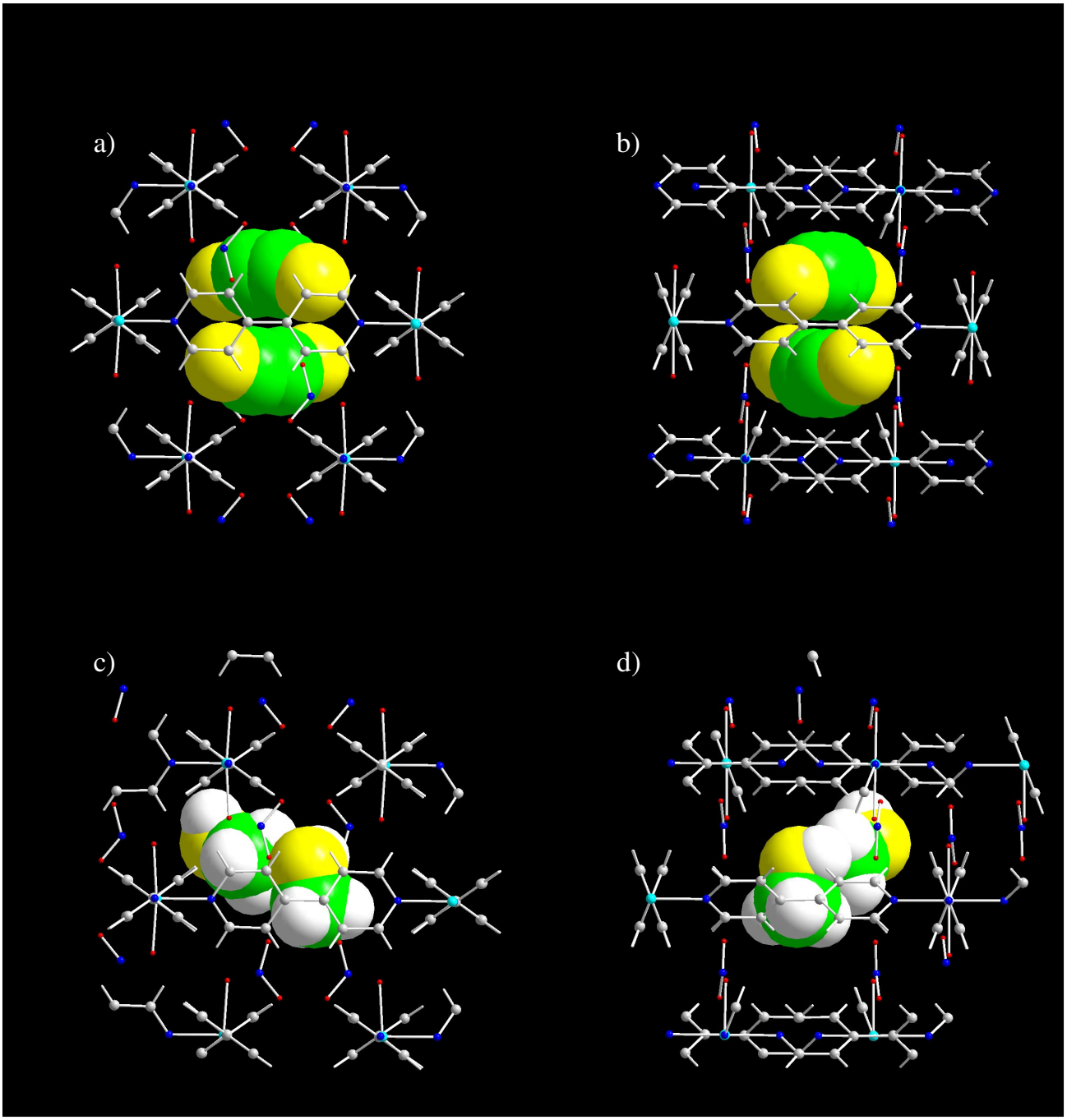



Figure S1

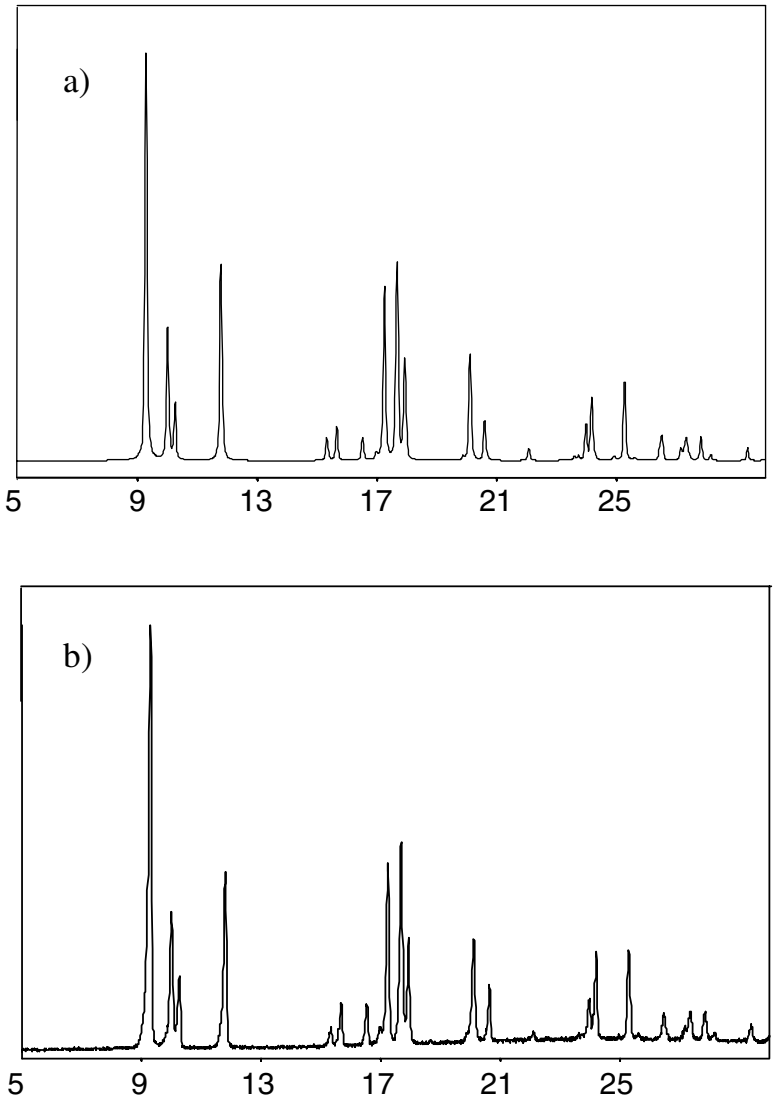



Figure S2

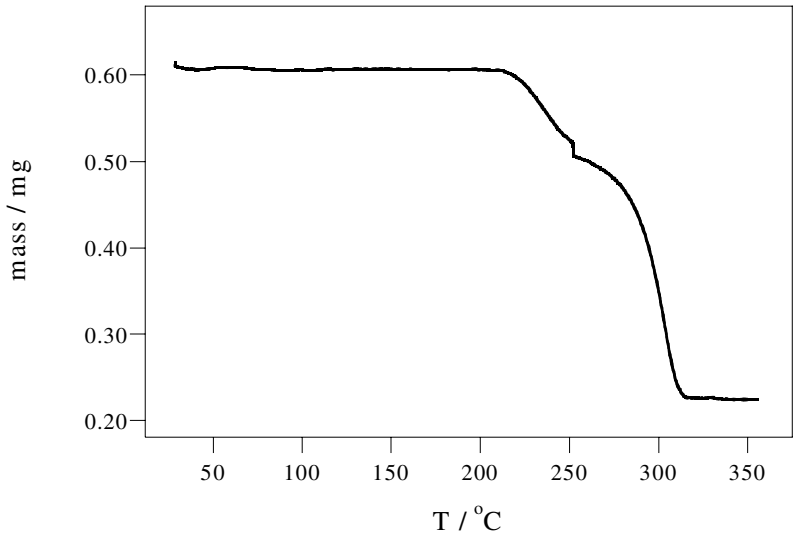



Figure S3

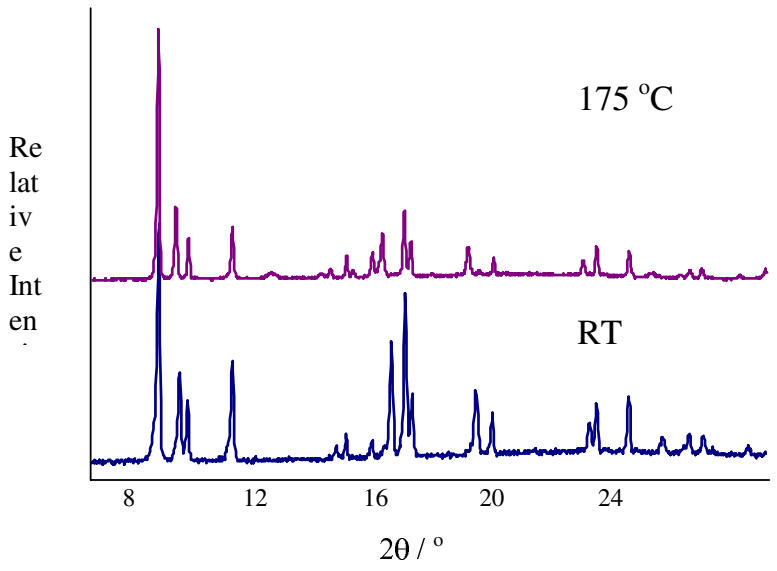
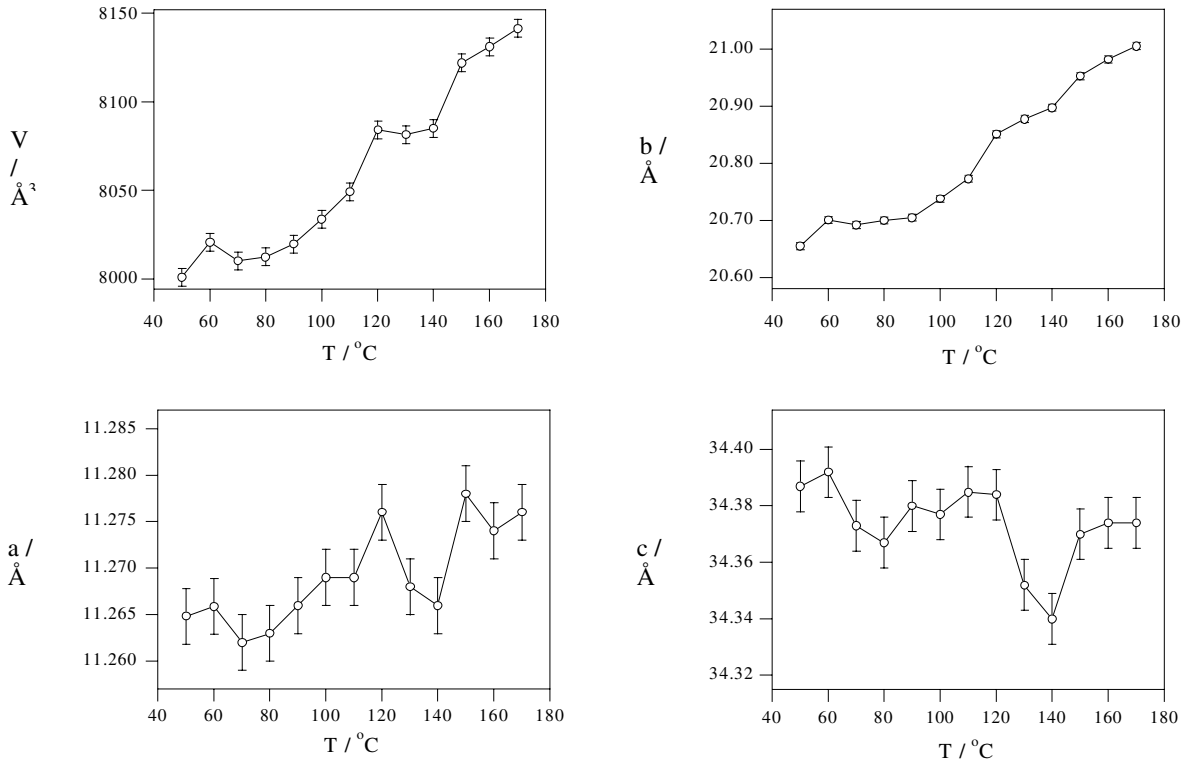



Figure S4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b / Å
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20.60
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T / °C
a / Å
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11.280
11.275
11.270
11.265
11.260
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34.36
34.34
34.32
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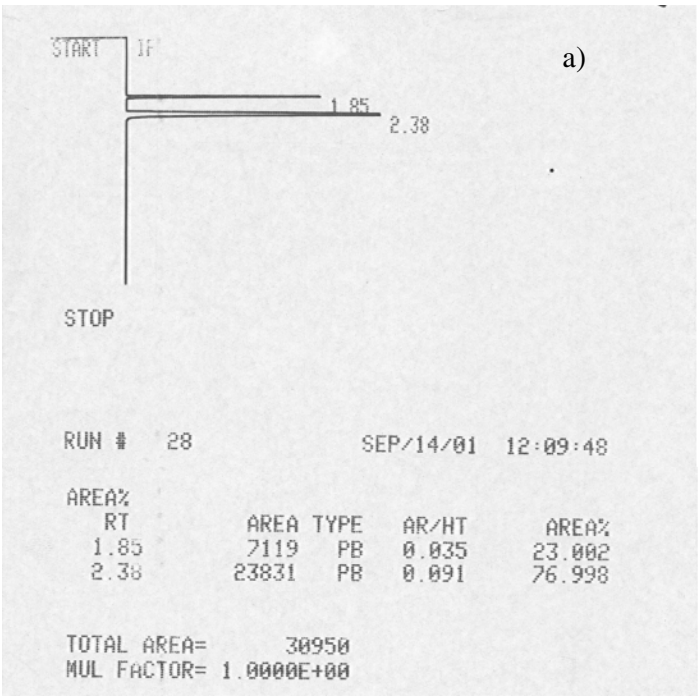
T / °C

Figure S5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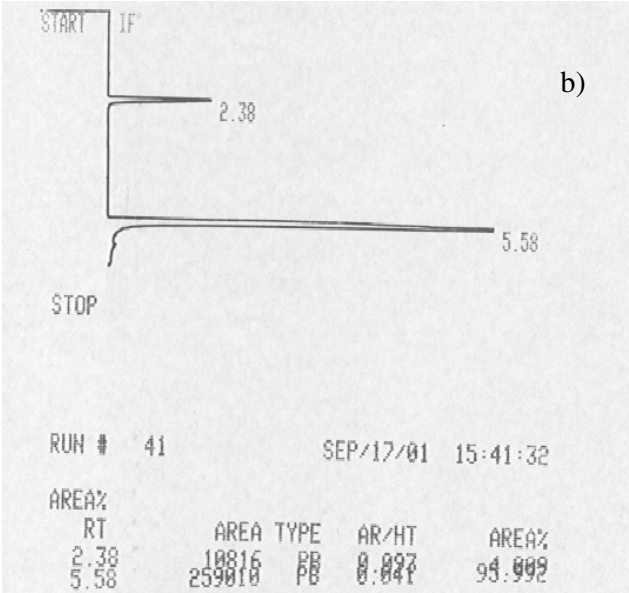
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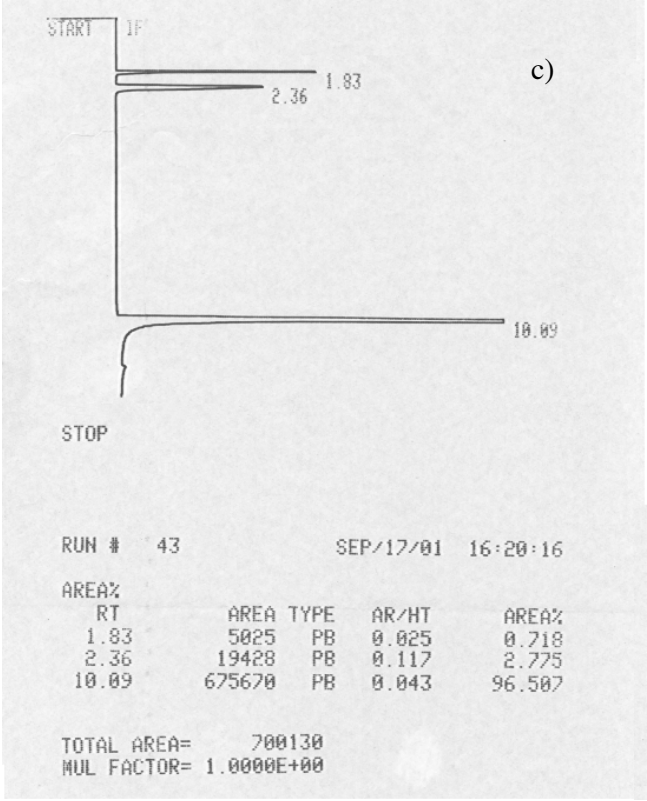
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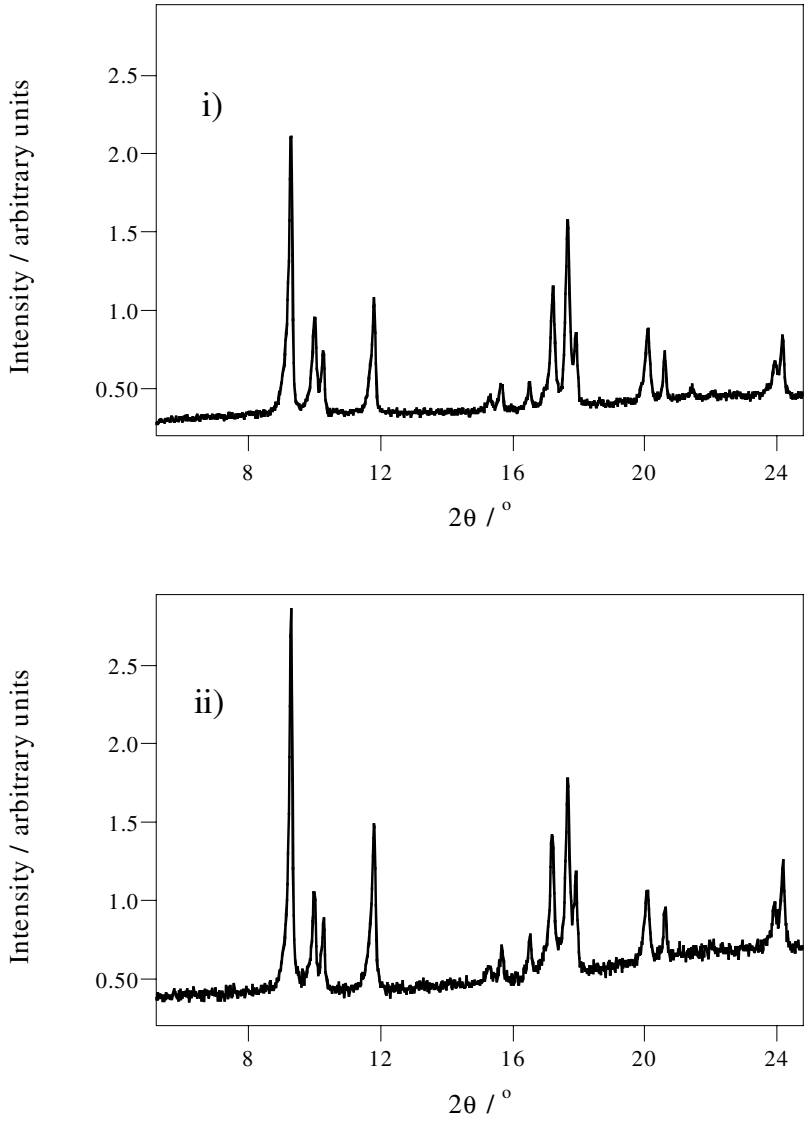
Figure S6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1.5
1.0
0.50
8
12
16
20
24
2θ / °
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Intensity / arbitrary units
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1.5
1.0
0.50
8
12
16
20
24
2θ / °

Figure S7

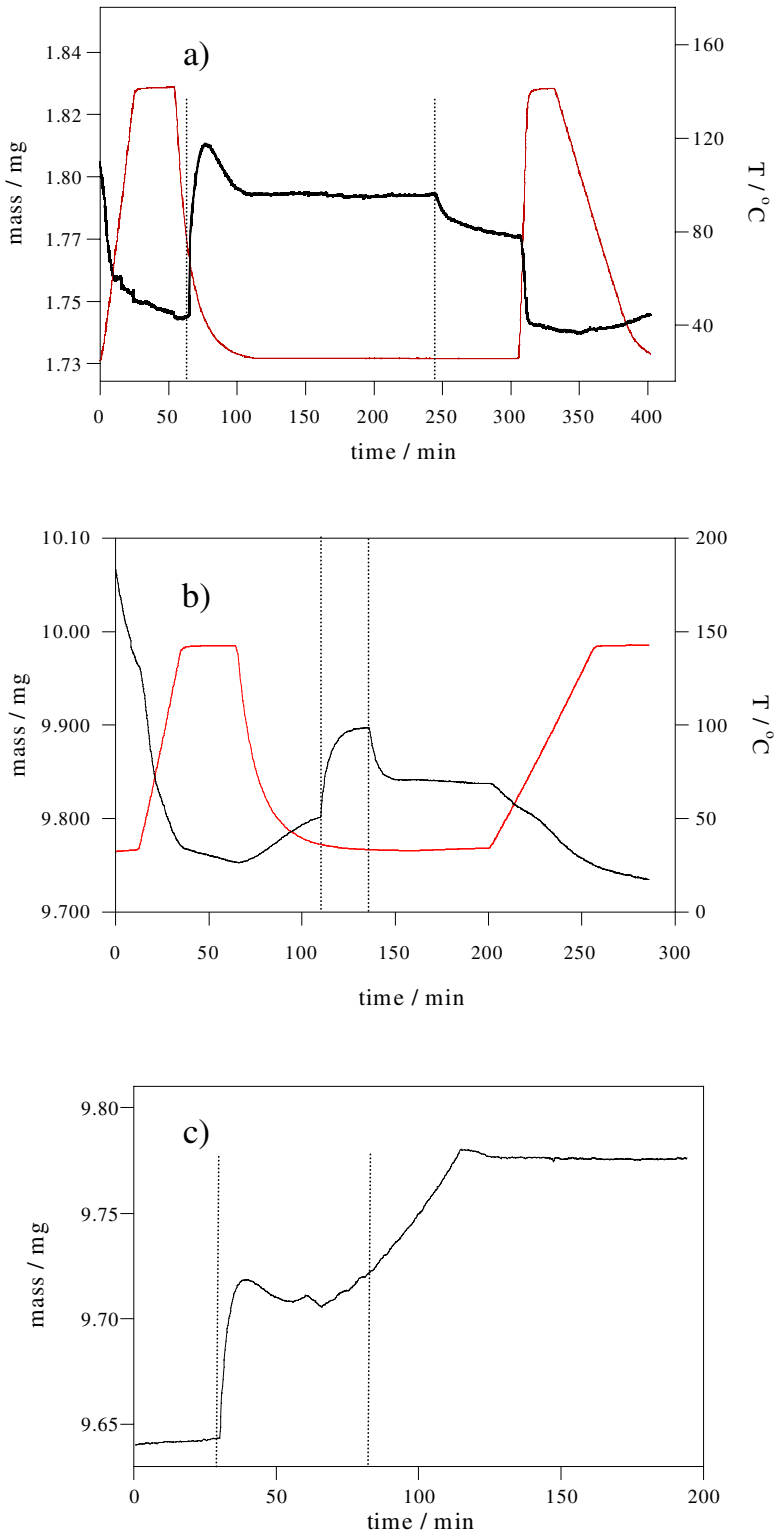
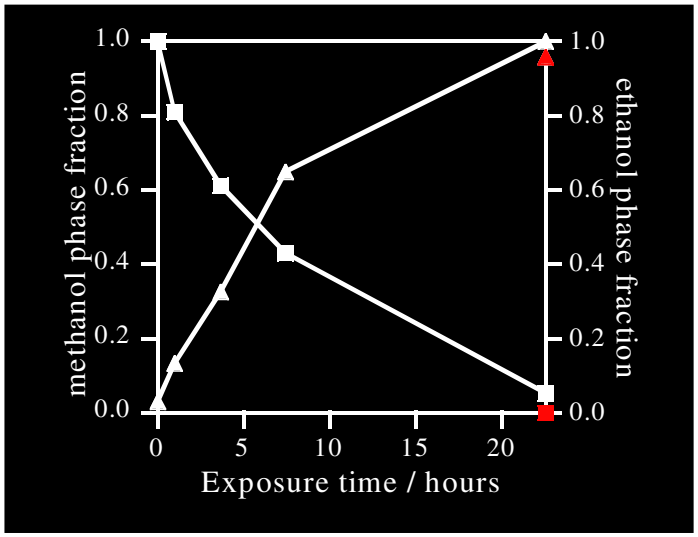



Figure S8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15
20
Exposure time / hours

Figure S9

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of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc.
and is
 not relevant to the choice of reflections for refinement.  R-factors
based
 on F^2^ are statistically about twice as large as those based on F,
and R-
 factors based on ALL data will be even larger.

This material contains a framework composed of Ni atoms linked by
bipyridyl
molecules which form ladders directed along the c-direction of the
unit
cell.  The bypyridyl molecules link Ni atoms atoms along this
direction are
disordered.  They rock around the axis of the molecule and this has
been
modelled by splitting of these atoms over two sites.  The temperature
factors of the split atoms were refined isotropically.  The occupancy
of
the two sites refined to 0.557(6)/0.443(6).  The bypyridyl molecules
forming the cross struts of the ladder were succesfully modelled
without
the introduction of split atomic positions.

Careful inspection of the cavities within the framework has allowed us
to locate methanol molecules.The methanol is disordered about a 2-fold
axis and has 2 1/2-occupied orientations.  In trial refinements the
```

```
C-O bond length was shorter (1.35A) than the literature value of
1.43A.
It was therefore restained to the literature value with no appreciable
effect on the R-factors for the fit.

Elemental microanalysis and thermogravimetric experiments are
consistent
with the stoichiometry determined from the single crystal diffraction
experiment.
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 and torsion angles; correlations between esds in cell parameters are
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C2B N1 1.325(11) . ?
C2B C5B 1.359(14) . ?
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C3 C4A 1.374(12) . ?
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C3 C4B 1.430(11) . ?
C3 C3 1.498(9) 12_654 ?
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N3 C9 1.325(8) 12_554 ?
N3 C9 1.325(8) . ?
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C9 N3 C9 116.5(8) 12_554 . ?
C9 N3 Ni1 121.7(4) 12_554 . ?
C9 N3 Ni1 121.7(4) . . ?
O2 N4 O3 125.7(8) . . ?
O2 N4 O1 116.2(8) . . ?
O3 N4 O1 118.2(7) . . ?
C8 C7 C8 117.3(8) 12_554 . ?
C8 C7 C7 121.3(4) 12_554 18_565 ?
C8 C7 C7 121.3(4) . 18_565 ?
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR
and
 goodness of fit S are based on F^2^, conventional R-factors R are
based
 on F, with F set to zero for negative F^2^. The threshold expression
of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc.
and is
 not relevant to the choice of reflections for refinement.  R-factors
based
 on F^2^ are statistically about twice as large as those based on F,
and R-
 factors based on ALL data will be even larger.

 This material contains a framework composed of Ni atoms linked by
bipyridyl
 molecules which form ladders directed along the c-direction of the
unit
 cell.  The bypyridyl molecules link Ni atoms atoms along this
direction are
 disordered.  They rock around the axis of the molecule and this has
been
 modelled by splitting of these atoms over two sites.  The temperature
 factors of the split atoms were refined isotropically.  The occupancy
of
 the two sites refined to 0.557(6)/0.443(6).  The bypyridyl molecules
 forming the cross struts of the ladder were succesfully modelled
without
 the introduction of split atomic positions.  Data were collected from
a
 crystal which  had been desolvated ex-situ.
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P=(Fo^2^+2Fc^2^)/3'
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C1A C 0.6201(15) 0.3729(13) 0.0711(3) 0.025(2) Uiso 0.479(11) d P . .
H1A H 0.5771 0.3706 0.0941 0.030 Uiso 0.479(11) calc PR . .
H1B H 0.5816 0.3152 0.0872 0.030 Uiso 0.521(11) d PR . .
C1B C 0.6240(16) 0.3385(10) 0.0683(3) 0.025(2) Uiso 0.521(11) d P . .
C2A C 0.6281(14) 0.3749(14) 0.0051(4) 0.033(3) Uiso 0.479(11) d P . .
H2A H 0.5891 0.3750 -0.0187 0.040 Uiso 0.479(11) calc PR . .
H2B H 0.5832 0.4356 -0.0038 0.040 Uiso 0.521(11) d PR . .
C2B C 0.6234(17) 0.4094(11) 0.0146(4) 0.033(3) Uiso 0.521(11) d P . .
C3 C 0.8093(6) 0.3746(7) 0.04097(16) 0.030(2) Uani 1 d . . .
C4A C 0.7415(13) 0.3746(13) 0.0743(4) 0.024(2) Uiso 0.479(11) d P . .
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H4B H 0.7851 0.3159 0.0883 0.028 Uiso 0.521(11) d PR . .
C4B C 0.7434(14) 0.3392(11) 0.0692(3) 0.024(2) Uiso 0.521(11) d P . .
C5A C 0.7477(14) 0.3754(15) 0.0059(4) 0.029(3) Uiso 0.479(11) d P . .
H5A H 0.7898 0.3763 -0.0174 0.035 Uiso 0.479(11) calc PR . .
H5B H 0.7842 0.4333 -0.0059 0.035 Uiso 0.521(11) d PR . .
C5B C 0.7449(14) 0.4101(11) 0.0128(4) 0.029(3) Uiso 0.521(11) d P . .
O1 O 0.3771(6) 0.2742(4) 0.04178(13) 0.059(2) Uani 1 d . . .
N1 N 0.5609(5) 0.3741(6) 0.03976(15) 0.046(2) Uani 1 d . . .
N3 N 0.3750 0.3750 -0.0225(2) 0.048(4) Uani 1 d S . .
O2 O 0.3571(7) 0.3062(6) 0.09918(19) 0.111(4) Uani 1 d . . .
N4 N 0.3691(8) 0.2594(7) 0.07641(19) 0.061(3) Uani 1 d . . .
C7 C 0.3750 0.3750 -0.1029(3) 0.054(6) Uani 1 d S . .
O3 O 0.3739(10) 0.2031(9) 0.0861(3) 0.152(7) Uani 1 d . . .
C8 C 0.3377(9) 0.4278(8) -0.0827(2) 0.064(4) Uani 1 d . . .
H8 H 0.325(9) 0.473(7) -0.094(2) 0.077 Uiso 1 d . . .
C9 C 0.3391(8) 0.4262(7) -0.0424(2) 0.070(5) Uani 1 d . . .
H9 H 0.3135 0.4631 -0.0288 0.084 Uiso 1 calc R . .

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O1 0.034(3) 0.106(8) 0.039(3) -0.002(3) 0.001(3) 0.005(5)
N1 0.016(4) 0.085(8) 0.036(3) 0.009(4) -0.004(3) 0.002(6)
N3 0.020(5) 0.099(13) 0.026(4) 0.000 0.000 0.013(8)
O2 0.082(6) 0.183(13) 0.069(4) -0.075(6) -0.034(4) 0.055(7)
N4 0.035(5) 0.109(12) 0.039(4) 0.015(5) 0.002(4) -0.011(7)
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C7 0.019(7) 0.11(2) 0.029(6) 0.000 0.000 0.000(9)
O3 0.098(8) 0.197(19) 0.162(9) 0.099(11) -0.036(7) -0.042(11)
C8 0.068(8) 0.094(14) 0.031(4) -0.003(5) -0.018(4) 0.019(8)
C9 0.052(7) 0.125(15) 0.034(4) -0.014(5) -0.016(4) 0.020(7)

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planes)
 are estimated using the full covariance matrix.  The cell esds are
taken
 into account individually in the estimation of esds in distances,
angles
 and torsion angles; correlations between esds in cell parameters are
only
 used when they are defined by crystal symmetry.  An approximate
(isotropic)
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planes.
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Ni1 O1 2.062(9) . ?
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Ni1 N1 2.095(5) 12_554 ?
Ni1 N1 2.095(5) . ?
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C1A C4A 1.37(2) . ?
C1B C4B 1.34(2) . ?
C1B N1 1.412(18) . ?
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C2B N1 1.328(19) . ?
C2B C5B 1.37(2) . ?
C3 C4A 1.377(15) . ?
C3 C5A 1.390(15) . ?
C3 C5B 1.410(19) . ?
C3 C4B 1.418(19) . ?
C3 C3 1.479(13) 12_654 ?
O1 N4 1.231(8) . ?
N3 C9 1.313(12) . ?
N3 C9 1.313(12) 12_554 ?
O2 N4 1.242(15) . ?
N4 O3 1.197(17) . ?
C7 C8 1.349(13) . ?
C7 C8 1.349(13) 12_554 ?
C7 C7 1.518(18) 18_565 ?
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O1 Ni1 N3 93.77(13) 12_554 . ?
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O1 Ni1 N1 88.7(4) 12_554 12_554 ?
O1 Ni1 N1 91.0(4) . 12_554 ?
N3 Ni1 N1 91.82(15) . 12_554 ?
O1 Ni1 N1 91.0(4) 12_554 . ?
O1 Ni1 N1 88.7(4) . . ?
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N1 Ni1 N1 176.4(3) 12_554 . ?
N1 C1A C4A 126.4(12) . . ?
C4B C1B N1 120.9(14) . . ?
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N1 C2B C5B 124.3(15) . . ?
C4A C3 C5A 116.4(9) . . ?
C4A C3 C5B 106.6(12) . . ?
C5A C3 C5B 30.9(14) . . ?
C4A C3 C4B 30.8(13) . . ?
C5A C3 C4B 109.7(12) . . ?
C5B C3 C4B 117.5(10) . . ?
C4A C3 C3 123.7(7) . 12_654 ?
C5A C3 C3 119.9(7) . 12_654 ?
C5B C3 C3 120.6(11) . 12_654 ?
C4B C3 C3 122.0(10) . 12_654 ?
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C2B C5B C3 118.6(14) . . ?
N4 O1 Ni1 107.9(8) . . ?
C1A N1 C2B 106.6(12) . . ?
C1A N1 C2A 115.7(10) . . ?
C2B N1 C2A 32.8(12) . . ?
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C2B N1 C1B 117.7(11) . . ?
C2A N1 C1B 108.8(11) . . ?
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C2B N1 Ni1 120.2(9) . . ?
C2A N1 Ni1 120.6(7) . . ?
C1B N1 Ni1 122.0(9) . . ?
C9 N3 C9 117.2(10) . 12_554 ?
C9 N3 Ni1 121.4(5) . . ?
C9 N3 Ni1 121.4(5) 12_554 . ?
O3 N4 O1 120.0(13) . . ?
O3 N4 O2 124.6(10) . . ?
O1 N4 O2 115.4(13) . . ?
C8 C7 C8 118.0(12) . 12_554 ?
C8 C7 C7 121.0(6) . 18_565 ?
C8 C7 C7 121.0(6) 12_554 18_565 ?
C7 C8 C9 119.5(11) . . ?
N3 C9 C8 122.9(11) . . ?

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