Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Structural Variety in Ytterbium Dicarboxylate Frameworks and In Situ Study Diffraction of their Solvothermal Crystallisation

Matthew I. Breeze, Thomas W. Chamberlain, Guy. J. Clarkson, Raíssa Pires de Camargo,Yue Wu, Juliana Fonseca de Lima, Franck Millange, Osvaldo A. Serra, Dermot O'Hare and Richard I. Walton

S1: Single Crystal Analysis: Further Details

The structure of (**1**) we recently reported in a preliminary communication (reference 17 of main text).

For (**2**) the asymmetric unit contains an Yb coordinated to three half anions of terephthalate, a DMF and a water. The three terephtalate anions all lie on inversion centres. Two of the terephthalate carboxylate oxygens (O101/O102 and O201/O202) are coordinated to the Yb by both oxygens and one bridges between Yb1 and a symmetry equivalent Yb1 across an inversion centre (O301/O302). The hydrogens on the coordinated water (O501) were located in a difference map and they were allowed to refine with a distance restraint (DFIX 0.85) and thermal parameters equal to 1.5 times that of O501 to which they were attached.

The structure of (**3**) was refined as a twin with matrices relating the two twin components:

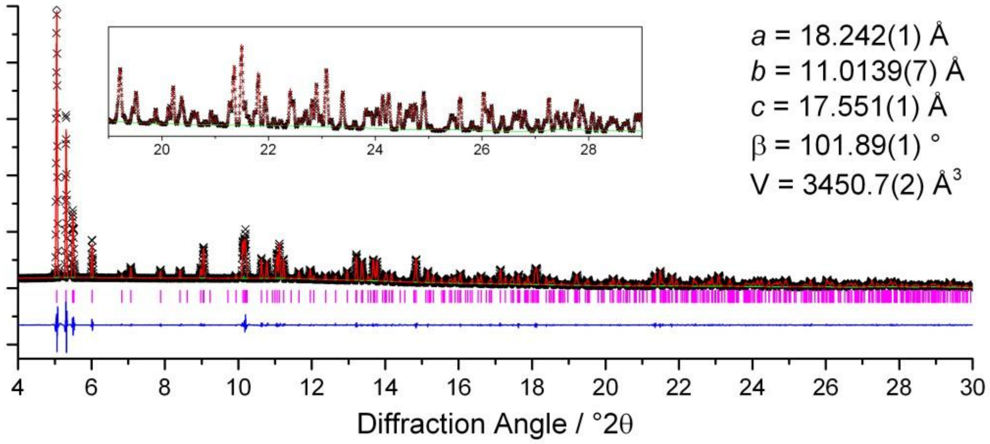
1 1.0000 0.0000 0.0000 0.0000 1.0000 0.0000 0.0000 0.0000 1.0000
2 -1.0000 0.0007 -0.2907 -0.0007 -1.0001 -0.0003 0.0004 -0.0002 1.0001

The refined scale factors (twin ratios) were 0.7145(18) 0.2855(18)

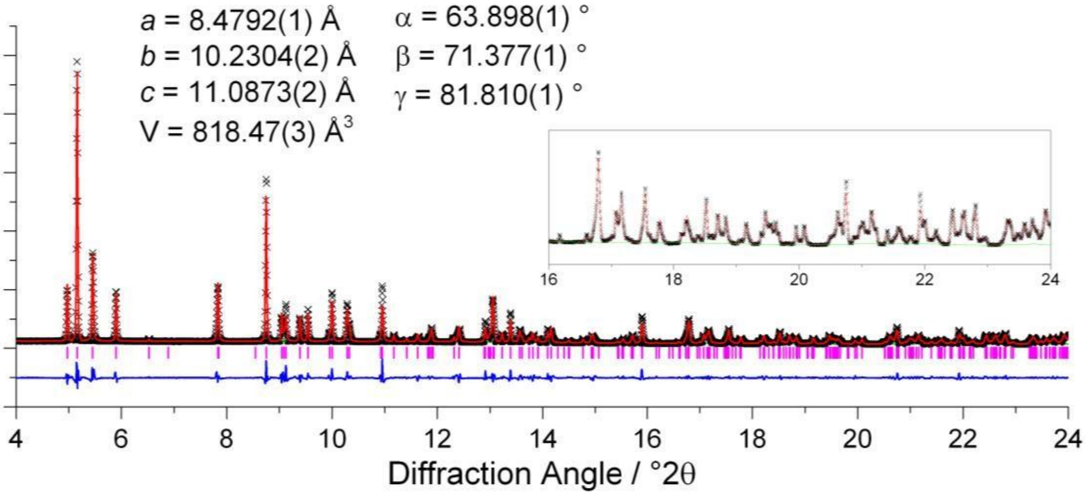
All the crystals of (**4**) examined were twinned. A suitable twin refinement could not be realized so the refinement was conducted on the major twin component. The asymmetric unit contains a Yb with two water ligands and three naphthalene dicarboxylates. The three naphthalene dicarboxylate acids all lie on inversion centres (so only half of them appear in asymmetric unit). Two are bound using both oxygens of the same carboxyl to Yb1 (naphthalene A and B) and one is bridged between symmetry related Yb ions (naphthalene C). Some of the hydrogens were located on the bound waters in a difference map but due to large satellite Q peaks from unresolved twinning it was preferable to place all of them at calculated positions for the refinement.

S2: Powder XRD

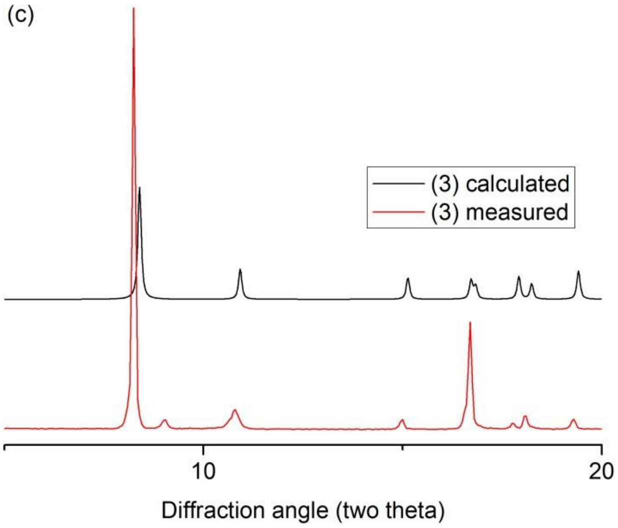
(a)



(b)



(c)



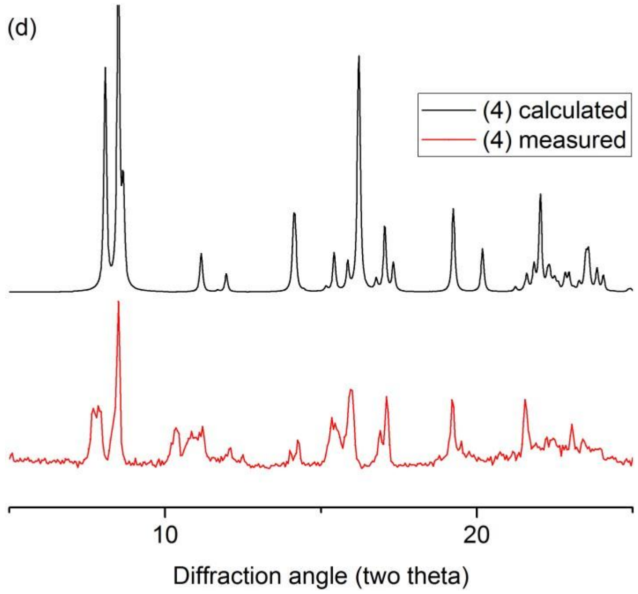


Figure S2.1: Measured and calculated room temperature powder XRD of compounds (a) (1), (b) (2), (c) (3), and (d) (4). For (1) and (2) Beamline I11 of the Diamond Light Source was used with λ = 0.825174 Å and the fitted obtained using a Le Bail with the lattice parameters shown (space groups $C2/c$ and $P\bar{1}$ respectively) with Black crosses experimental data; Green, background; Red, profile fit, Magenta lines: allowed reflections; and Blue line difference between experimental data and fit. Insets are Profile fit at higher angle. For (3) and (4) and laboratory instrument was used with Cu Kα radiation. Note the effects of preferred orientation for (3) and (4) and for (3) a small amount of (2) as impurity.

S3: Thermogravimetric Analysis

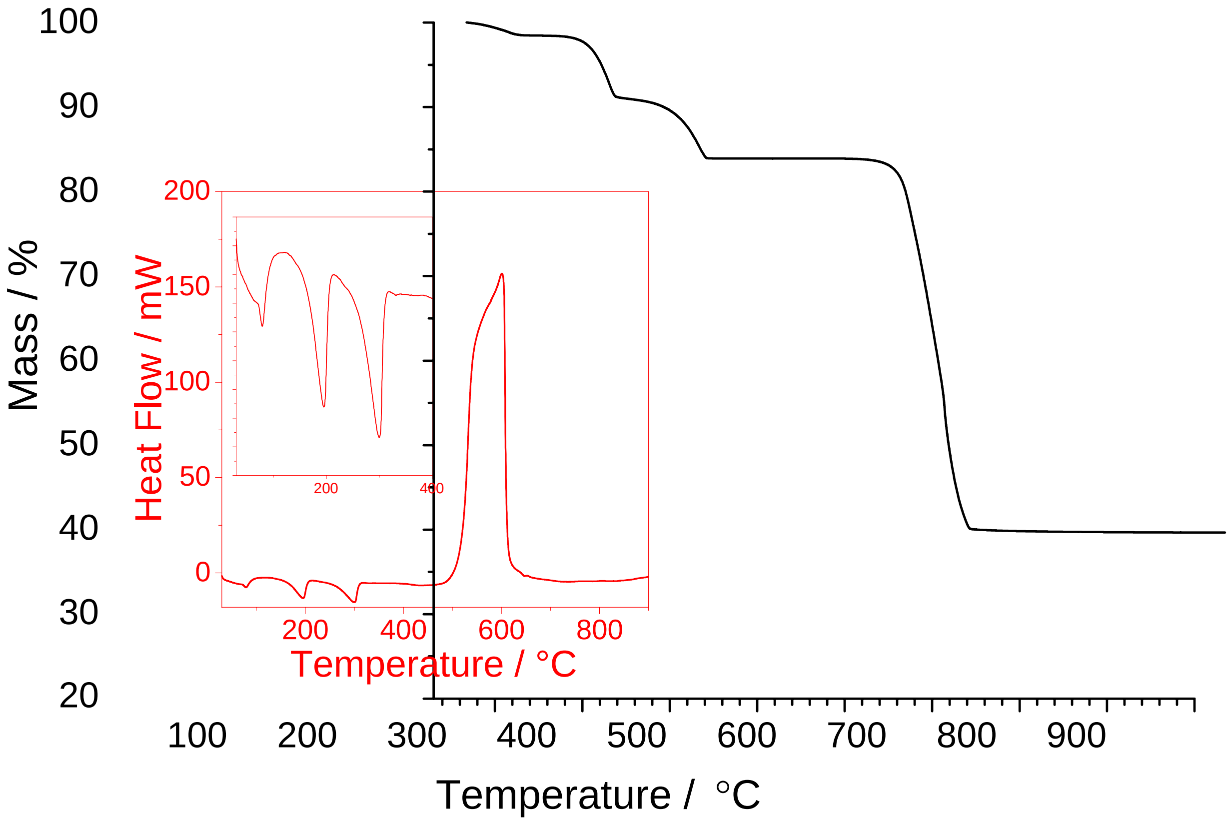


Figure S3.1: TGA of (1) with DSC inset.

Table S3.1: Analysis of TGA data of (1)

	Temperature	Total % Mass Measured	Total % Mass Expected
$[Yb_2(BDC)_3(DMF)_2H_2O].0.45DMF$	25 °C	100.00	100.00
$Yb_2(DMF)_2(BDC)_3(DMF)_2$	135 °C	94.95	95.03
$Yb_2(BDC)_3(DMF)$	202 °C	88.50	87.90
$Yb_2(BDC)_3$	390 °C	81.32	80.76
Yb_2O_3	900 °C	43.47	38.50

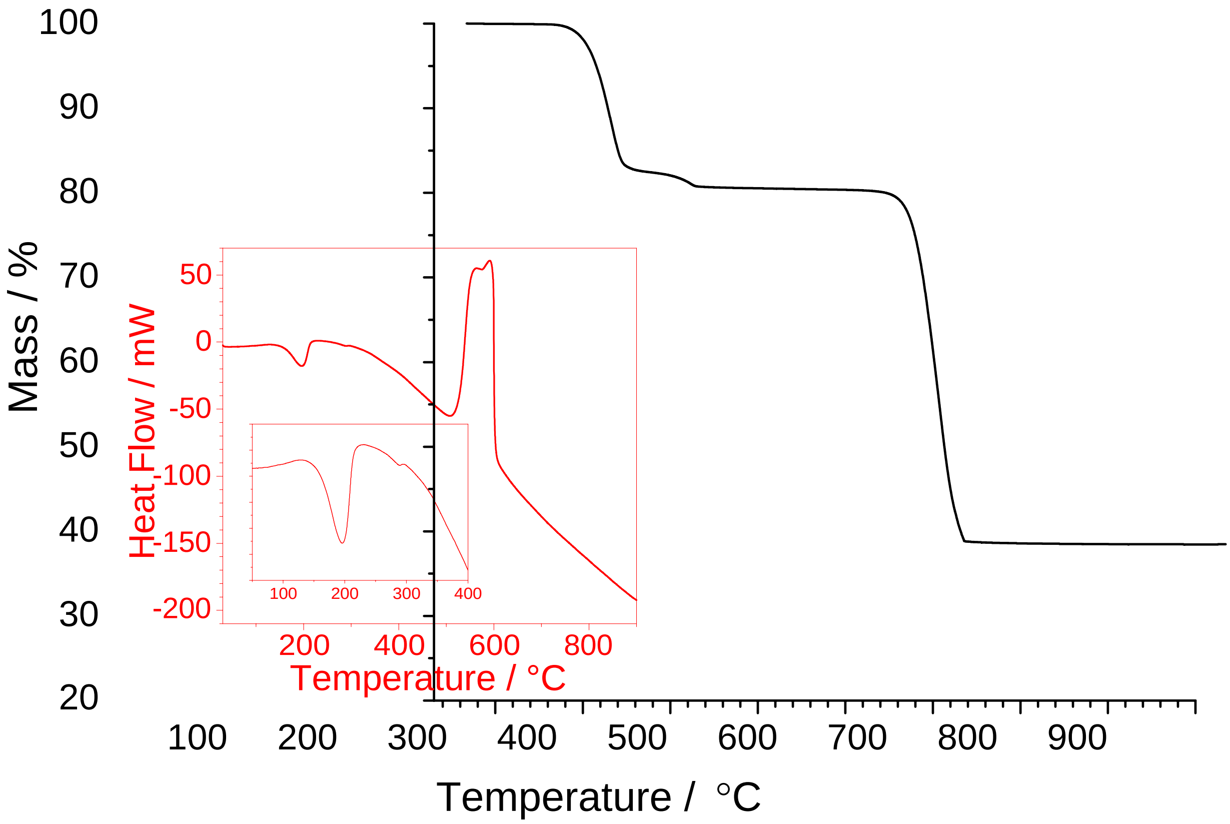


Figure S3.2: TGA of (2) with DSC inset.

Table S3.2: Analysis of TGA data of (2)

	Temperature	Total % Mass Measured	Total % Mass Expected
$Yb_2(BDC)_3(DMF)_2(H_2O)_2$	25 °C	100.00	100.00
$Yb_2(BDC)_3(H_2O)_2$	225 °C	82.67	83.92
$Yb_2(BDC)_3$	315 °C	80.67	82.16
Yb_2O_3	900 °C	38.46	38.63

S4: Analysis of $Yb_2(BDC)_3$

Elemental analysis: C 33.92 % (expected 34.38 %); H 1.68 % (expected 1.44 %)

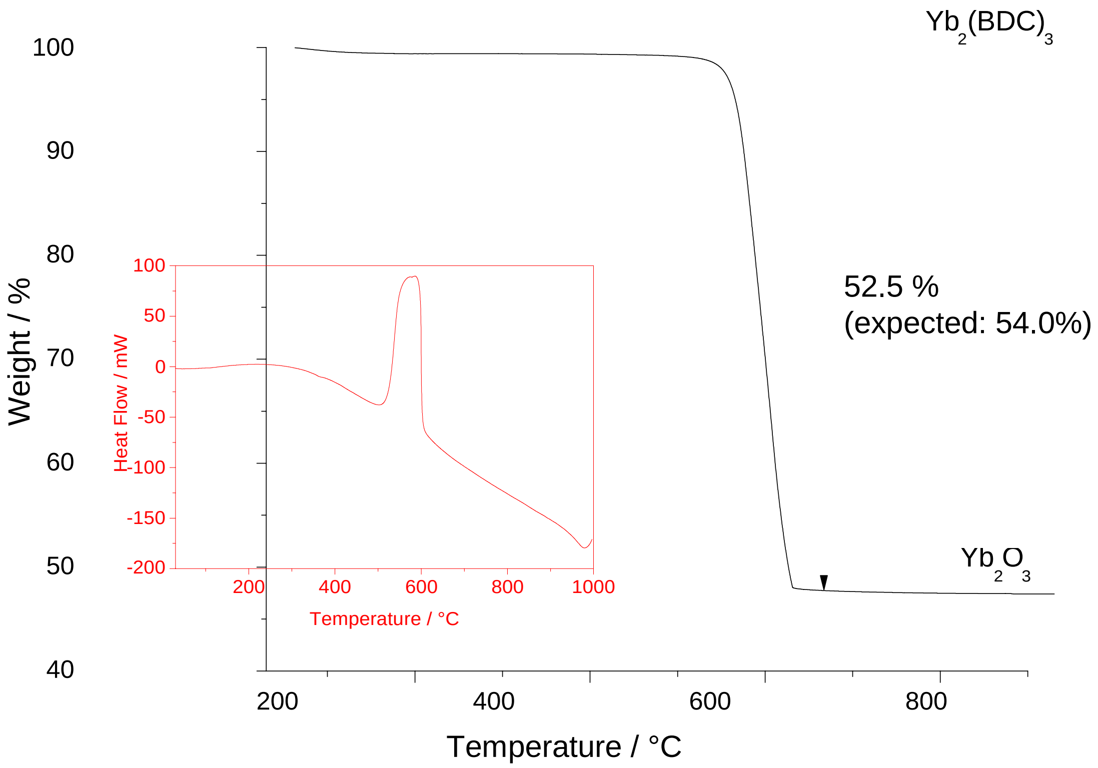


Figure S4.1: TGA of $Yb_2(BDC)_3$ with DSC inset.

S5. Kinetic Analysis of *in situ* XRD

The model of Gualtieri was used to analysis crystallisation kinetics:

$$\alpha = \frac{1}{1+\exp\left\{-\left(\frac{t-a}{b}\right)\right\}}.\left\{1-\exp\left[-\left(k_g t\right)^N\right]\right\} \tag{1}$$

α is the extent of crystallisation (normalised to 1), N is the dimensionality of crystal growth. k_g is the rate constant of crystal growth, while a and b are constants related to nucleation. Induction time as this is accounted for in the constants a and b.

Since not all of the reactions we studied reached completion, we introduced a normalisation factor, A, in our fitting. Thus we used the equation:

$$I = A\left[\frac{1}{1+\exp\left\{-\left(\frac{t-a}{b}\right)\right\}}.\left\{1-\exp\left[-\left(k_g t\right)^N\right]\right\}\right] \tag{2}$$

Where I is the total Bragg peak intensity. Fitting was performed with least-squares refinements using the Origin software.

The rate constant for nucleation, k_n, is given by:

$$k_n = 1/a \tag{3}$$

The probability of nucleation, P_N *vs* time can be calculated.

$$P_N = \exp\left\{-\frac{(t-a)^2}{2b^2}\right\} \tag{4}$$

The relative magnitudes of k_g and k_n can then be used to infer which is the rate-determining process in crystallisation. In addition, the value of b can be used to deduce information about the nature of nucleation: if $b \sim 15$ nucleation is heterogeneous, if $b \sim 20$ nucleation is homogeneous, and if $b > 20$ then nucleation is autocatalytic.

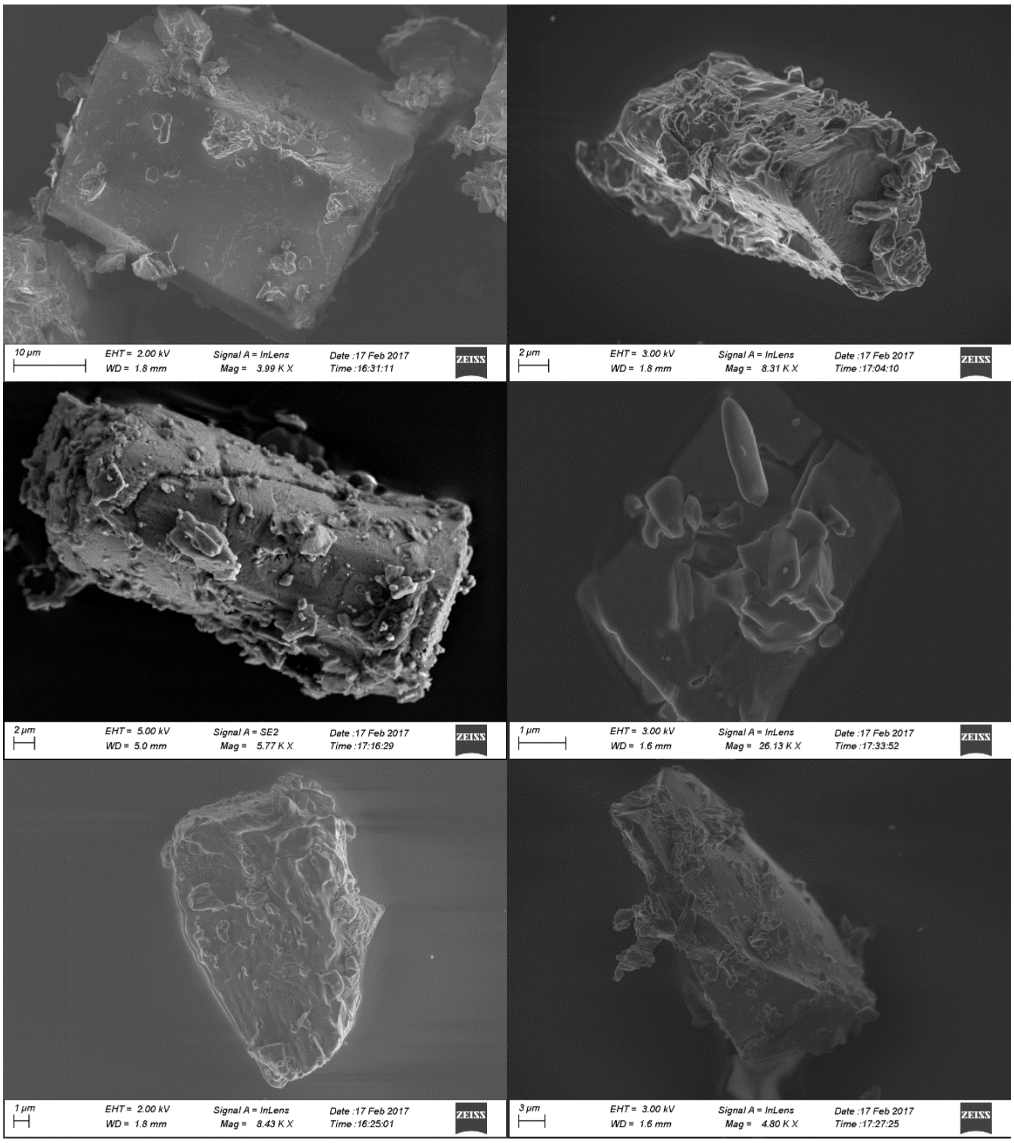


Figure S5.1 SEM images of (2)

S6: Topological analysis of (1)

The program SYSTRE was used to assign topology.[1]

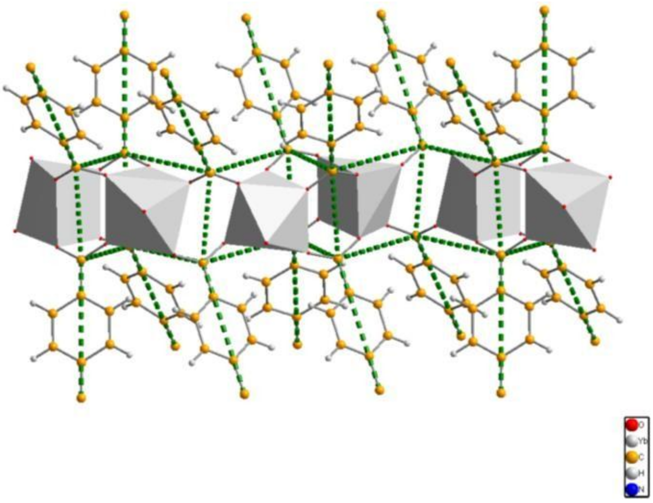
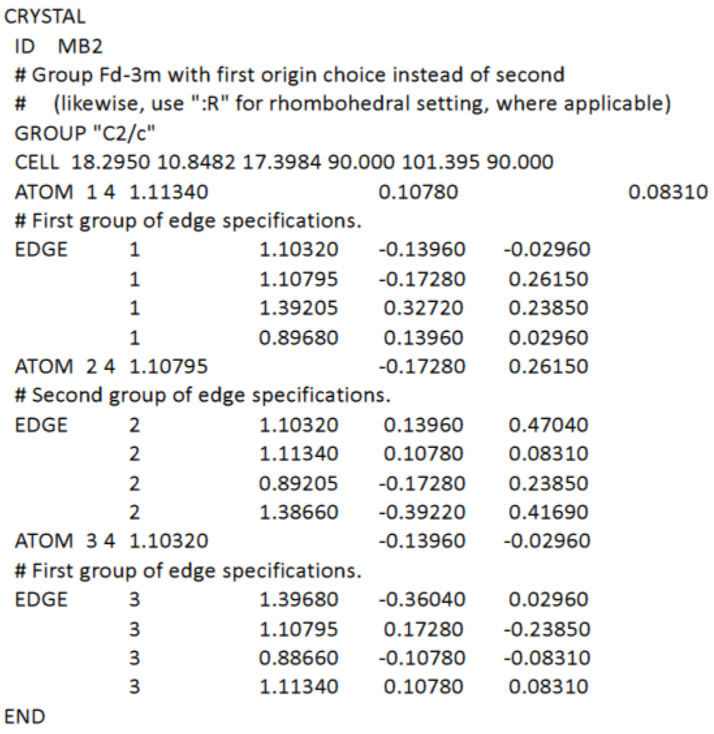
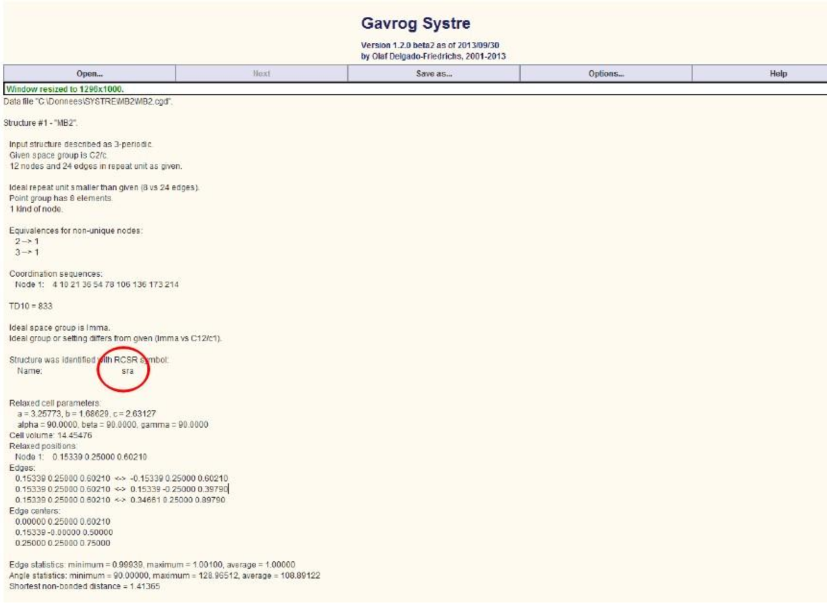


Figure S6.1: Selection of nodes to define topology (bridging carboxylate connection points)



```
CRYSTAL
 ID   MB2
 # Group Fd-3m with first origin choice instead of second
 #    (likewise, use ":R" for rhombohedral setting, where applicable)
 GROUP "C2/c"
 CELL  18.2950 10.8482 17.3984 90.000 101.395 90.000
 ATOM  1 4  1.11340               0.10780                0.08310
 # First group of edge specifications.
 EDGE        1          1.10320    -0.13960    -0.02960
             1          1.10795    -0.17280     0.26150
             1          1.39205     0.32720     0.23850
             1          0.89680     0.13960     0.02960
 ATOM  2 4  1.10795               -0.17280     0.26150
 # Second group of edge specifications.
 EDGE        2          1.10320     0.13960     0.47040
             2          1.11340     0.10780     0.08310
             2          0.89205    -0.17280     0.23850
             2          1.38660    -0.39220     0.41690
 ATOM  3 4  1.10320               -0.13960    -0.02960
 # First group of edge specifications.
 EDGE        3          1.39680    -0.36040     0.02960
             3          1.10795     0.17280    -0.23850
             3          0.88660    -0.10780    -0.08310
             3          1.11340     0.10780     0.08310
END
```

Figure S6.2: Input for SYSTRE software



```
Window resized to 1296x1000.
Data file "C:\Donnees\SYSTRE\MB2\MB2.cgd".

Structure #1 - "MB2".

  Input structure described as 3-periodic.
  Given space group is C2/c.
  12 nodes and 24 edges in repeat unit as given.

  Ideal repeat unit smaller than given (8 vs 24 edges).
  Point group has 8 elements.
  1 kind of node.

  Equivalences for non-unique nodes:
    2 --> 1
    3 --> 1

  Coordination sequences:
    Node 1:    4 10 21 36 54 78 106 136 173 214

  TD10 = 833

  Ideal space group is Imma.
  Ideal group or setting differs from given (Imma vs C12/c1).

  Structure was identified with RCSR symbol:
     Name:                 sra


  Relaxed cell parameters:
     a = 3.25773, b = 1.68629, c = 2.63127
     alpha = 90.0000, beta = 90.0000, gamma = 90.0000
  Cell volume: 14.45476
  Relaxed positions:
    Node 1:    0.15339 0.25000 0.60210
  Edges:
    0.15339 0.25000 0.60210  <->  -0.15339 0.25000 0.60210
    0.15339 0.25000 0.60210  <->  0.15339 -0.25000 0.39790
    0.15339 0.25000 0.60210  <->  0.34661 0.25000 0.89790
  Edge centers:
    0.00000 0.25000 0.60210
    0.15339 -0.00000 0.50000
    0.25000 0.25000 0.75000

  Edge statistics: minimum = 0.99939, maximum = 1.00100, average = 1.00000
  Angle statistics: minimum = 90.00000, maximum = 128.96512, average = 108.89122
  Shortest non-bonded distance = 1.41365
```

Figure S6.3: Output from SYSTRE software

[1] O. Delgado-Friedrichs and M. O'Keeffe, *Acta Crystallogr. Sect. A*, 2003, **59**, 351-360.