Supplementary Information

Transformation from non- to double-interpenetration in robust Cd(II) doubly-pillared-layered metal-organic frameworks

Himanshu Aggarwal,[a] Prem Lama[a] and Leonard J. Barbour[a]*

*Department of Chemistry and Polymer Science, University of Stellenbosch, Stellenbosch 7600, South Africa

Synthesis

Both [Cd(tp)(4,4′-bipy)] and [Cd(atp)(4,4′-bipy)] non-interpenetrated frameworks were synthesized following previously reported procedures.[1,2]

Single Crystal Parameters

Table S1. Comparison of unit cell parameters of non-interpenetrated, activated and twofold interpenetrated [Cd(tp)(4,4′-bipy)]**.**

Non-interpenetrated [Cd(tp)(4,4′-bipy)] (CCDC REFCODE CUHPUR)	**Activated [Cd(tp)(4,4′-bipy)] (this study)**	**Twofold interpenetrated [Cd(tp)(4,4′-bipy)] CCDC REFCODE LOTXIB**
Space Group = *Pbam*	Space Group = *C2/c*	Space Group = *C2/c*
Temperature (K) = 100	Temperature (K) = 100	Temperature (K) = 294
a (Å) = 12.949(<1)	*a* (Å) = 15.902(3)	*a* (Å) = 16.108(3)
b (Å) = 21.290 (<1)	*b* (Å) = 11.664(3)	*b* (Å) = 11.675(2)
c (Å) = 11.683 (<1)	*c* (Å) = 20.202(2)	*c* (Å) = 20.171(4)
α (º) = 90	*α* (º) = 90	*α* (º) = 90
β (º) = 90	*β* (º) = 112.093(3)	*β* (º) = 111.99(3)
γ (º) = 90	*γ* (º) = 90	*γ*(º) = 90
V (Å^3) = 3220.82	*V* (Å^3) = 3472.04(3)	*V*(Å^3) = 3517.4(11)

Table S2. Comparison of unit cell parameters of non-interpenetrated, activated and twofold interpenetrated [Cd(atp)(4,4′-bipy)].

Non-interpenetrated [Cd(atp)(4,4′-bipy)] CCDC REFCODE YUXQOY	**Activated [Cd(atp)(4,4′-bipy)] (this study)**	**Twofold interpenetrated [Cd(atp)(4,4′-bipy)] CCDC REFCODE YUXQUE**
Space Group = *Pbam*	Space Group = *C*2/*m*	Space Group = *C*2/*m*
Temperature (K) = 293	Temperature (K) = 100	Temperature (K) = 293
a (Å) = 13.700(3)	*a* (Å) = 16.202(2)	*a* (Å) = 15.950(3)
b (Å) = 21.050(4)	*b* (Å) = 11.921(3)	*b* (Å) = 11.700(2)
c (Å) = 11.720(2)	*c* (Å) = 10.438(3)	*c* (Å) = 10.210(2)
α (°) = 90	*α* (°) = 90	*α* (°) = 90
β (°) = 90	*β* (°) = 112.683 (3)	*β* (°) = 112.77(3)
γ (°) = 90	*γ* (°) = 90	*γ*(°) = 90
V (Å^3) = 3379.87	*V* (Å^3) = 1860.13 (3)	*V*(Å^3) = 1756.8(6)

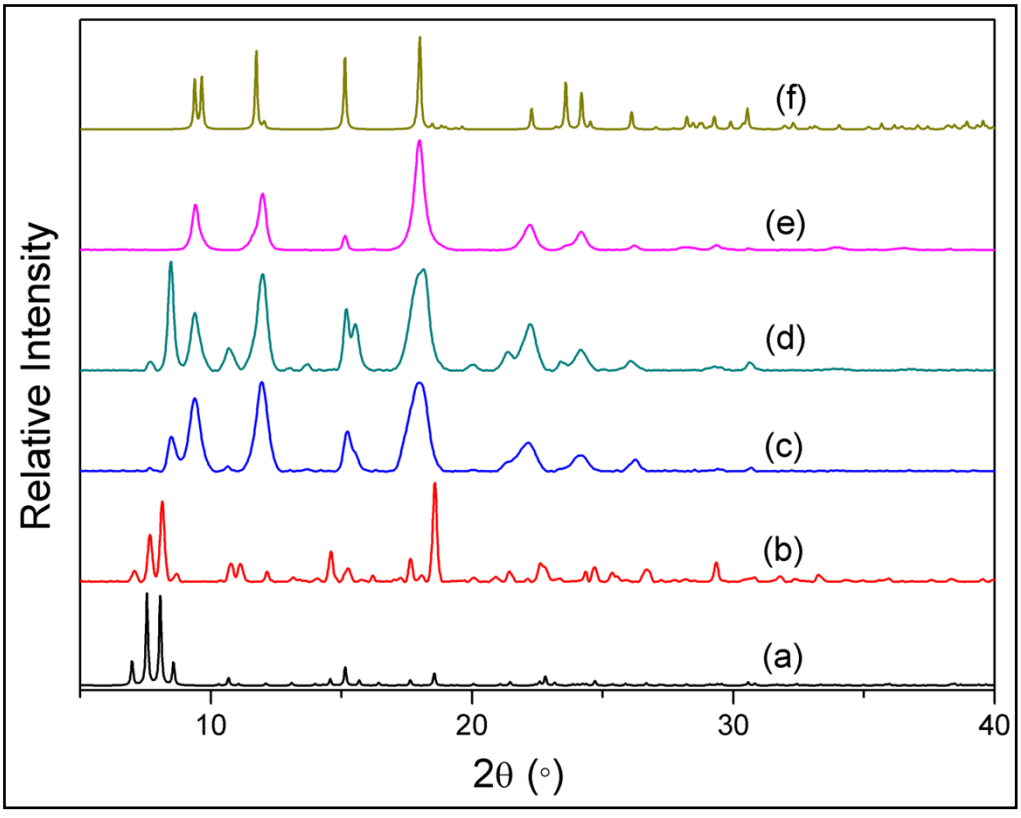

Figure S1: PXRD patterns of (a) simulated non-interpenetrated **2**, (b) as-synthesized non-interpenetrated **2**, (c) activated **2** at 150 °C, (d) activated **2** at 200 °C, (e) activated **2** at 270 °C and (f) (a) simulated doubly interpenetrated **2**.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a TA Instruments Q500 analyser. The sample was heated at 40 °C/min from room temperature to decomposition.

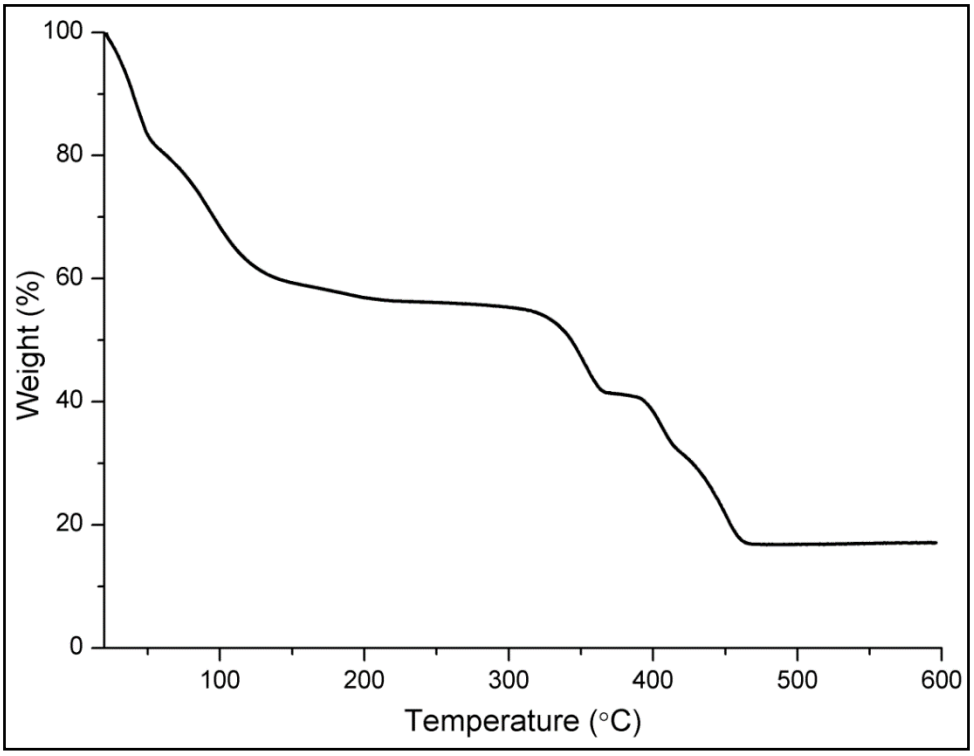

Figure S2: TGA for **1**.

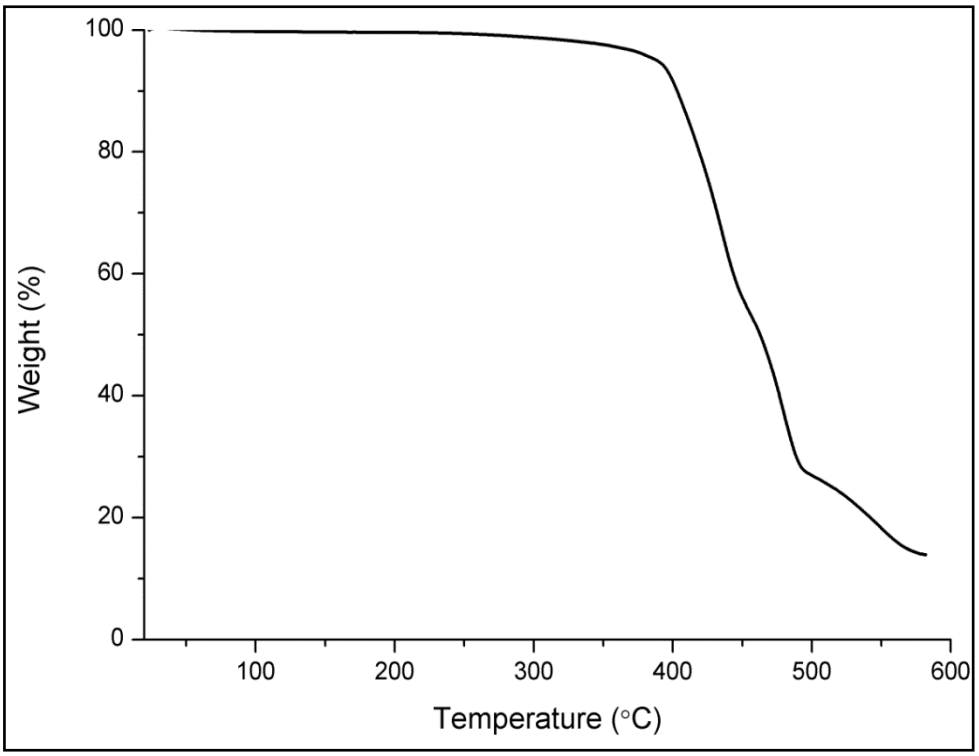

Figure S3: TGA for activated **1**.

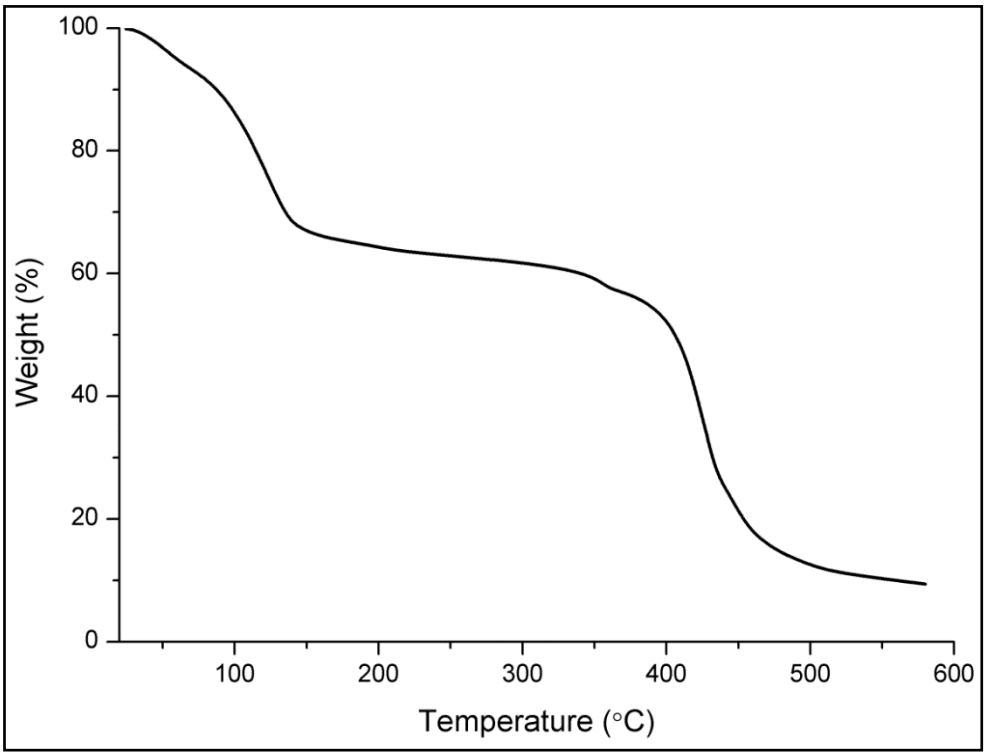

Figure S4: TGA for **2**.

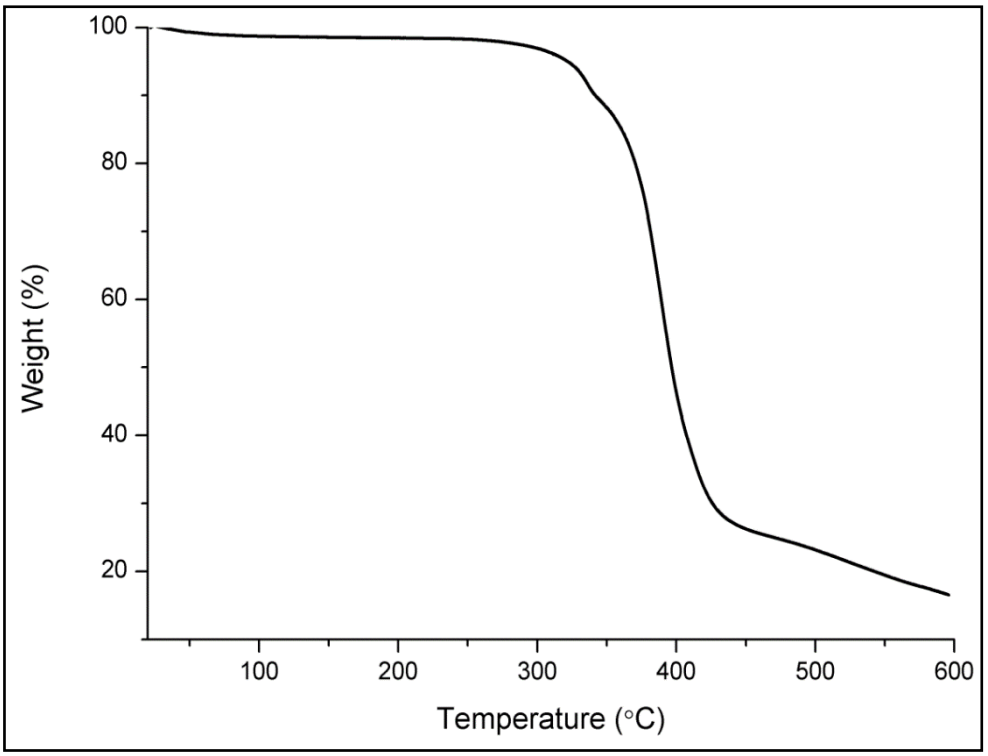

Figure S5: TGA for activated **2**.

Differential Scanning Calorimetry (DSC)

DSC experiments were carried out on a TA Instruments Q100 with the sample heated to 270 °C at a rate of 40 °C/min.

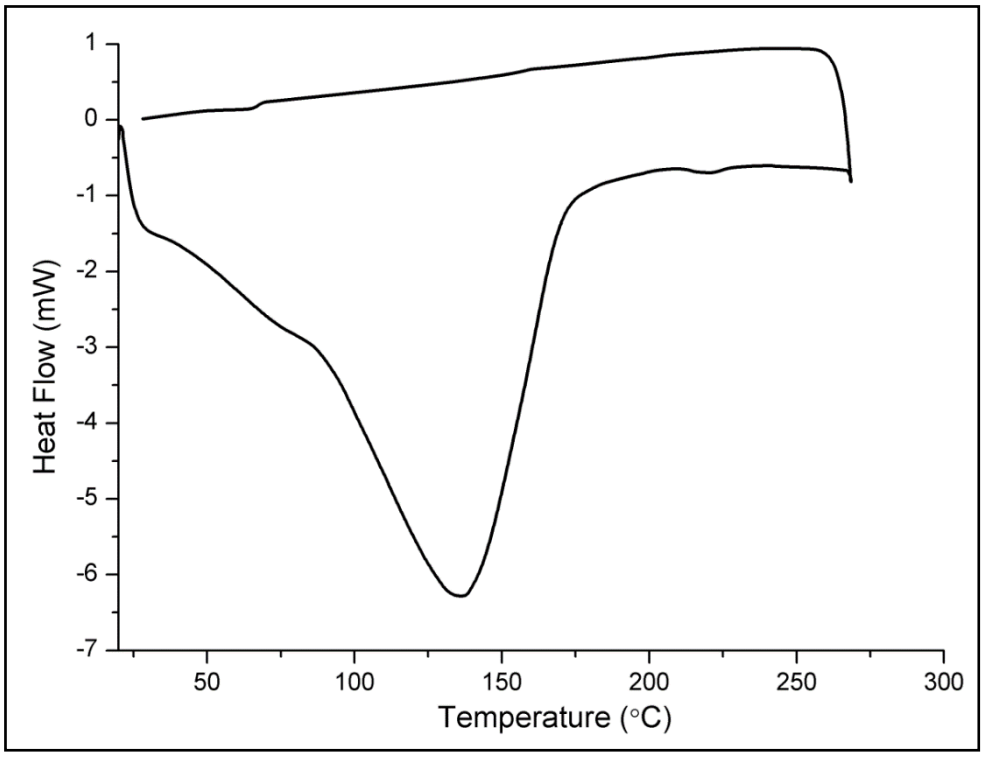

Figure S6: DSC for **1**.

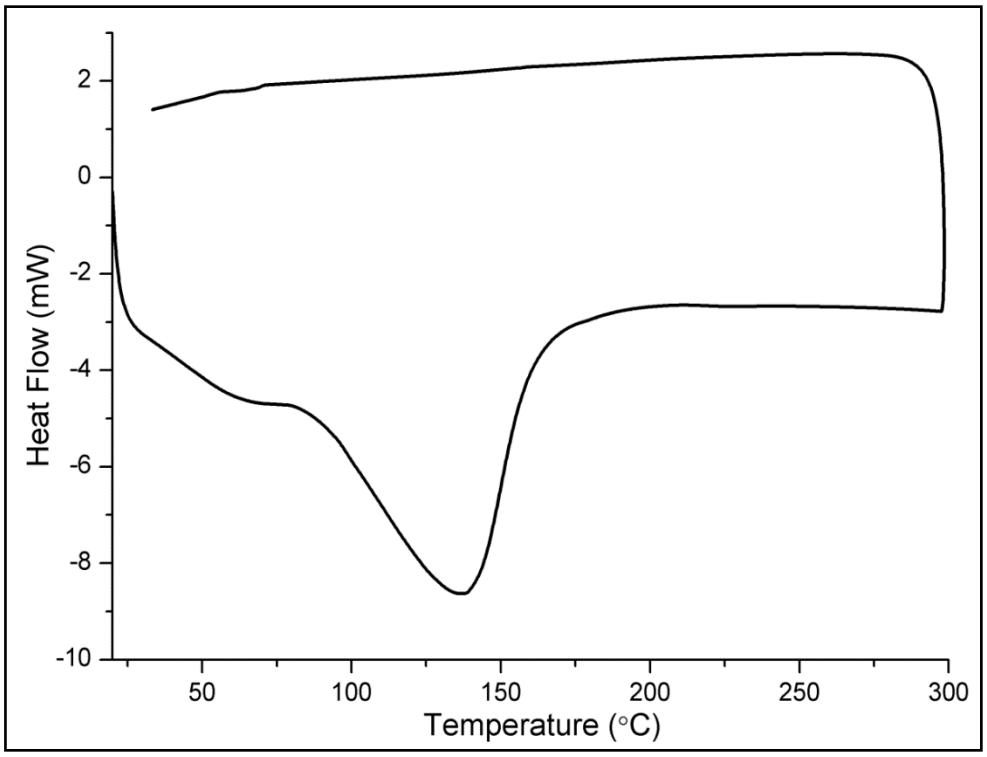

Figure S7: DSC for **2**.

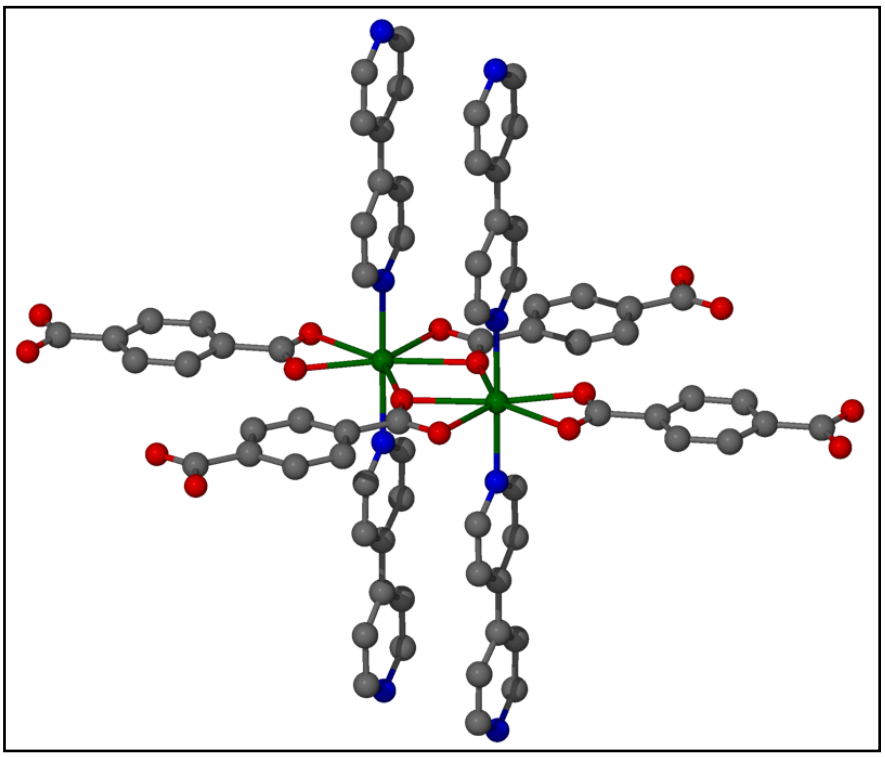

Figure S8: Dinuclear unit in **1**.

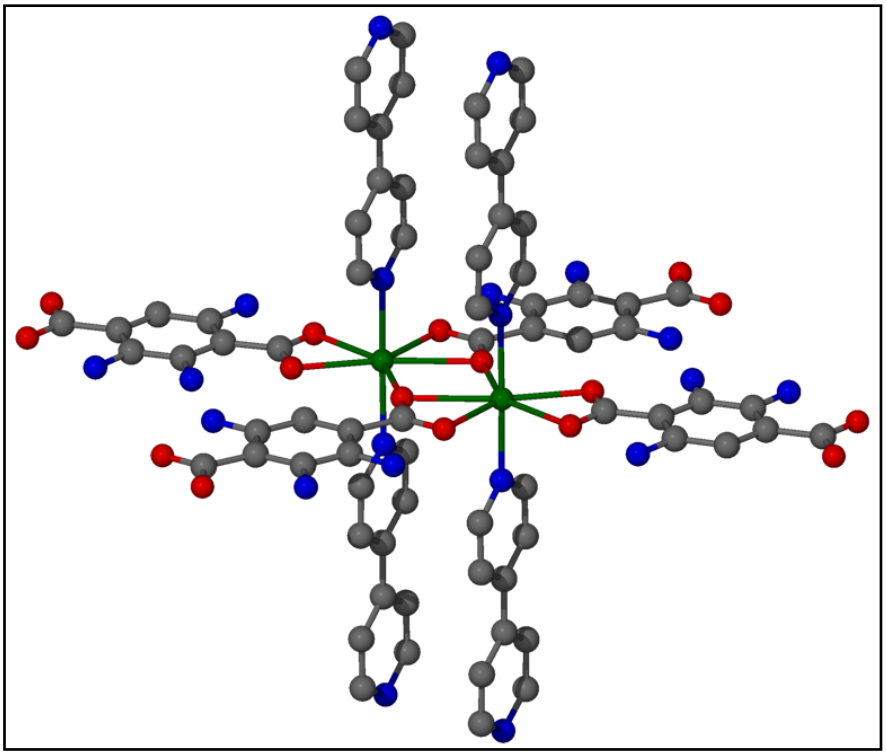

Figure S9: Dinuclear unit in **2**.

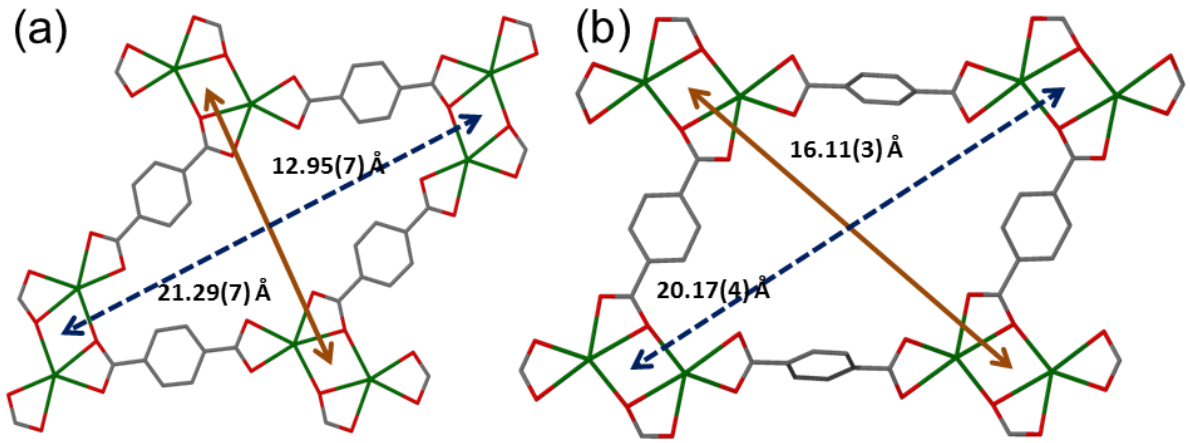

Figure S10: Packing diagram showing the diagonal distances between metal cluster centres (i.e. the Cd···Cd centroid) in (a) non-interpenetrated **1** and (b) doubly interpenetrated **1**.

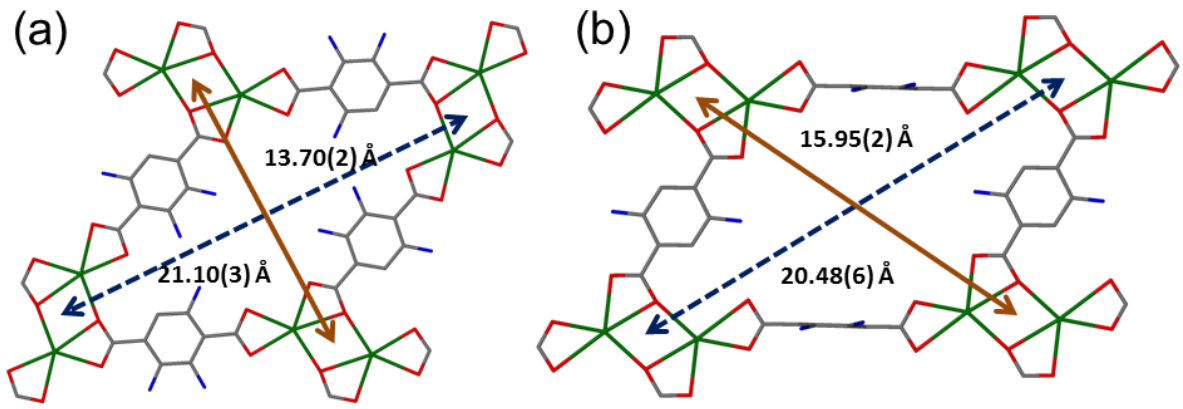

Figure S11: Packing diagram showing the diagonal distances between metal cluster centres (i.e. the Cd···Cd centroid) in (a) non-interpenetrated **2** and (b) doubly interpenetrated **2**.

Rietveld Refinement

The observed X-ray powder patterns were refined using Rietveld[3] method. We employed the program TOPAS[3] using as the corresponding published single-crystal X-ray structures as starting models. The resultant difference plots thus generated are given below.

Table S3 Final Rietveld refinement parameters for the four structures:

Compound	**1** Non-interpenetrated	**1** Doubly-interpenetrated	**2** Non-interpenetrated	**2** Doubly-interpenetrated
$R_p$fitted	0.074	0.037	0.043	0.024
$_wR_p$fitted	0.101	0.051	0.056	0.031
Bragg R-factor	2.20	0.79	0.47	0.56
GoF (χ)	3.05	3.71	2.00	1.51
Temperature (K)	298(2)	298(2)	298(2)	298(2)
Space group	*Pbam*	*C*2/*c*	*Pbam*	*C*2/*m*
a (Å)	12.9018(5)	15.8442(3)	13.4882(6)	16.1576(7)
b (Å)	21.3502(6)	11.6038(2)	21.1458(3)	11.6540(9)
c (Å)	11.6964(4)	20.0921(3)	11.5206(8)	10.1833(13)
α, γ (°)	90	90	90	90

β (°)	90	112.461(12)	90	113.403(15)
No. of parameters	1612	369	2749	402

Table S4: Comparison of Rietveld parameters with the reported unit cell parameters for Non-interpenetrated and doubly-interpenetrated compound **1**.

Compound	Non-interpenetrated **1**		Doubly-interpenetrated **1**	
	Rietveld	Reported	Rietveld	Reported
Temperature (K)	298	100	298	294
Space group	*Pbam*	*Pbam*	*C*2/*c*	*C*2/*c*
a (Å)	12.901(5)	12.949(5)	15.844(3)	16.108(3)
b (Å)	21.350(6)	21.290(6)	11.603(2)	11.675(2)
c (Å)	11.696(4)	11.682(5)	20.092(3)	20.171(4)
α, γ (°)	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	112.46(12)	111.99(3)

Table S5: Comparison of Rietveld parameters with the reported unit cell parameters for non-interpenetrated and doubly-interpenetrated compound **2**.

Compound	Non-interpenetrated **2**		Doubly-interpenetrated **2**	
	Rietveld	Reported	Rietveld	Reported
Temperature (K)	298	293	298	293
Space group	*Pbam*	*Pbam*	*C*2/*m*	*C*2/*m*
a (Å)	13.488(6)	13.700(3)	16.157(7)	15.950(3)
b (Å)	21.145(3)	21.050(4)	11.654(9)	11.700(2)
c (Å)	11.520(8)	11.720(2)	10.183(13)	10.210(2)
α, γ (°)	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	113.40(15)	112.77(3)

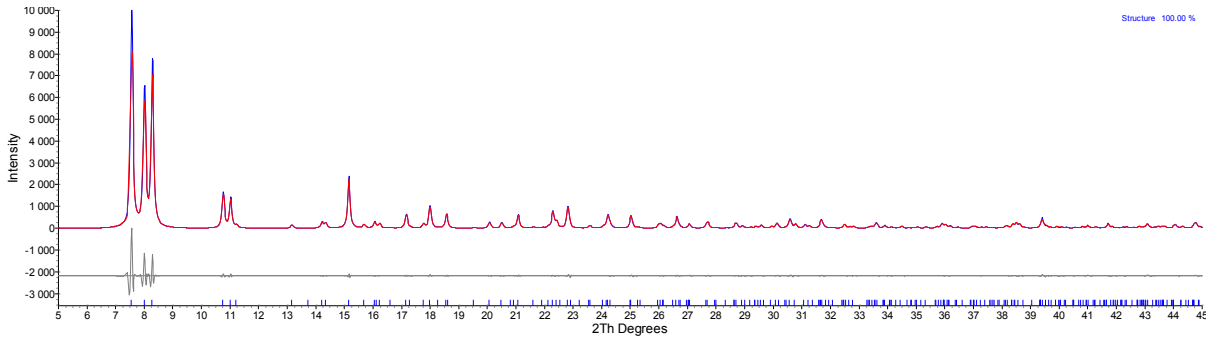

Figure S12: Observed (blue) and refined (red) X-ray powder diffractograms (the latter obtained from Rietveld refinement) as well as the difference plot (grey) for non-interpenetrated compound **1**.

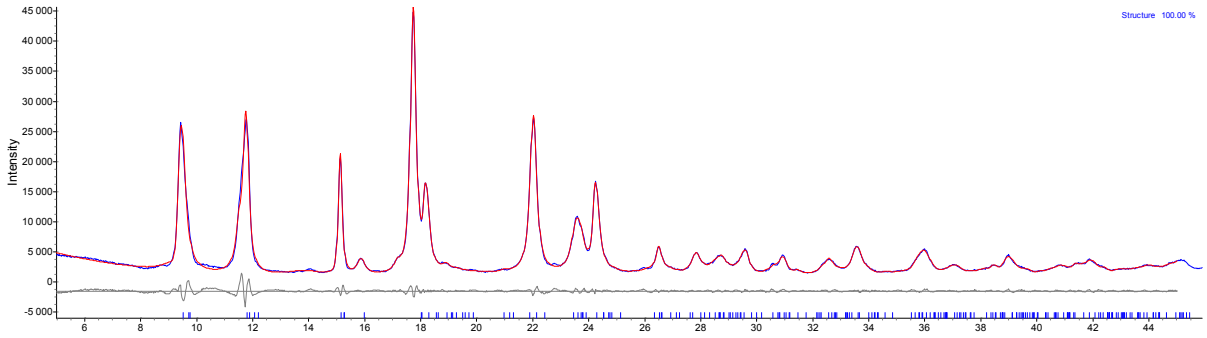

Figure S13: Observed (blue) and refined (red) X-ray powder diffractograms (the latter obtained from Rietveld refinement) as well as the difference plot (grey) for doubly-interpenetrated compound **1**.

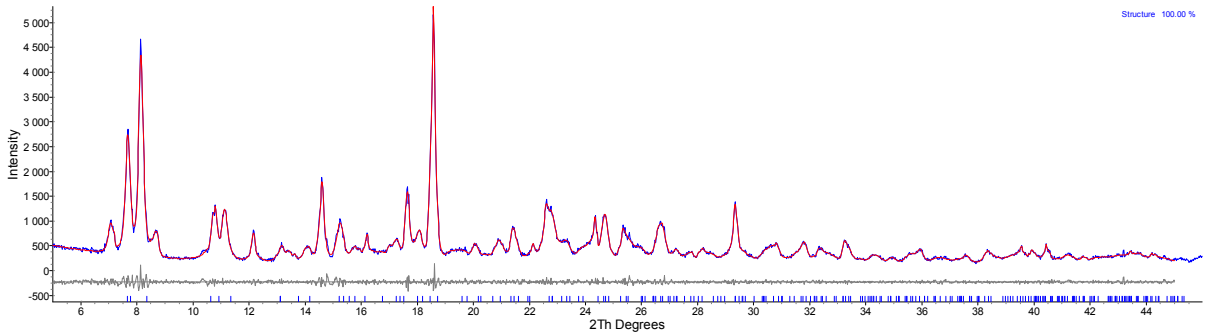

Figure S14: Observed (blue) and refined (red) X-ray powder diffractograms (the latter obtained from Rietveld refinement) as well as the difference plot (grey) for non-interpenetrated compound **2**.

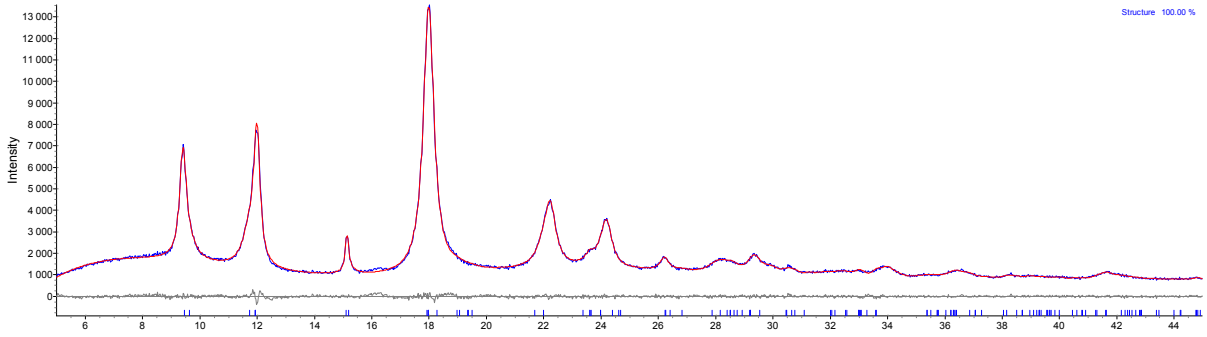

Figure S15: Observed (blue) and refined (red) X-ray powder diffractograms (the latter obtained from Rietveld refinement) as well as the difference plot (grey) for doubly-interpenetrated compound **2**.

Phase purity analysis

The as-synthesized and activated PXRD patterns for both compounds **1** and **2** were compared with those generated from the corresponding published CIF files using X'Pert Highscore Plus[4] to quantify phase purity.

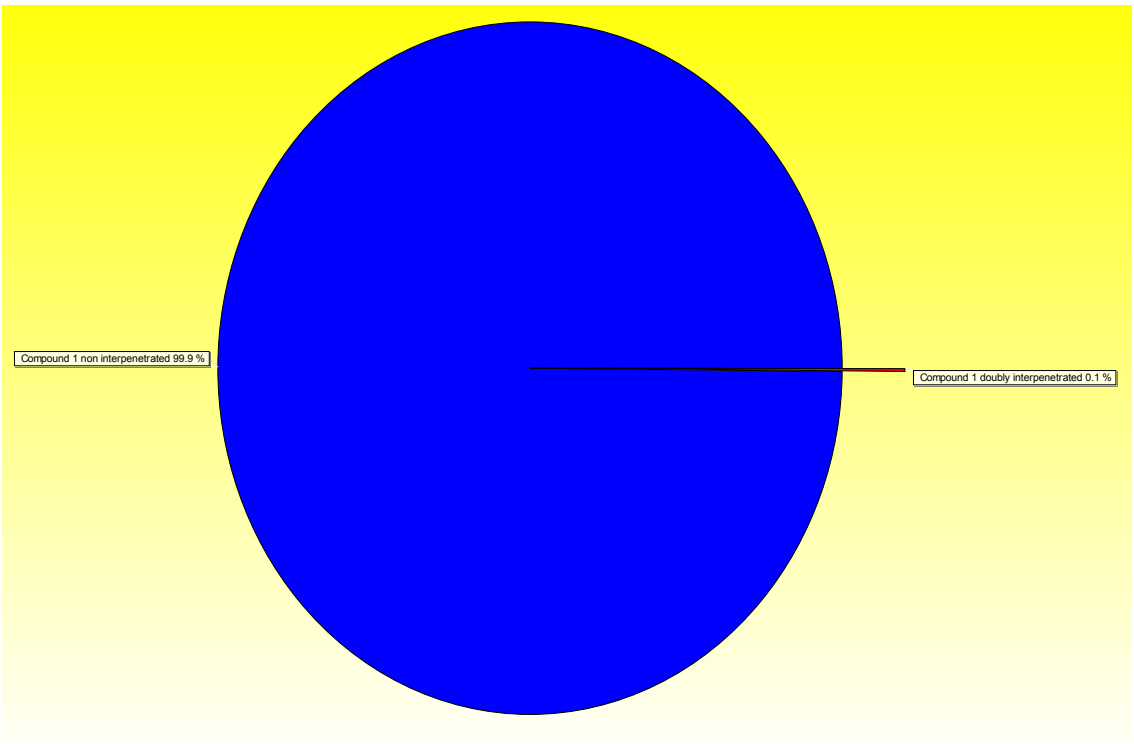

Figure S16: Quantification plot for as-synthesized **1** generated by X'Pert Highscore Plus (using the non-interpenetrated (blue) and doubly interpenetrated (red) CIF files of **1**).

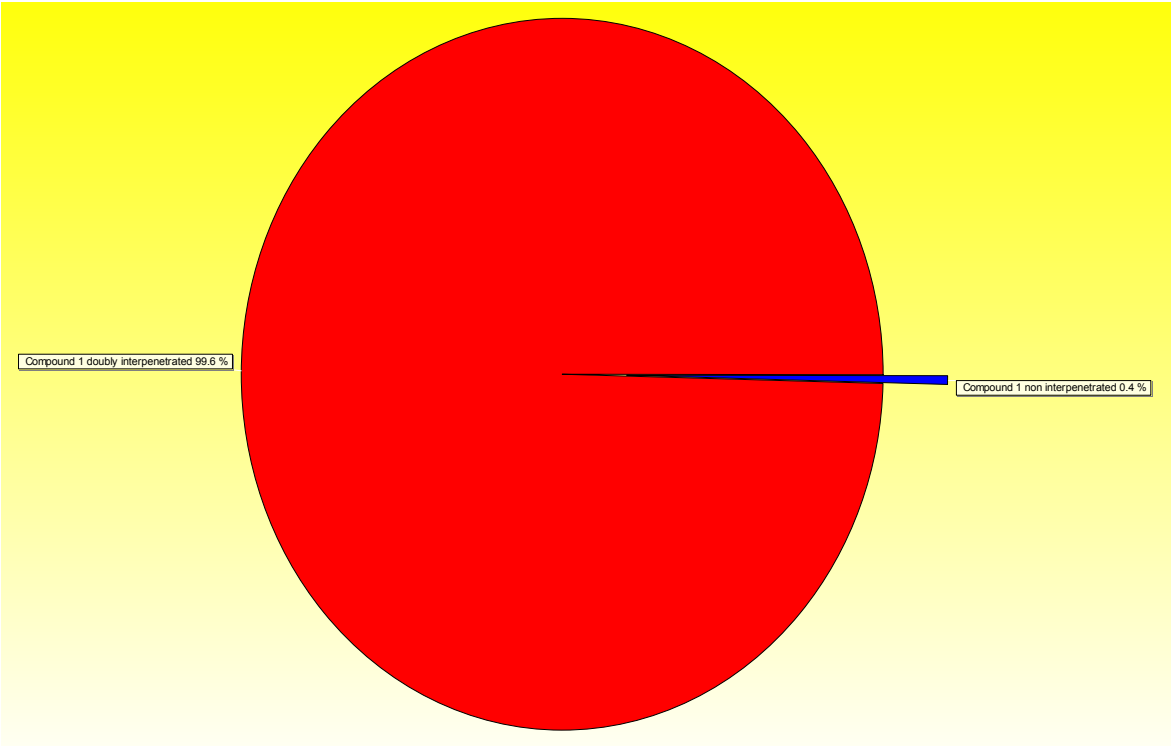

Figure S17: Quantification plot for activated **1** generated by X'Pert Highscore Plus (using the non-interpenetrated (blue) and doubly interpenetrated (red) CIF files of **1**).

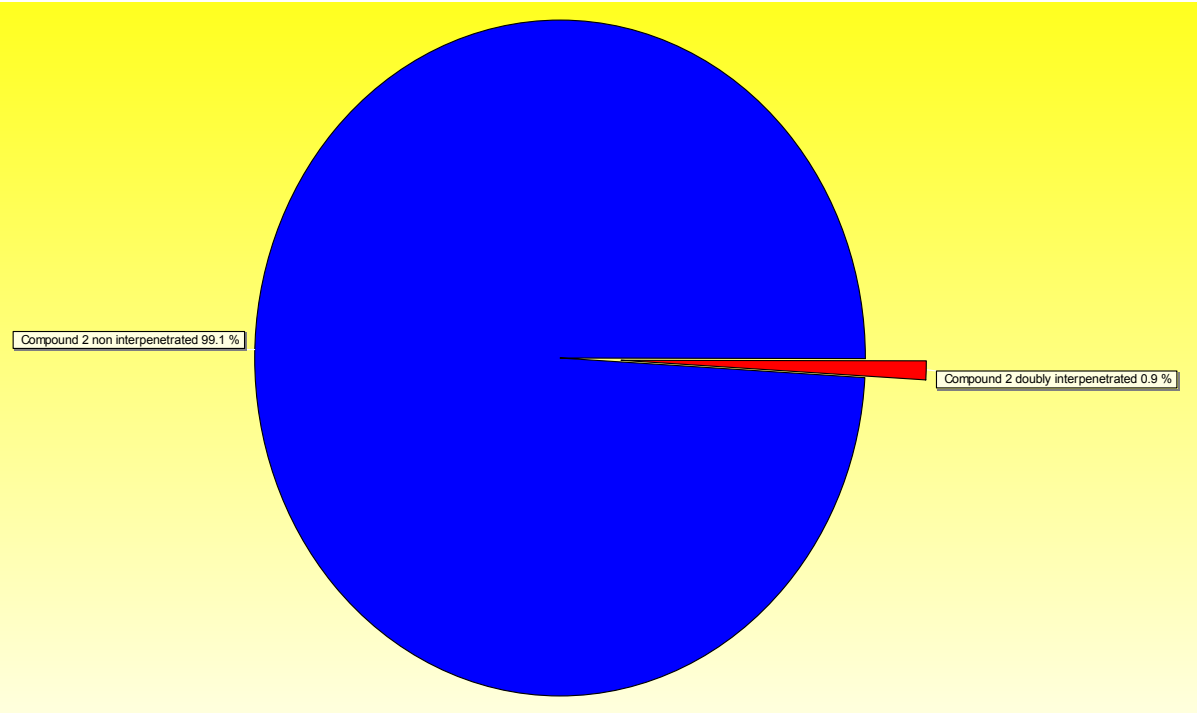

Figure S18: Quantification plot for as-synthesised **2** generated by X'Pert Highscore Plus (using the non-interpenetrated (blue) and doubly interpenetrated (red) CIF files of **2**).

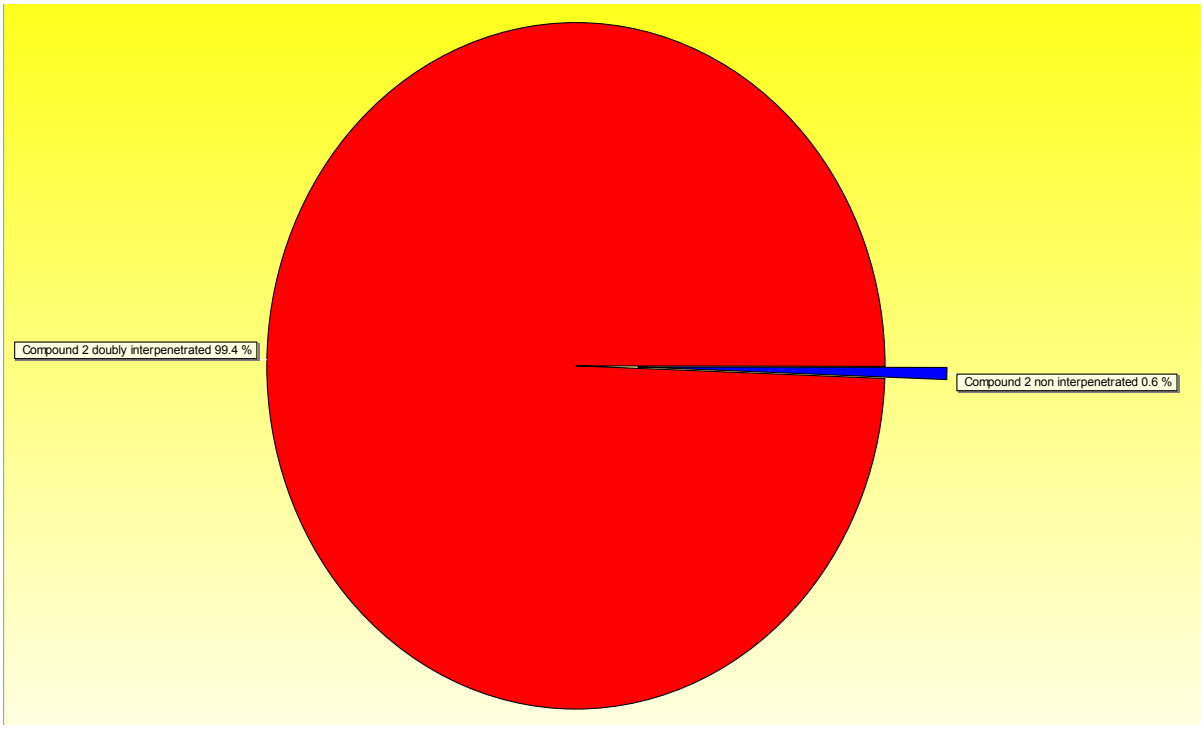

Figure S19: Quantification plot for activated **2** generated by X'Pert Highscore Plus (using the non-interpenetrated (blue) and doubly interpenetrated (red) CIF files of **2**).

References:

1. J. Zhang, L. Wojtas, R. W. Larsen, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.,* **2009**, *131*, 17040-17041.

2. H.-L. Jiang, Yo. Tatsu, Z.-H. Lu and Q. Xu, *J. Am. Chem. Soc.,* **2010**, *132*, 5586-5587.

3. A. Coelho, *J. Appl. Crystallogr.*, **2000**, *33*, 899–908.

4. PANalytical B. V. Almelo, The Netherlands, **2009**, X'Pert Highscore Plus Version 2.2e.