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Effect of Coordinated and Lattice Neutral Co-ligands on the Dielectric Properties of Cadmium and Magnesium Based Coordination Polymers

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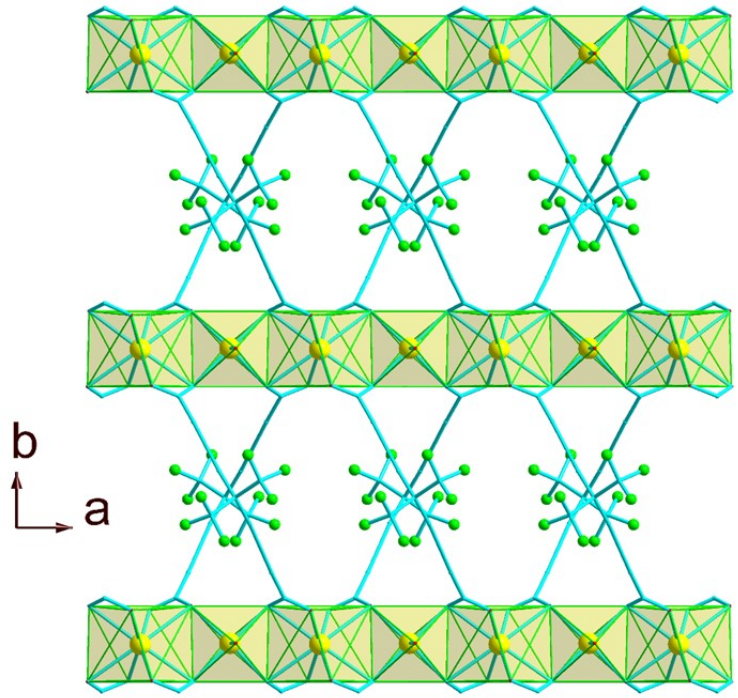


Fig. S1 Cadmium carboxylate column connected by *FBA* forming a 2D sheet on ab-plane in solid **1**.

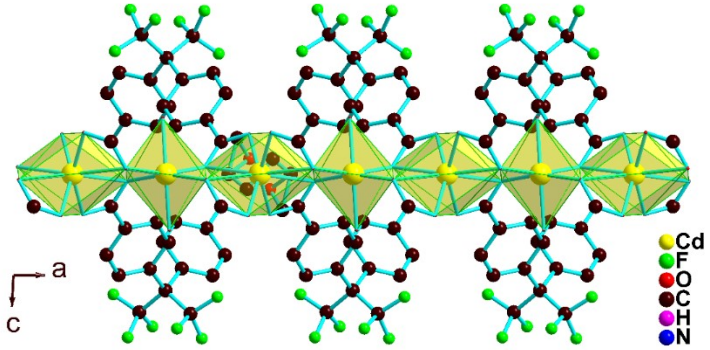


Fig. S2 Crystal structure of **1** viewed on ac-plane showing the linking of cadmium carboxylate column through FBA^{2-} ligands resulting in a 1D square-shaped channel.

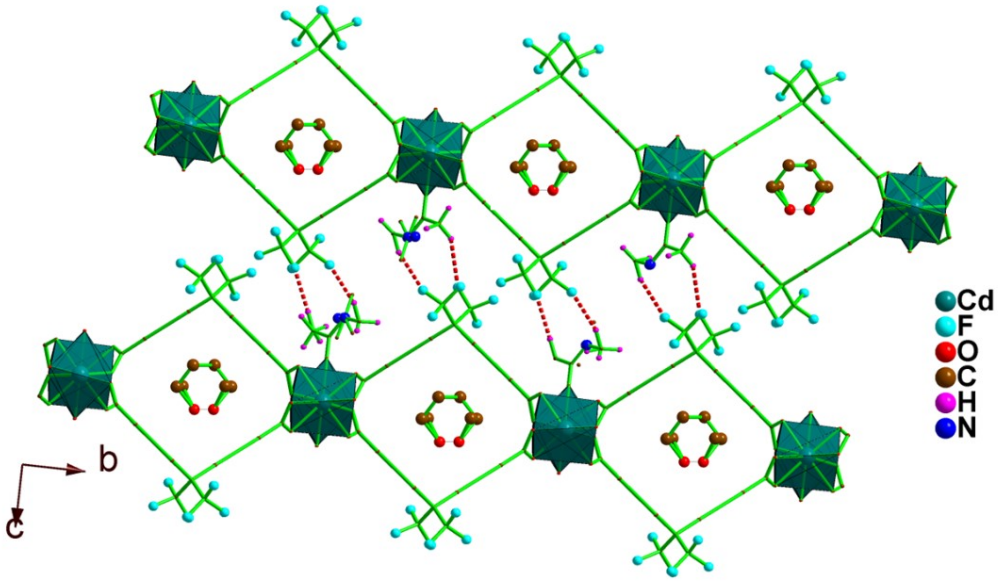


Fig. S3 Crystal structure of **1** viewed on bc-plane showing the linking of cadmium carboxylate column through FBA^{2-} ligands and THF molecules resides in 2D square-shaped channel.

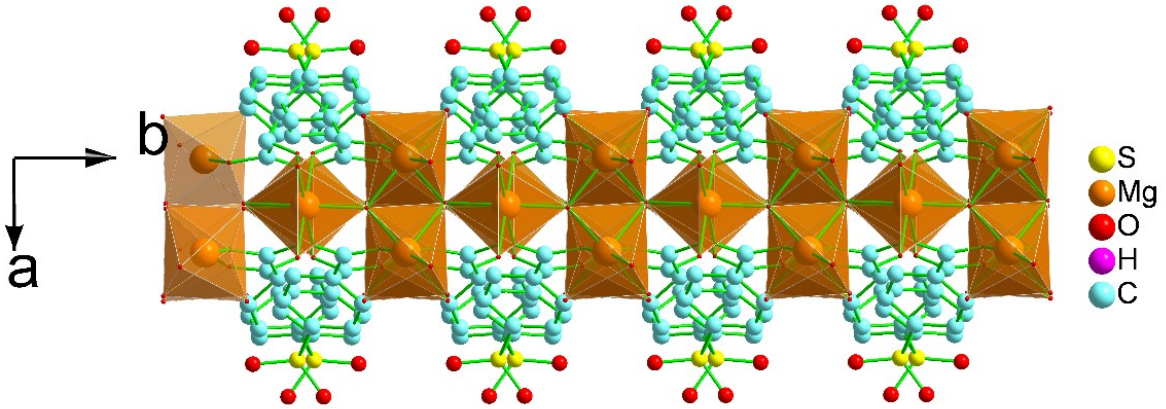


Fig. S4 (a) 1D chain structure of Solid **2** viewed along the c axis.

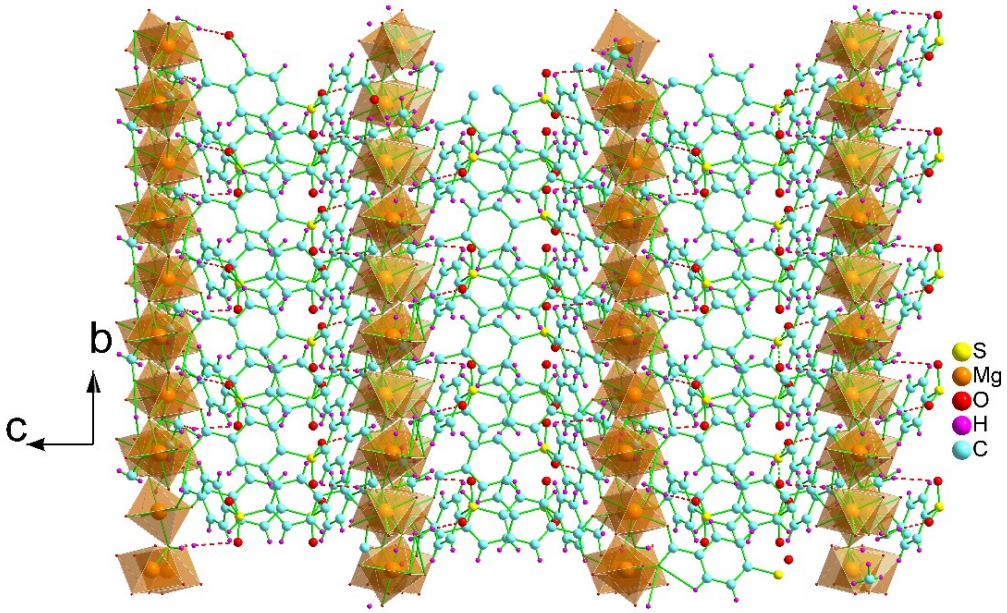


Fig. S5 2D structure of Solid **2** resulting from the C−H···O_{SBA} interaction between the EtOH molecules and oxygens of SBA^{2-} ligands.

Table S1. Analysis of Cd1(II) coordination geometry using SHAPE.

	Structure†											
	OP-8	HPY-8	HBPY-8	**CU-8**	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8	JSD-8	TT-8	ETBPY-8
Cd1_CShM	30.518	23.131	10.600	**3.686**	11.873	9.317	15.722	19.566	13.789	13.650	15.107	4.551	18.981

†OP-8: Octagon (D_{8h}); HPY-8: Heptagonal pyramid (C_{7v}); HBPY-8: Hexagonal bipyramid (D_{6h}); CU-8 Cube (O_h); SAPR-8: Square antiprism (D_{4d}); TDD-8: Triangular dodecahedron (D_{2d}); JGBF-8: Johnson gyrobifastigium J26 (D_{2d}); JETBPY-8: Johnson elongated triangular bipyramid J14 (D_{3h}); JBTPR-8: Biaugmented trigonal prism J50 (C_{2v}); BTPR-8: Biaugmented trigonal prism (C_{2v}); JSD-8 Snub diphenoid J84 (D_{2d}); TT-8: Triakis tetrahedron (T_d) ETBPY-8: Elongated trigonal bipyramid (D_{3h})

Table S2. Analysis of Cd2(II) coordination geometry using SHAPE.

	Structure†				
	HP-6	PPY-6	**OC-6**	TPR-6	JPPY-6
Cd2_CShM	30.680	24.187	**1.112**	12.188	27.678

†HP-6: Hexagon (D_{6h}); PPY-6: Pentagonal pyramid (C_{5v}); OC-6: Octahedron (O_h); TPR-6: Trigonal prism (D_{3h}); JPPY-6: Johnson pentagonal pyramid J2 (C_{5v})

Various combination of cadmium salts and V-shaped ligands applied for the synthesis of Solid 1

The reaction between different cadmium salts and 4,4' (hexafluoroisopropylidene)bisbenzoic acid was carried out in various combinations of polar aprotic solvents at different temperature. The composition of cadmium salts (0.30 mmol), *H_2FBA* ligand (0.15 mmol), and Phen (0.15 mmol) were kept constant. Every solution was 30 minutes magnetically stirred in beaker and were Teflon's sealed off and the synthesis was completed in an 8 ml reactor system. For crystal formation suitable for X-ray diffraction, the reaction was conducted in the temperature range 120-140 °C which was suitable to get the crystalline phase as per suggested by the database analysis. The outcome of the products resulted in a variety of phases, including liquid, powder, and crystalline. Only the data of solid **1** was solved using the single crystal diffraction method. By varying the metal, ligand, and solvent composition, this synthesis screening also raised the possibility of new phases.

Table S3: Outcome of the reactions between cadmium salts, *H_2FBA*, Phen with DMA, H_2O and THF.

S.No	Metal salt	Solvent/solvent combinations	Solution after stirring about 30 minutes	Teflon (size)	Temperature (°C) and duration	Result
(1)	$Cd(NO_3)_2{\cdot}4H_2O$ (0.30 mmol)	DMA (8ml)	Yellow colour homogenous solution	8ml	140 °C for 4 days	Powder
(2)	$Cd(NO_3)_2{\cdot}4H_2O$ (0.30 mmol)	DMA/H_2O (4ml/4ml)	Colourless solution	8ml	140 °C for 4 days	Powder
(3)	$Cd(NO_3)_2{\cdot}4H_2O$ (0.30 mmol)	DMA/EtOH (4ml/4ml)	Colourless homogenous solution	8ml	140 °C for 4 days	Block shape colourless crystals $[Cd_2(FBA)_2(phen)_2]$. DMA[1]
(4)	$Cd(NO_3)_2{\cdot}4H_2O$ (0.30 mmol)	DMA/MeOH (4ml/4ml)	Colourless homogenous solution	8ml	140 °C for 4 days	Powder
(5)	$Cd(NO_3)_2{\cdot}4H_2O$ (0.30 mmol)	DMA/THF (4ml/4ml)	Colourless homogenous solution		140 °C for 4 days	Needle shape crystal of **Solid 1**
(6)	$Cd(OAc)_2{\cdot}2H_2O$ (0.30 mmol)	DMA (8ml)	White colour solution	8ml	140 °C for 4 days	Powder
(7)	$Cd(OAc)_2{\cdot}2H_2O$ (0.30 mmol)	DMA/H_2O (4ml/4ml)	Milky white colour solution	8ml	140 °C for 4 days	Powder
(8)	$Cd(OAc)_2{\cdot}2H_2O$ (0.30 mmol)	DMA/EtOH (4ml/4ml)	Milky white colour solution	8ml	140 °C for 4 days	Colourless very fine crystals Very poor diffracting
(9)	$Cd(OAc)_2{\cdot}2H_2O$ (0.30 mmol)	DMA/MeOH (4ml/4ml)	Milky white colour solution	8ml	140 °C for 4 days	Clear solution

	$Cd(OAc)_2·2H_2O$ (0.30 mmol)	DMA/THF (4ml/4ml)	Milky white colour solution	8ml	140 °C for 4 days	Needle shape crystals Poor diffracting
(10)	$CdCl_2·4H_2O$ (0.30 mmol)	DMA (8ml)	Colourless homogenous solution	8ml	140 °C for 4 days	Powder
(11)	$CdCl_2·4H_2O$ (0.30 mmol)	DMA/H_2O (4ml/4ml)	Milky white colour solution	8ml	140 °C for 4 days	Powder
(12)	$CdCl_2·4H_2O$ (0.30 mmol)	DMA/EtOH (4ml/4ml)	Colourless homogenous solution	8ml	140 °C for 4 days	Colourless very fine crystals Poor diffracting
(13)	$CdCl_2·4H_2O$ (0.30 mmol)	DMA/MeOH (4ml/4ml)	Colourless homogenous solution	8ml	140 °C for 4 days	Powder
(14)	$CdCl_2·4H_2O$ (0.30 mmol)	DMA/THF (4ml/4ml)	Colourless homogenous solution	8ml	140 °C for 4 days	Needle shaped crystals; cell parameter matched with **solid 1** but could not solved
(15)	$Cd(NO_3)_2·4H_2O$ (0.30 mmol)	DMA (8ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Powder
(16)	$Cd(NO_3)_2·4H_2O$ (0.30 mmol)	DMA/H_2O (4ml/4ml)	Colourless solution	8ml	120 °C for 4 days	Needle shaped crystals: Poorly diffracting
(17)	$Cd(NO_3)_2·4H_2O$ (0.30 mmol)	DMA/EtOH (4ml/4ml)	White colour solution	8ml	120 °C for 4 days	Block shaped crystal: Poorly diffracting
(18)	$Cd(NO_3)_2·4H_2O$ (0.30 mmol)	DMA/MeOH (4ml/4ml)	Milky white colour solution	8ml	120 °C for 4 days	Powder
(19)	$Cd(NO_3)_2·4H_2O$ (0.30 mmol)	DMA/THF (4ml/4ml)	White colour solution	8ml	120 °C for 4 days	Needle shaped crystal of **solid 1**
(20)	$Cd(OAc)_2·2H_2O$ (0.30 mmol)	DMA (8ml)	White colour solution	8ml	120 °C for 4 days	Powder
(21)	$Cd(OAc)_2·2H_2O$ (0.30 mmol)	DMA/H_2O (4ml/4ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Powder
(22)	$Cd(OAc)_2·2H_2O$ (0.30 mmol)	DMA/EtOH (4ml/4ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Colourless very fine crystals Very poor diffracting
(23)	$Cd(OAc)_2·2H_2O$ (0.30 mmol)	DMA/MeOH (4ml/4ml)	Milky white colour solution	8ml	120 °C for 4 days	Clear solution
	$Cd(OAc)_2·2H_2O$ (0.30 mmol)	DMA/THF (4ml/4ml)	Milky white colour solution	8ml	120 °C for 4 days	Powder
(24)	$CdCl_2·4H_2O$ (0.30 mmol)	DMA/EtOH (4ml/4ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Powder
(25)	$CdCl_2·4H_2O$ (0.30 mmol)	DMA/MeOH (4ml/4ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Powder
(26)	$CdCl_2·4H_2O$ (0.30 mmol)	DMA/THF (4ml/4ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Powder

Outcomes of the reactions

The Phen is incorporated in the structure suggesting it is working as template for the crystallization of solid **1**. The reaction without Phen resulted the powder phase as the end product which couldn't be characterized through single crystals. Solid $[Cd_2(FBA)_2(phen)_2]$.DMA reported by our group was also obtained in the crystalline phase which were confirmed by checking the cell parameters on single crystals diffraction.

Various combination of cadmium salts and SBA ligand applied for the synthesis of solid 2

Magnesium salts and 4,4′-sulfonyldibenzoic acid were reacted in various combinations of polar aprotic solvents at different temperatures. The composition of salts (1 mmol) and ligand *H_2SBA* (0.50 mmol) were kept constant. Each solution was magnetically agitated in a beaker for 30 minutes before being sealed with Teflon and the synthesis was completed in an 8 ml reactor setup. The reaction was carried out at temperatures ranging from 120 to 130 °C, which were appropriate for obtaining the crystalline phase suggested by the database analysis. The reactions resulted in variety of phases, including liquid, powder, and crystalline. Only the data of new phase solid **2** was solved using the single crystal diffraction method.

Table S4: Outcome of the reactions between Magnesium salts, *H_2SBA* and various solvents.

S. No	Metal salt	Solvent/solvent combinations	Solution after stirring about 30 minutes	Teflon (size)	Temperature (°C) and duration	Result
(1)	$MgCl_2 \cdot 4H_2O$ (1 mmol)	DMA (8ml)	Milky white colour solution	8ml	130 °C for 4 days	Powder
(2)	$MgCl_2 \cdot 4H_2O$ (1 mmol)	DMA/H_2O (4ml/4ml)	Colourless solution	8ml	130 °C for 4 days	Needle shaped crystals: Poorly diffracting
(3)	$MgCl_2 \cdot 4H_2O$ (1 mmol)	DMA/EtOH (4ml/4ml)	Colourless homogenous solution	8ml	130 °C for 4 days	Needle shaped crystal of **Solid 2**
(4)	$MgCl_2 \cdot 4H_2O$ (1 mmol)	DMA/MeOH (4ml/4ml)	Colourless homogenous solution	8ml	130 °C for 4 days	Powder
(5)	$MgCl_2 \cdot 4H_2O$ (1 mmol)	DMA/THF (4ml/4ml)	Colourless homogenous solution		130 °C for 4 days	Powder
(6)	$Mg(OAc)_2 \cdot 4H_2O$ (1 mmol)	DMA (8ml)	White colour solution	8ml	130 °C for 4 days	Powder
(7)	$Mg(OAc)_2 \cdot 4H_2O$ (1 mmol)	DMA/H_2O (4ml/4ml)	Milky white colour solution	8ml	130 °C for 4 days	Powder
(8)	$Mg(OAc)_2 \cdot 4H_2O$ (1 mmol)	DMA/EtOH (4ml/4ml)	Milky white colour solution	8ml	130 °C for 4 days	Needle shaped crystals; cell parameter matched with Solid **2** but could not solved
(9)	$Mg(NO_3)_2 \cdot 6H_2O$ (1 mmol)	DMA/MeOH (4ml/4ml)	Milky white colour solution	8ml	130 °C for 4 days	Clear solution
	$Mg(NO_3)_2 \cdot 6H_2O$ (1 mmol)	DMA/THF (4ml/4ml)	Milky white colour solution	8ml	130 °C for 4 days	Powder
(10)	$Mg(NO_3)_2 \cdot 6H_2O$ (1 mmol)	DMA (8ml)	Colourless homogenous solution	8ml	130 °C for 4 days	Powder
(11)	$Mg(NO_3)_2 \cdot 6H_2O$ (1 mmol)	DMA/H_2O (4ml/4ml)	Milky white colour solution	8ml	130 °C for 4 days	Powder

(12)	$Mg(NO_3)_2 \cdot 6H_2O$ (1 mmol)	DMA/EtOH (4ml/4ml)	Colourless homogenous solution	8ml	130 °C for 4 days	Colourless very fine crystals Poor diffracting
(13)	$Mg(NO_3)_2 \cdot 6H_2O$ (1 mmol)	DMA/MeOH (4ml/4ml)	Colourless homogenous solution	8ml	130 °C for 4 days	Powder
(14)	$Mg(NO_3)_2 \cdot 6H_2O$ (1 mmol)	DMA/THF (4ml/4ml)	Colourless homogenous solution	8ml	130 °C for 4 days	Powder
(15)	$MgCl_2 \cdot 4H_2O$ (1 mmol)	DMA (8ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Powder
(16)	$MgCl_2 \cdot 4H_2O$ (1 mmol)	DMA/H_2O (4ml/4ml)	Colourless solution	8ml	120 °C for 4 days	Needle shaped crystals: Poorly diffracting
(17)	$MgCl_2 \cdot 4H_2O$ (1 mmol)	DMA/EtOH (4ml/4ml)	White colour solution	8ml	120 °C for 4 days	Needle shaped crystal **Solid 2**
(18)	$MgCl_2 \cdot 4H_2O$ (1 mmol)	DMA/MeOH (4ml/4ml)	Milky white colour solution	8ml	120 °C for 4 days	Powder
(19)	$MgCl_2 \cdot 4H_2O$ (1 mmol)	DMA/THF (4ml/4ml)	White colour solution	8ml	120 °C for 4 days	Needle shaped crystal Poorly diffracting
(20)	$Mg(OAc)_2 \cdot 4H_2O$ (1 mmol)	DMA (8ml)	White colour solution	8ml	120 °C for 4 days	Powder
(21)	$Mg(OAc)_2 \cdot 4H_2O$ (1 mmol)	DMA/H_2O (4ml/4ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Powder
(22)	$Mg(OAc)_2 \cdot 4H_2O$ (1 mmol)	DMA/EtOH (4ml/4ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Colourless very fine crystals Very poor diffracting
(23)	$Mg(OAc)_2 \cdot 4H_2O$ (1 mmol)	DMA/MeOH (4ml/4ml)	Milky white colour solution	8ml	120 °C for 4 days	Clear solution
	$Mg(OAc)_2 \cdot 4H_2O$ (1 mmol)	DMA/THF (4ml/4ml)	Milky white colour solution	8ml	120 °C for 4 days	Powder
(24)	$Mg(NO_3)_2 \cdot 6H_2O$ (1 mmol)	DMA/EtOH (4ml/4ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Powder
(25)	$Mg(NO_3)_2 \cdot 6H_2O$ (1 mmol)	DMA/MeOH (4ml/4ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Powder
(26)	$Mg(NO_3)_2 \cdot 6H_2O$ (1 mmol)	DMA/THF (4ml/4ml)	Colourless homogenous solution	8ml	120 °C for 4 days	Powder

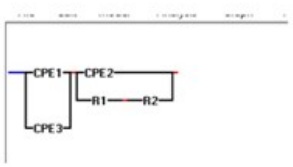
Outcomes of the reactions

The screening of the reactions suggested the temperature 120 °C and 130 °C were the suitable for the aggregation of the molecules in the crystalline phase. The variation in the composition of the ligand and salts resulted mostly the powder form of the product. The solid **2** crystalline phase was obtained when the same concentration of different salts of magnesium were used.

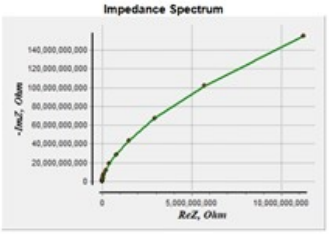
EIS software data fitting Report

Solid 1.

Equivalent Electric Circuit



Impedance Spectrum



Parameters of the Equivalent Electric Circuit

Parameters	Values of the Parameters	Errors, %
R1	1.8728E05	0.02
R2	9.3842E05	0.003
P1	6.0544E-13	0.24956
n1	0.38325	0.40688
P2	1.2292E-08	0.002
n2	0.96186	0.01
P3	7.2904E-12	0.020065
n3	1	0.010452

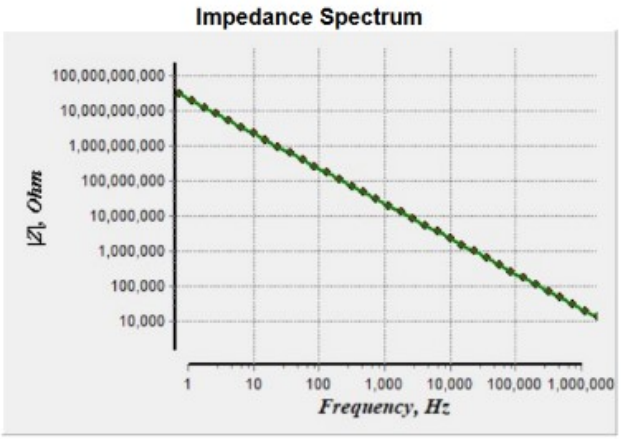
Statistics of the model

r^2 (complex) = 2.0107E14
r^2 (Z'' values) = 1.3396E14
r^2 (Z' values) = 6.7109E13
r^2 (parametric) = 0.57684
r^2 (amplitude) = 7.4985E-05

ALGORITHM: NM Simp

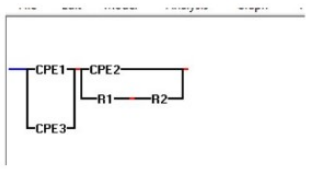
number of iterations = 0

Function selected: Unweighted

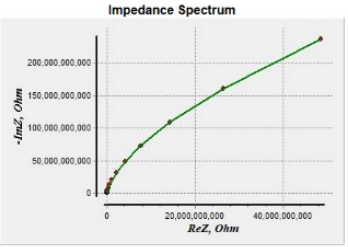


Solid 2.

Equivalent Electric Circuit



Impedance Spectrum



Parameters of the Equivalent Electric Circuit

Parameters	*Values of the Parameters*	*Errors, %*
R1	2.4216E05	0.001451
R2	1.4793E05	0.032121
P1	6.5807E-12	0.038376
n1	0.98898	0.024033
P2	0.00015429	0.002145
n2	0.19505	0.003254
P3	1.1115E-12	0.177692
n3	0.34521	0.030662

Statistics of the model

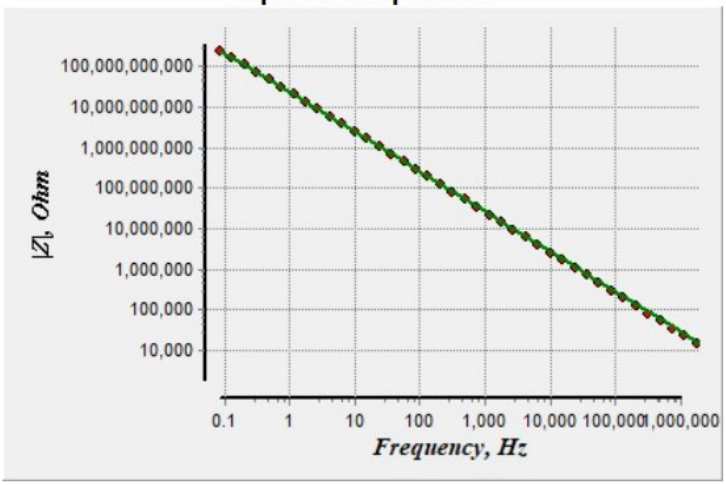
r^2 (complex) = 1.5797E15
r^2 (Z** values) = 7.3318E14
r^2 (Z* values) = 8.4656E14
r^2 (parametric) = 1568.2
r^2 (amplitude) = 0.0082456

ALGORITHM: NM Simp

number of iterations = 0

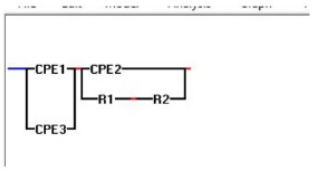
Function selected: Unweighted

Impedance Spectrum

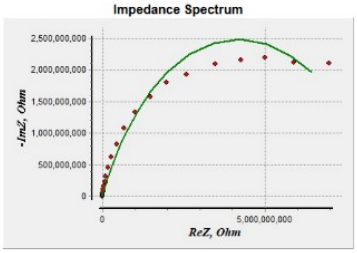


Solid 1'.

Equivalent Electric Circuit



Impedance Spectrum



Parameters of the Equivalent Electric Circuit

Parameters	*Values of the Parameters*	*Errors, %*
R1	9.9988E05	0.1202
R2	9.9858E05	0.0123
P1	1.22E-10	0.9661
n1	0.015939	10.8910
P2	9.9434E-09	0.0232
n2	0.7067	0.0321
P3	5.1713E-11	0.4017
n3	0.69722	0.5049

Statistics of the model

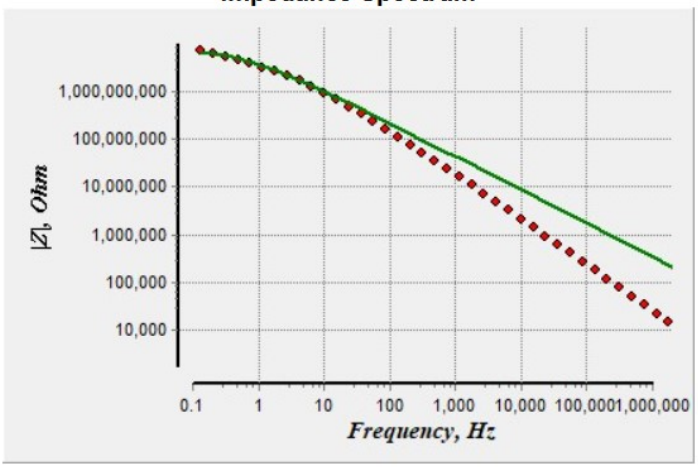
r^2 (complex) = 2.4395E16
r^2 (Z'' values) = 1.2695E16
r^2 (Z' values) = 1.17E16
r^2 (parametric) = 8043.9
r^2 (amplitude) = 87.178

ALGORITHM: NM Simp

number of iterations = 0

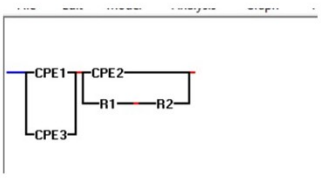
Function selected: Unweighted

Impedance Spectrum

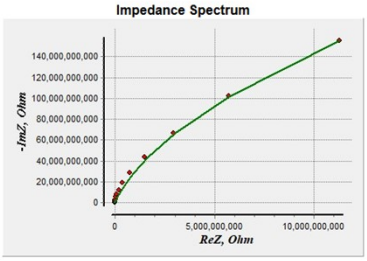


Solid 2'

Equivalent Electric Circuit



Impedance Spectrum



Parameters of the Equivalent Electric Circuit

Parameters	*Values of the Parameters*	*Errors, %*
R1	38206	0.0036
R2	6.3129E05	0.0032
P1	7.6191E-12	0.14687
n1	0.98485	0.089951
P2	0.0005	0.0014
n2	0.63449	0.0024
P3	3.1477E-13	3.5076
n3	0.032743	0.0821

Statistics of the model

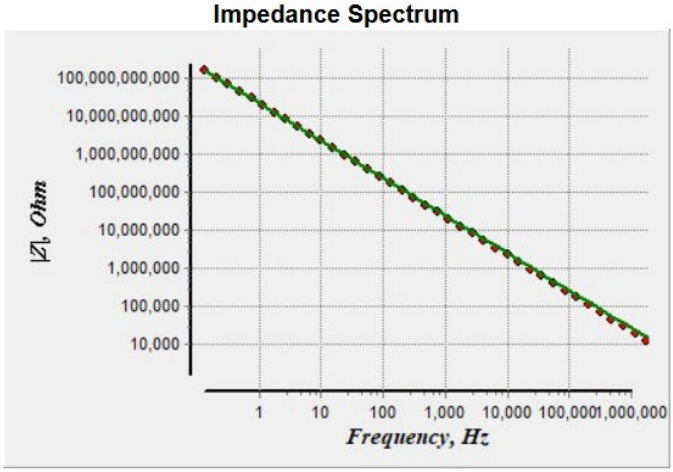
r^2 (complex) = 1.1245E16
r^2 (Z** values) = 7.1279E15
r^2 (Z* values) = 4.1171E15
r^2 (parametric) = 506.51
r^2 (amplitude) = 0.019449

ALGORITHM: NM Simp

number of iterations = 0

Function selected: Unweighted

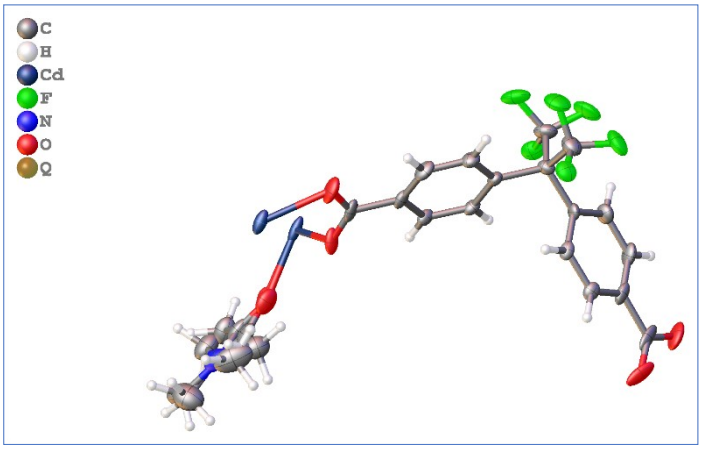
Impedance Spectrum



Solid1

R_1=4.29%

Crystal Data and Experimental



Experimental. Single Colorless needle shape-shaped crystals of **Solid1** were used as supplied. A suitable crystal with dimensions 0.32 × 0.21 × 0.12 mm^3 was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the olex2.solve 1.5 (Bourhis et al., 2015) solution program using iterative methods and by using Olex2 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with XL (Sheldrick, 2008) using full matrix least squares minimisation on F^2.

Crystal Data. $C_{23}H_{21}CdF_6NO_{5.5}$, M_r = 625.81, monoclinic, $P2/n$ (No. 13), a = 7.5048(14) Å, b = 12.3263(19) Å, c = 26.274(5) Å, β = 92.904(5)°, $\alpha = \gamma$ = 90°, V = 2427.4(8) Å^3, T = 100(2) K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.983, 36864 reflections measured, 4522 unique (R_{int} = 0.0968) which were used in all calculations. The final wR_2 was 0.0893 (all data) and R_1 was 0.0429 (I≥2 σ(I)).

Compound	**Solid1**
Formula	$C_{23}H_{21}CdF_6NO_{5.5}$
$D_{calc.}$/ g cm^{-3}	1.712
μ/mm^{-1}	0.983
Formula Weight	625.81
Colour	Colorless
Shape	needle shape-shaped
Size/mm^3	0.32×0.21×0.12
T/K	100(2)
Crystal System	monoclinic
Space Group	$P2/n$
a/Å	7.5048(14)
b/Å	12.3263(19)
c/Å	26.274(5)
α/°	90
β/°	92.904(5)
γ/°	90
V/Å^3	2427.4(8)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK_α
Θ_{min}/°	2.267
Θ_{max}/°	25.500
Measured Refl's.	36864
Indep't Refl's	4522
Refl's I≥2 σ(I)	3061
R_{int}	0.0968
Parameters	378
Restraints	90
Largest Peak	0.515
Deepest Hole	-0.727
GooF	1.045
wR_2 (all data)	0.0893
wR_2	0.0795
R_1 (all data)	0.0838
R_1	0.0429

Structure Quality Indicators

Reflections:	d min (MoKα) 2Θ=51.0° 0.83	I/σ(I) 16.4	Rint m=8.38 9.68%	Full 50.5° 99.8
Refinement:	Shift 0.000	Max Peak 0.5	Min Peak -0.7	GooF 1.045

A Colorless needle shape-shaped-shaped crystal with dimensions 0.32 × 0.21 × 0.12 mm^3 was mounted. Data were collected using a Bruker APEX-II CCD diffractometer operating at T = 100(2) K.

Data were measured using ϕ and ω scans with MoK_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program Bruker D8 Quest. The maximum resolution that was achieved was Θ = 25.500˚ (0.83 Å).

The unit cell was refined using SAINT v8.37A (Bruker, 2015) on 917 reflections, 2% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using SAINT v8.37A (Bruker, 2015). The final completeness is 99.80 % out to 25.500˚ in Θ. No absorption correction was performed. The absorption coefficient μ of this material is 0.983 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.780 and 0.888.

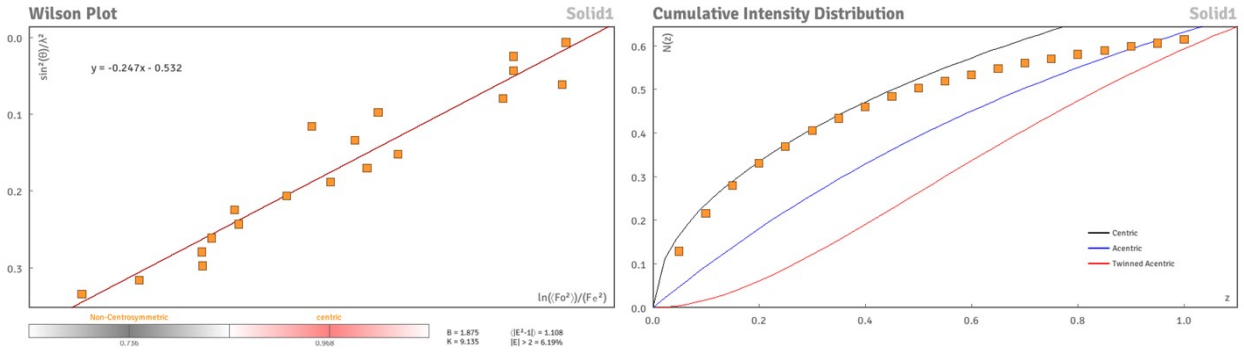
The structure was solved and the space group $P2/n$ (# 13) determined by the olex2.solve 1.5 (Bourhis et al., 2015) structure solution program using using iterative methods and refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2014/7 of XL (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

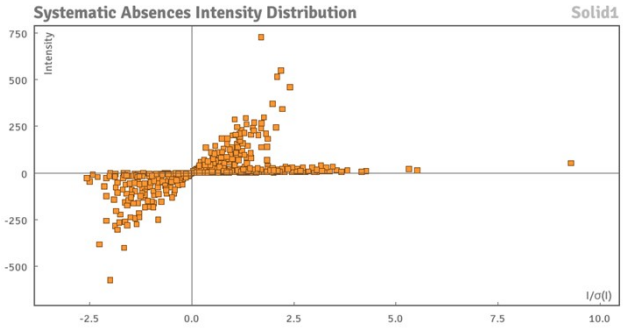
_exptl_absorpt_process_details: SADABS-2016/2 (Bruker,2016/2) was used for absorption correction.wR_2(int) was 0.0968 before and 0.0559 after correction.The Ratio of minimum to maximum transmission is 0.9252.The $\lambda/2$ correction factor is Not present.

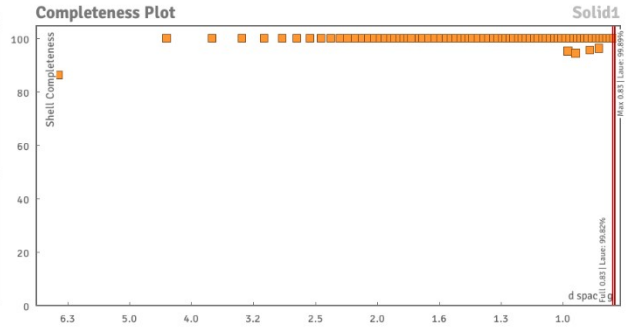
_smtbx_masks_special_details: A solvent mask was calculated and 84 electrons were found in a volume of 336$Å^3$ in 1 void per unit cell. This is consistent with the presence of 1[C4H8O] per Formula Unit which account for 80 electrons per unit cell.

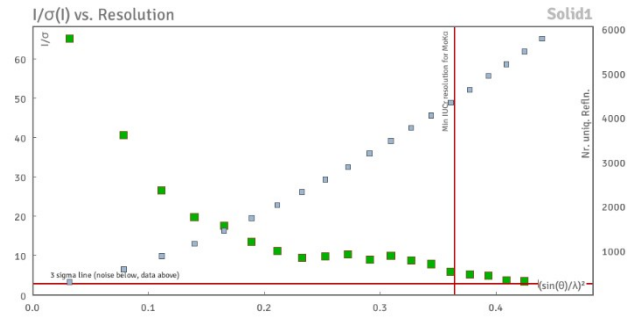
There is a single formula unit in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1. The moiety formula is C21 H17 Cd F6 N O5, 0.5[C4H8O].

Data Plots: Diffraction Data

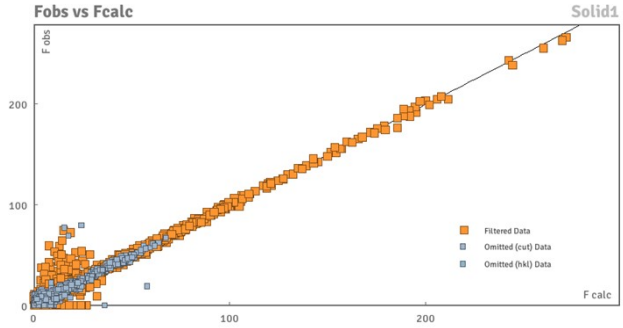


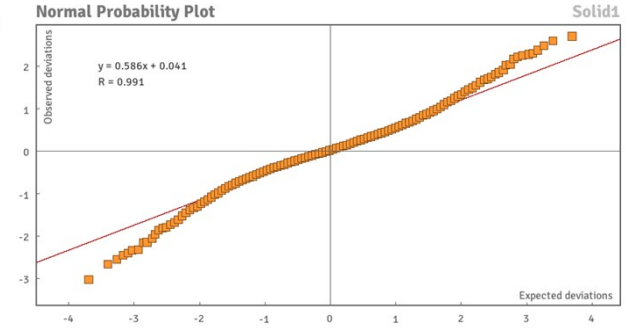






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	37885	Unique reflections	4522
Completeness	0.999	Mean I/σ	17.83
hkl_{max} collected	(8, 16, 35)	hkl_{min} collected	(-10, -16, -34)
hkl_{max} used	(9, 14, 31)	hkl_{min} used	(-9, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.83
d_{max} used	8.98	d_{min} used	0.83
Friedel pairs	7687	Friedel pairs merged	1
Inconsistent equivalents	483	R_{int}	0.0968
R_{sigma}	0.061	Intensity transformed	0
Omitted reflections	6	Omitted by user (OMIT hkl)	0
Multiplicity	(5438, 6538, 5008, 1874, 528, 86, 11)	Maximum multiplicity	21
Removed systematic absences	1021	Filtered off (Shel/OMIT)	6376

Table S5: Selected Bond Lengths in Å for Solid1.

Atom	Atom	Length/Å
Cd1	O1	2.235(3)
Cd1	O1[1]	2.235(3)
Cd1	O3[2]	2.247(4)
Cd1	O3[3]	2.247(4)
Cd2	O2[4]	2.250(3)
Cd2	O2	2.250(3)
Cd2	O4[3]	2.251(3)
Cd2	O4[5]	2.251(3)
Cd2	O5[4]	2.266(9)
Cd2	O5	2.266(9)
Cd2	O5A[4]	2.231(10)
Cd2	O5A	2.231(10)
O4	Cd2[6]	2.251(3)
O3	Cd1[7]	2.247(4)

[1]3/2-x,+y,1/2-z; [2]1+x,-1+y,+z; [3]1/2-x,-1+y,1/2-z; [4]1/2-x,+y,1/2-z; [5]+x,-1+y,+z; [6]+x,1+y,+z; [7]-1+x,1+y,+z

Table S6: Selected Bond Angles in ˚ for Solid1.

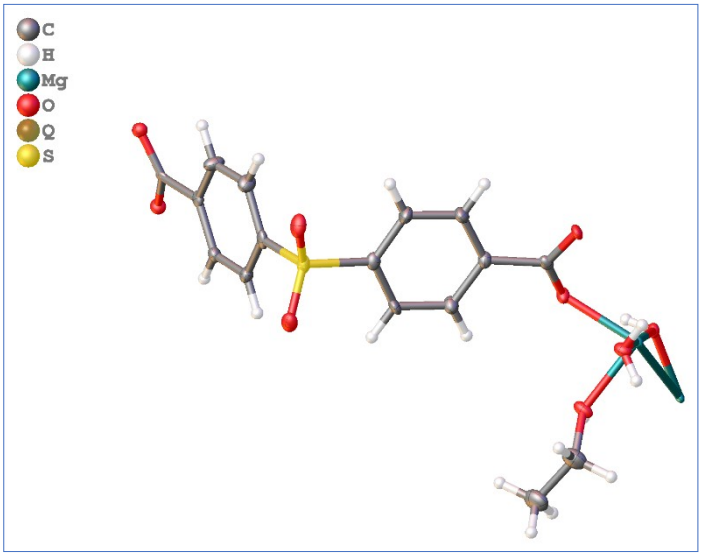
Atom	Atom	Atom	Angle/˚
O1	Cd1	O1[1]	100.92(18)
O1	Cd1	O3[2]	86.28(13)
O1	Cd1	O3[3]	157.22(13)
O1[1]	Cd1	O3[3]	86.28(13)
O1[1]	Cd1	O3[2]	157.22(13)
O3[3]	Cd1	O3[2]	95.38(18)
O2	Cd2	O2[4]	92.47(16)
O2	Cd2	O4[5]	166.73(14)
O2	Cd2	O4[3]	90.31(11)
O2[4]	Cd2	O4[3]	166.73(14)
O2[4]	Cd2	O4[5]	90.31(11)
O2[4]	Cd2	O5[4]	102.5(3)
O2	Cd2	O5	102.5(3)
O2[4]	Cd2	O5	80.2(5)
O2	Cd2	O5[4]	80.2(5)
O4[5]	Cd2	O4[3]	89.93(19)
O4[3]	Cd2	O5[4]	90.7(3)
O4[5]	Cd2	O5[4]	86.6(5)
O4[5]	Cd2	O5	90.8(3)
O4[3]	Cd2	O5	86.6(5)
O5[4]	Cd2	O5	176.2(9)
O5A	Cd2	O2[4]	84.2(6)
O5A[4]	Cd2	O2	84.2(6)
O5A	Cd2	O2	92.6(4)
O5A[4]	Cd2	O2[4]	92.6(4)
O5A[4]	Cd2	O4[3]	100.6(4)
O5A	Cd2	O4[3]	82.7(6)
O5A[4]	Cd2	O4[5]	82.7(6)
O5A	Cd2	O4[5]	100.6(4)
O5A[4]	Cd2	O5A	175.5(11)

[1]3/2-x,+y,1/2-z; [2]1+x,-1+y,+z; [3]1/2-x,-1+y,1/2-z; [4]1/2-x,+y,1/2-z; [5]+x,-1+y,+z; [6]+x,1+y,+z; [7]-1+x,1+y,+z

Solid2

R_1=4.98%

Crystal Data and Experimental



Experimental. Single Colourless needle-shaped crystals of **Solid2** were used as supplied. A suitable crystal with dimensions 0.30 × 0.20 × 0.10 mm^3 was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 100 K during data collection. The structure was solved with the olex2.solve 1.5 (Bourhis et al., 2015) solution program using iterative methods and by using Olex2 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with XL (Sheldrick, 2008) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal Data. $C_{36}H_{43}Mg_3NO_{19}S_2$, M_r = 930.76, monoclinic, $C2/c$ (No. 15), a = 25.095(16) Å, b = 6.440(4) Å, c = 28.376(18) Å, β = 114.671(18)°, $\alpha = \gamma = 90°$, V = 4168(5) Å^3, T = 100 K, Z = 4, Z' = 0.5, μ(MoK$_\alpha$) = 0.253, 7133 reflections measured, 3231 unique (R_{int} = 0.0991) which were used in all calculations. The final wR_2 was 0.1356 (all data) and R_1 was 0.0498 (I≥2 σ(I)).

Compound	**Solid2**
Formula	$C_{36}H_{43}Mg_3NO_{19}S_2$
$D_{calc.}$/ g cm^{-3}	1.483
μ/mm^{-1}	0.253
Formula Weight	930.76
Colour	Colorless
Shape	needle-shaped
Size/mm^3	0.30×0.20×0.10
T/K	100
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	25.095(16)
b/Å	6.440(4)
c/Å	28.376(18)
α/°	90
β/°	114.671(18)
γ/°	90
V/Å^3	4168(5)
Z	4
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.836
Θ_{max}/°	23.995
Measured Refl's.	7133
Indep't Refl's	3231
Refl's I≥2 σ(I)	2564
R_{int}	0.0991
Parameters	257
Restraints	0
Largest Peak	0.340
Deepest Hole	-0.581
GooF	1.041
wR_2 (all data)	0.1356
wR_2	0.1262
R_1 (all data)	0.0659
R_1	0.0498

Structure Quality Indicators

Reflections:	d min (MoKα) 2Θ=48.0° 0.87	I/σ(I) 14.2	Rint m=2.35 9.91%	Full 48.0° 98.7
Refinement:		Max Peak 0.3	Min Peak -0.6	GooF 1.041

A Colourless needle-shaped-shaped crystal with dimensions 0.30 × 0.20 × 0.10 mm^3 was mounted. Data were collected using a Bruker APEX-II CCD diffractometer operating at T = 100 K.

Data were measured using ϕ and ω scans with MoK_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program Bruker D8 Quest. The maximum resolution that was achieved was Θ = 23.995˚ (0.87 Å).

The unit cell was refined using SAINT v8.37A (Bruker, 2015) on 3358 reflections, 47% of the observed reflections.

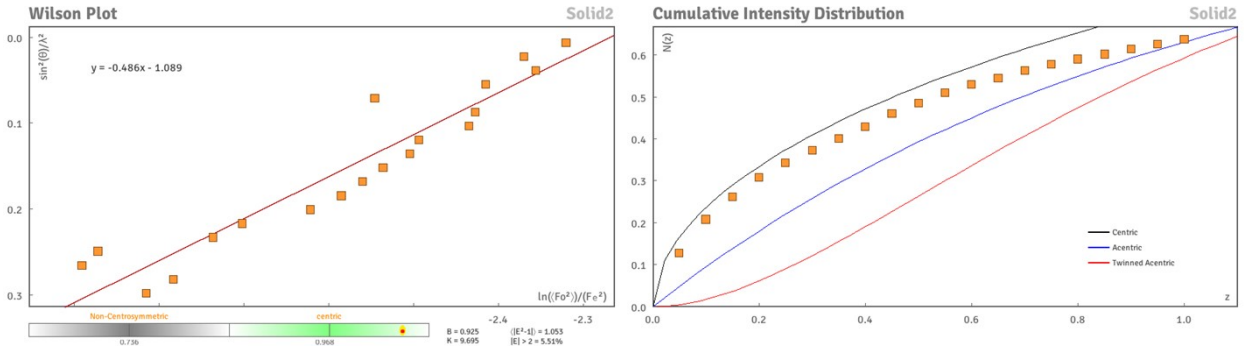
Data reduction, scaling and absorption corrections were performed using SAINT v8.37A (Bruker, 2015). The final completeness is 98.60 % out to 23.995˚ in Θ. A multi-scan absorption correction was performed. The absorption coefficient μ of this material is 0.253 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0 and 0.

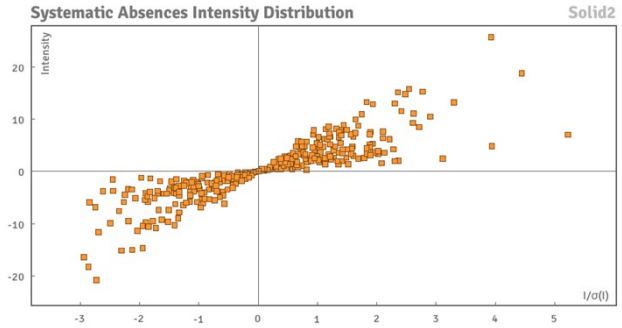
The structure was solved and the space group $C2/c$ (# 15) determined by the olex2.solve 1.5 (Bourhis et al., 2015) structure solution program using using iterative methods and refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2014/7 of XL (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

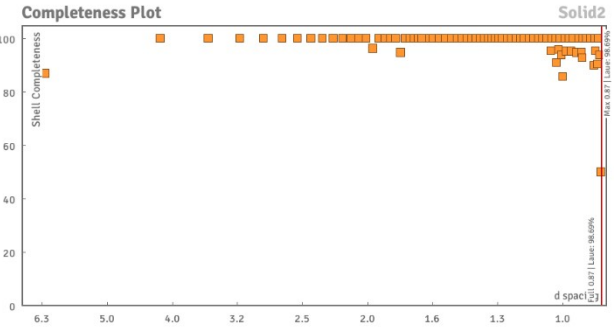
_smtbx_masks_special_details: A solvent mask was calculated and 196 electrons were found in a volume of 752Å^3 in 1 void per unit cell. This is consistent with the presence of 1[C4H9NO] per formula unit which account for 192 electrons per unit cell.

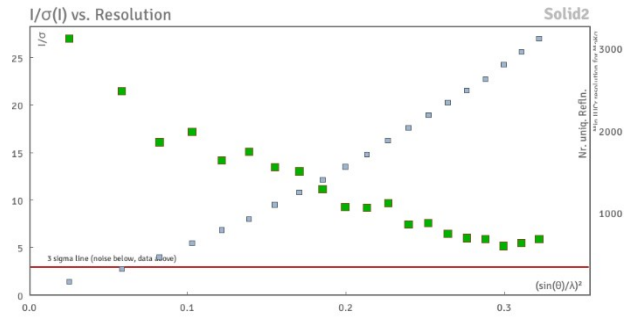
The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms. The moiety formula is C32 H34 Mg3 O18 S2, 1[C4H9NO].

Data Plots: Diffraction Data

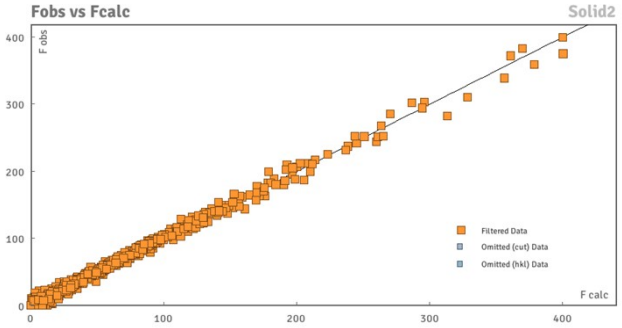


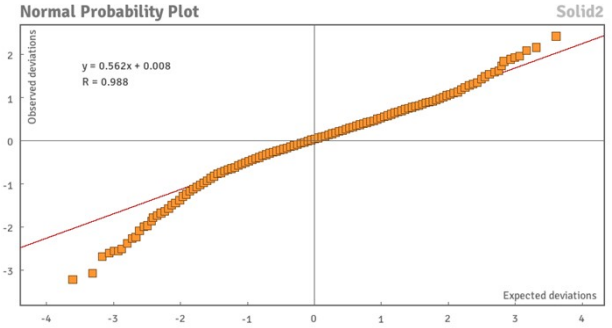






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	7581	Unique reflections	3231
Completeness	0.987	Mean I/σ	11.4
hkl_{max} collected	(28, 7, 32)	hkl_{min} collected	(-23, -7, -32)
hkl_{max} used	(26, 7, 32)	hkl_{min} used	(-28, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.84
d_{max} used	9.12	d_{min} used	0.87
Friedel pairs	1448	Friedel pairs merged	1
Inconsistent equivalents	263	R_{int}	0.0991
R_{sigma}	0.0707	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(6853, 364)	Maximum multiplicity	6
Removed systematic absences	448	Filtered off (Shel/OMIT)	0

Table S7: **Selected Bond Lengths in Å for Solid2.**

Atom	Atom	Length/Å
Mg2	Mg1[1]	3.554(2)
Mg2	Mg1[2]	3.568(2)
Mg2	Mg1	3.554(2)
Mg2	Mg1[3]	3.568(2)
Mg2	O2[1]	2.050(2)
Mg2	O2	2.050(2)
Mg2	O9[4]	2.084(2)
Mg2	O9[5]	2.084(2)
Mg2	O5[3]	2.094(2)
Mg2	O5[2]	2.094(2)
Mg2	H2	2.41(4)
Mg1	Mg2[6]	3.568(2)
Mg1	Mg1[2]	3.040(3)
Mg1	O2[2]	2.054(2)
Mg1	O2	2.045(2)
Mg1	O4	2.079(2)
Mg1	O8[5]	2.088(3)
Mg1	O1	2.104(2)
Mg1	O3	2.102(2)
Mg1	H2	2.33(4)
O2	Mg1[2]	2.055(2)
O9	Mg2[7]	2.084(2)
O5	Mg2[6]	2.094(2)
O8	Mg1[8]	2.088(2)

––––

[1]1-x,2-y,1-z; [2]1-x,1-y,1-z; [3]+x,1+y,+z; [4]1-x,1+y,3/2-z; [5]+x,1-y,-1/2+z; [6]+x,-1+y,+z; [7]1-x,-1+y,3/2-z; [8]+x,1-y,1/2+z

Table S8: **Selected Bond Angles in ˚ for Solid2.**

Atom	Atom	Atom	Angle/˚
Mg1	Mg2	Mg1[1]	179.999(12)
Mg1[2]	Mg2	Mg1[3]	180.0
Mg1[1]	Mg2	Mg1[3]	129.47(5)
Mg1	Mg2	Mg1[2]	129.47(5)
Mg1[1]	Mg2	Mg1[2]	50.53(5)
Mg1	Mg2	Mg1[3]	50.53(5)
Mg1[2]	Mg2	H2	138.5(9)
Mg1[1]	Mg2	H2	139.4(9)
Mg1	Mg2	H2	40.6(9)
Mg1[3]	Mg2	H2	41.5(9)
O2[1]	Mg2	Mg1[2]	29.66(6)
O2	Mg2	Mg1	29.73(6)
O2	Mg2	Mg1[1]	150.27(6)
O2[1]	Mg2	Mg1	150.27(6)
O2[1]	Mg2	Mg1[1]	29.73(6)
O2[1]	Mg2	Mg1[3]	150.34(6)
O2	Mg2	Mg1[3]	29.66(6)
O2	Mg2	Mg1[2]	150.34(6)
O2[1]	Mg2	O2	180.0
O2[1]	Mg2	O9[4]	94.46(8)
O2	Mg2	O9[4]	85.54(8)
O2[1]	Mg2	O9[5]	85.54(8)
O2	Mg2	O9[5]	94.46(8)
O2[1]	Mg2	O5[2]	94.75(8)
O2[1]	Mg2	O5[3]	85.25(8)
O2	Mg2	O5[2]	85.24(8)
O2	Mg2	O5[3]	94.76(8)
O2	Mg2	H2	17.3(9)
O2[1]	Mg2	H2	162.7(9)
O9[5]	Mg2	Mg1[1]	114.30(6)
O9[4]	Mg2	Mg1[1]	65.70(6)
O9[4]	Mg2	Mg1[3]	78.93(6)
O9[5]	Mg2	Mg1[2]	78.93(6)
O9[4]	Mg2	Mg1[2]	101.07(6)
O9[5]	Mg2	Mg1	65.70(6)
O9[4]	Mg2	Mg1	114.30(6)
O9[5]	Mg2	Mg1[3]	101.07(6)
O9[5]	Mg2	O9[4]	180.0
O9[4]	Mg2	O5[3]	89.98(10)
O9[5]	Mg2	O5[3]	90.02(10)
O9[5]	Mg2	O5[2]	89.98(10)
O9[4]	Mg2	O5[2]	90.02(10)
O9[5]	Mg2	H2	105.9(9)
O9[4]	Mg2	H2	74.1(9)
O5[3]	Mg2	Mg1	101.42(6)
O5[3]	Mg2	Mg1[2]	113.96(6)
O5[2]	Mg2	Mg1[3]	113.96(6)
O5[2]	Mg2	Mg1	78.58(6)
O5[3]	Mg2	Mg1[3]	66.04(6)
O5[3]	Mg2	Mg1[1]	78.58(6)
O5[2]	Mg2	Mg1[1]	101.42(6)
O5[2]	Mg2	Mg1[2]	66.04(6)
O5[3]	Mg2	O5[2]	180.0
O5[3]	Mg2	H2	107.3(9)
O5[2]	Mg2	H2	72.7(9)
Mg2	Mg1	Mg2[6]	129.47(5)
Mg2[6]	Mg1	H2	101.2(9)
Mg2	Mg1	H2	42.4(9)
Mg1[3]	Mg1	Mg2[6]	64.50(4)
Mg1[3]	Mg1	Mg2	64.97(4)
Mg1[3]	Mg1	H2	50.5(9)
O2	Mg1	Mg2	29.82(6)
O2[3]	Mg1	Mg2[6]	29.59(6)
O2[3]	Mg1	Mg2	103.73(8)
O2	Mg1	Mg2[6]	103.51(8)
O2	Mg1	Mg1[3]	42.26(7)

Atom	Atom	Atom	Angle/°
O2[3]	Mg1	Mg1[3]	42.00(7)
O2	Mg1	O2[3]	84.26(11)
O2	Mg1	O4	92.10(10)
O2[3]	Mg1	O4	94.30(10)
O2	Mg1	O8[5]	95.06(10)
O2[3]	Mg1	O8[5]	92.11(10)
O2[3]	Mg1	O1	176.30(10)
O2	Mg1	O1	92.76(10)
O2	Mg1	O3	176.71(10)
O2[3]	Mg1	O3	92.61(10)
O2[3]	Mg1	H2	90.1(9)
O2	Mg1	H2	18.7(9)
O4	Mg1	Mg2[6]	71.51(6)
O4	Mg1	Mg2	112.51(7)
O4	Mg1	Mg1[3]	94.32(7)
O4	Mg1	O8[5]	170.83(9)
O4	Mg1	O1	83.58(9)
O4	Mg1	O3	89.17(9)
O4	Mg1	H2	74.0(9)
O8[5]	Mg1	Mg2	72.13(7)
O8[5]	Mg1	Mg2[6]	112.17(7)
O8[5]	Mg1	Mg1[3]	94.83(7)
O8[5]	Mg1	O1	90.35(9)
O8[5]	Mg1	O3	84.00(9)
O8[5]	Mg1	H2	112.6(10)
O1	Mg1	Mg2[6]	150.46(7)
O1	Mg1	Mg2	74.41(8)
O1	Mg1	Mg1[3]	134.98(8)
O1	Mg1	H2	86.4(9)
O3	Mg1	Mg2	151.29(7)
O3	Mg1	Mg2[6]	74.02(8)
O3	Mg1	Mg1[3]	134.61(8)
O3	Mg1	O1	90.40(10)
O3	Mg1	H2	163.1(9)

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[1]1-x,2-y,1-z; [2]+x,1+y,+z; [3]1-x,1-y,1-z; [4]1-x,1+y,3/2-z; [5]+x,1-y,-1/2+z; [6]+x,-1+y,+z; [7]1-x,-1+y,3/2-z; [8]+x,1-y,1/2+z

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Bruker D8 Quest

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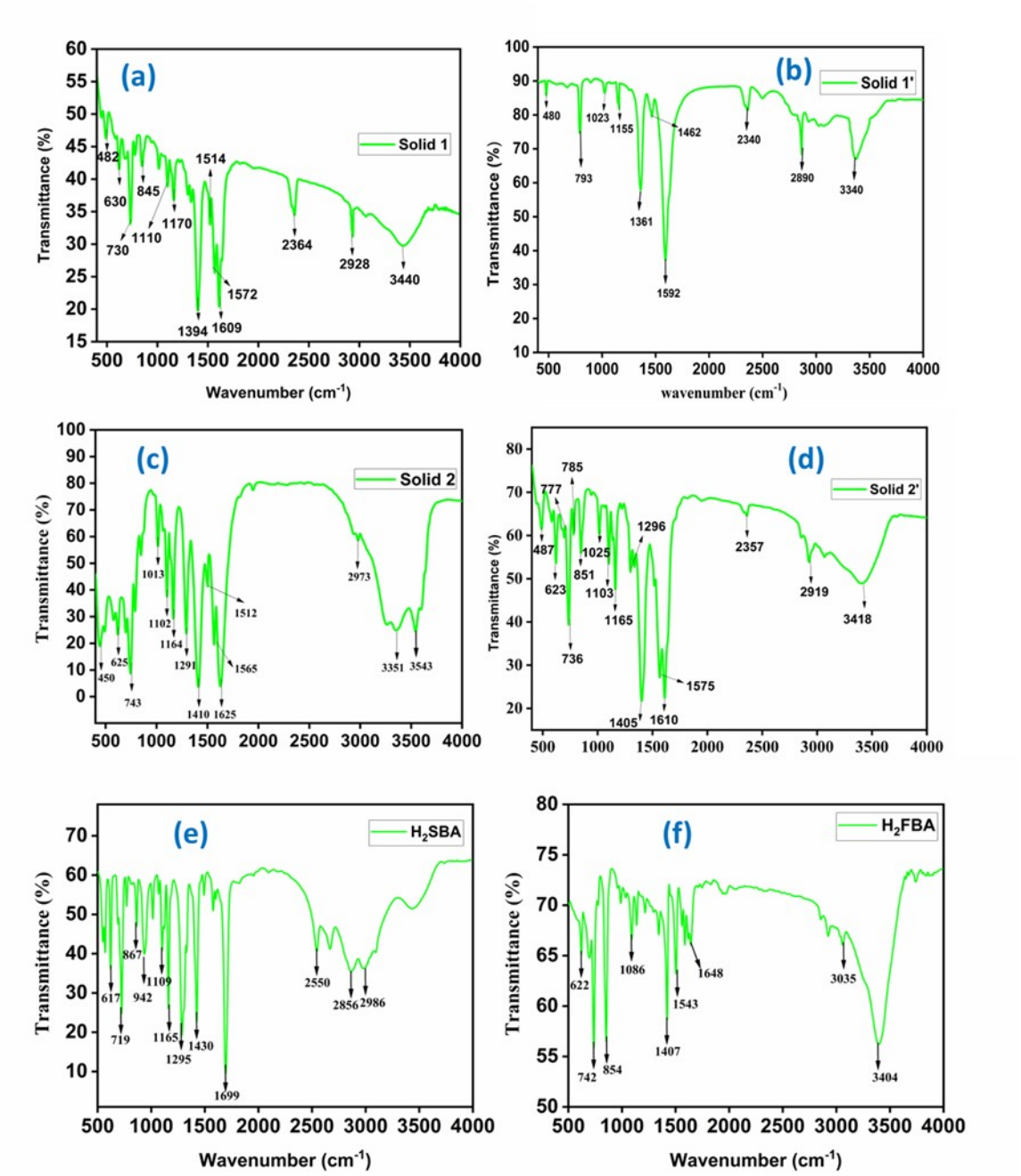

Fig. S6 FT-IR spectra of solids (a) **1**, (c) **2,** (b) **1'**, (d) **2'**, (e) *H_2SBA* and (f) *H_2FBA*

Table S9: Selected vibrational frequencies (cm^{-1}) for reported solids

	Solid **1**	Solid **1'**		Solid **2**	Solid **2'**
Cd-O stretch	482	480	Mg-O stretch	450	487
C-S stretch	—	—	C-S stretch	1013	1025
Cd-O-Cd Bending	730	793	Mg-O-Mg Bending	743	736
C-F stretch	1170	1023	S=O stretch	1013	1025
C-O stretch	1320	1361	C-O stretch	1410	1405
C-N (solvent)	1514	—	C-N (solvent)	1500	—
C=C (aromatic)	1394	1361	C=C (aromatic)	1291	1296
C=O (solvent)	1609	1592	C=O (solvent)	1625	1610
-OH stretch	3440	3340	-OH stretch	3418	3543

FT-IR spectra for solids **1** and **1'** with *FBA* ligand, displayed broad peak at 3440 cm^{-1} and 3340 cm^{-1} for O–H stretching of the carboxylic acid. However, the absence of water and corresponding hydrogen bonds can be felt in the absence of dominant broad peaks around 3300 cm^{-1} in solid **1'**. Sharp peaks around 2890cm^{-1} for **1** and 2928cm^{-1} for **1'** represent the sp^2 of the aromatic ring. Peaks from 1609 and 1592 cm^{-1} depict the symmetric stretch of carboxylate while the peaks around 1572-1462 cm^{-1} resulted from the asymmetric stretch of carbonyl of acid in solid **1** and **1'**. Multiple sharp peaks ranging from ~1390 to 1360cm^{-1} are from symmetric and antisymmetric stretch of C=C which is at lower end compared to isolated C=C depicting a partial single bond owing to resonance in the ring of solid **1** and **1'**. Peaks around 1170 cm^{-1} and 1110cm^{-1} in solid **1** as well as peaks around 1155 cm^{-1} and 1023 cm^{-1} in **1'** are from the asymmetric C–F bonds and sylllinetrical stretching respectively. Presence of peaks near 845cm^{-1}, 793cm^{-1}, 630cm^{-1} indicate the para-substitution of phenyl rings. The stretching peaks near 730-740cm^{-1} depict the presence of Cd–O–Cd bond. Cd-O symmetric stretch appears near 482–450cm^{-1}. The stretching peak at 1514cm^{-1} is due to the C–N bond whereas in **1'** this peak disappeared.

In solid **2**, EtOH and H_2O molecule displayed broad peaks peak at 3543 cm^{-1} and 3351 cm^{-1}. The broad range is because of the water, EtOH and presence of a hydrogen bonding in the vicinity of the oxygen. For solid **2'**, the broad peaks at 3418 cm^{-1} suggested the μ_3–OH and -OH stretching of carboxylic group. The absence of C–N bond stretching peaks near 1500 cm^{-1} in **2'** concluded that solvent molecules has been removed from the sample. The stretching peaks for **2** near 1013cm^{-1} and 1102 cm^{-1} as well as stretching peaks for **2'** near 1025cm^{-1} and 1125cm^{-1} depicts the presence of C–S bond. The asymmetric and symmetric O=S=O occur as strong absorption band near 1164 cm^{-1} and 1410 cm^{-1} for **2** and 1165cm^{-1} and 1405 cm^{-1} **2'** respectively. C=O symmetric stretch near 1291cm^{-1} and asymmetric around 1625 cm^{-1} in solid **2** and 1296cm^{-1}, 1610cm^{-1} in **2'** is due to the combination of the donation of electron to the metal and strong electronic effect present from the two sulfonyl oxygens which is a typical electron withdrawing effect. The stretching peaks near 743 and 736 cm^{-1} depict the presence of Mg–O–Mg bond in solid **2** and **2'**. Mg–O symmetric stretch appears near 450, 487cm^{-1} in both the solids. The stretching peaks 1013 cm^{-1} and 1025 cm^{-1} depicts the presence of S=O bonds in **2** and **2'**.

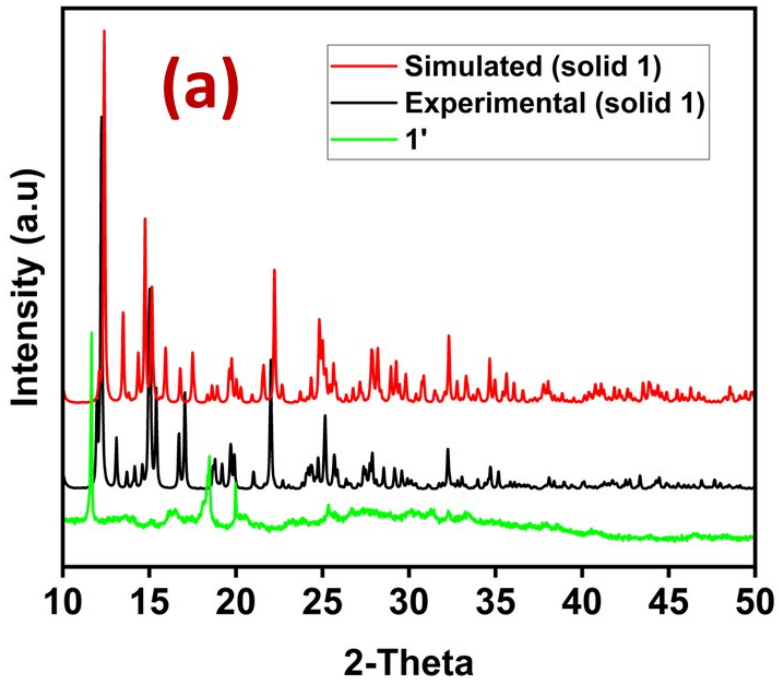

Fig. S7 PXRD pattern comparison of simulated (solid 1), as synthesized (solid 1) and heated sample (**Solid 1'**).

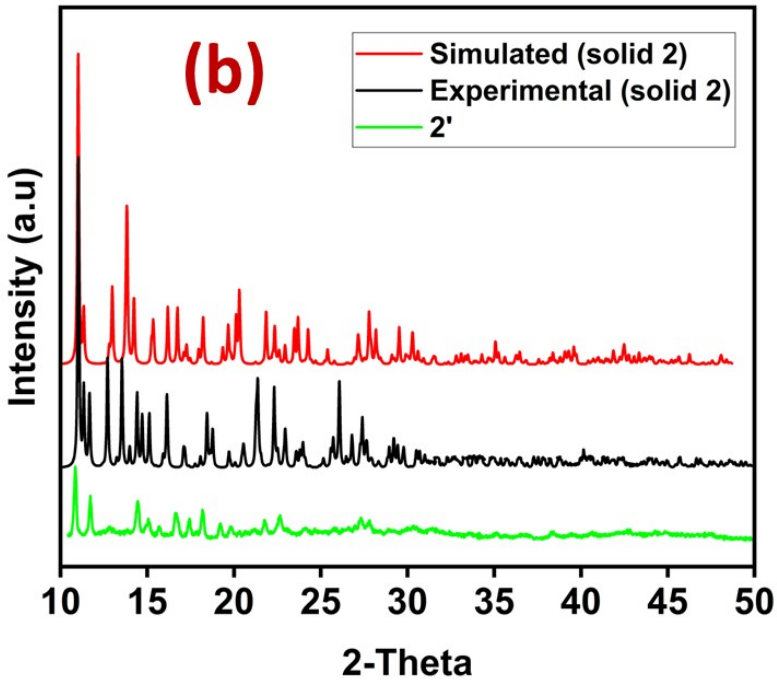

Fig. S8 PXRD pattern comparison of simulated (solid 2), as synthesized (solid 2) and heated sample (Solid 2').

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