Electronic Supplementary Material (ESI) for ChemComm.

A combined stretching-tilting mechanism produces negative, zero and positive linear thermal expansion in a semi-flexible Cd(II)-MOF

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Synthesis

All chemicals and solvent used in these experiments were purchased from Aldrich.

Synthesis of $\{[Cd(HBTC)(BPP)]\cdot 1.5DMF\cdot 2H_2O\}_n$, 1

1,3,5-Benzenetricarboxylic acid (20 mg, 0.095 mmol) and 1,3-bis(4-pyridyl)propane (19 mg, 0.095 mmol) were dissolved in 4.8 mL of DMF whereas $Cd(NO_3)_2.4H_2O$ (29 mg, 0.095 mmol) was dissolved in 3.6 mL of water and acidified with H_2SO_4 (1M, 0.2 mL). Both the solutions were heated and the hot clear solutions were combined in a sealed glass vial. The solution was heated at 80 °C for 24 hours followed by cooling to room temperature. The solution was then kept at -10 °C and after two weeks phase-pure single crystals **1** were obtained.

Calculation of the coefficients of linear thermal expansion

The unit cell parameters of single crystals of **1** were measured at 20 K intervals. The results of the measurements are summarised in **Tables S1-S3**. These values were used to calculate the linear thermal expansion coefficient, $\boldsymbol{\alpha}$, for each of the axes *a*, *b* and *c* using the following equation:

$$\propto = \frac{\Delta L}{L_0 \Delta T}$$

ΔL is the difference in length of the crystallographic axis, L_0 is the initial axis length at the initial temperature, T_0, and ΔT is the change in temperature. The volumetric expansion coefficient, $\boldsymbol{\alpha}_V$, can be calculated using a modified form of the above equation, *i.e.* by substituting ΔV for ΔL and V_0 for L_0. The standard deviations for thermal expansion coefficients are calculated using the "propagation of measurement uncertainty" method.[1] The crystal mosaicity remains approximately the same for the different unit cell determinations. The expansion coefficients were calculated using PAScal and Win_strain.[2,3]

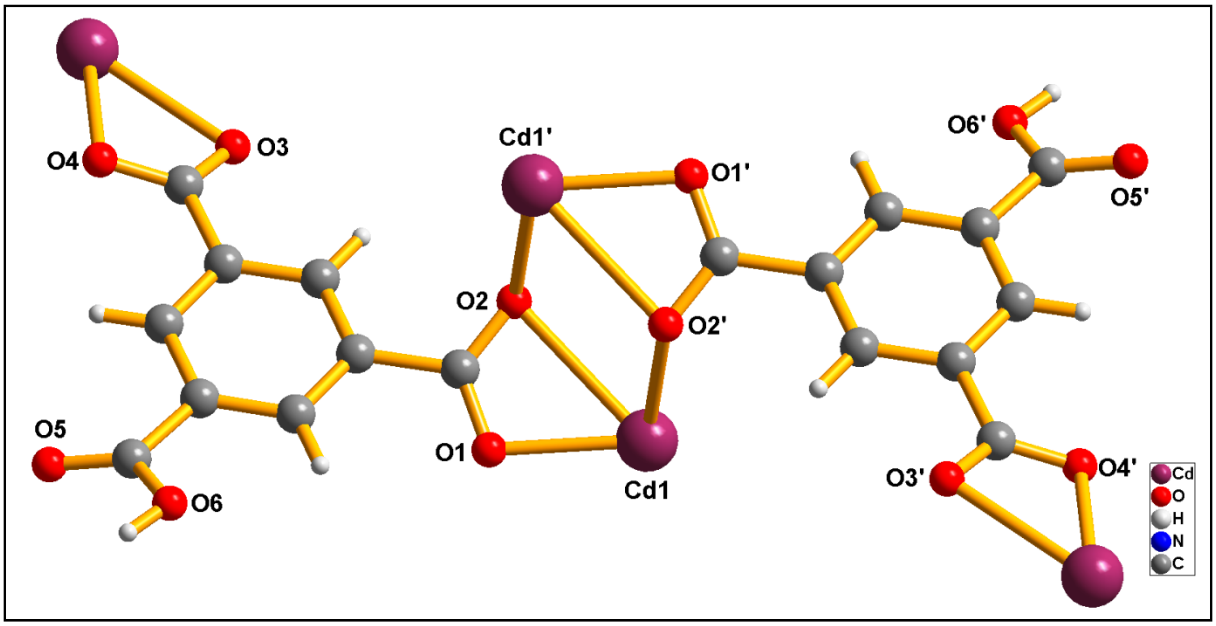

Figure S1. Coordination mode of carboxylic units along with dimeric Cd_2 unit in **1**.

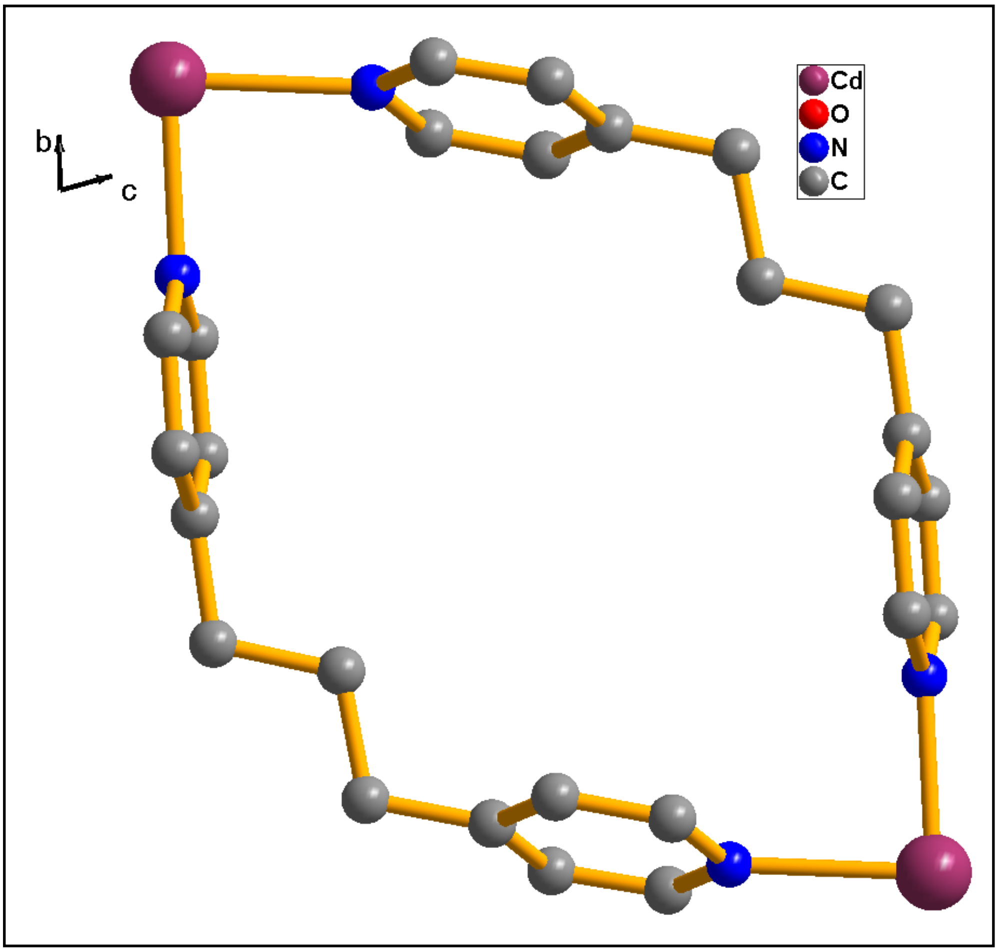

Figure S2. Perspective view showing schematic representation of the macrocyclic unit $Cd_2(BPP)_2$ in the crystallographic *bc* plane.

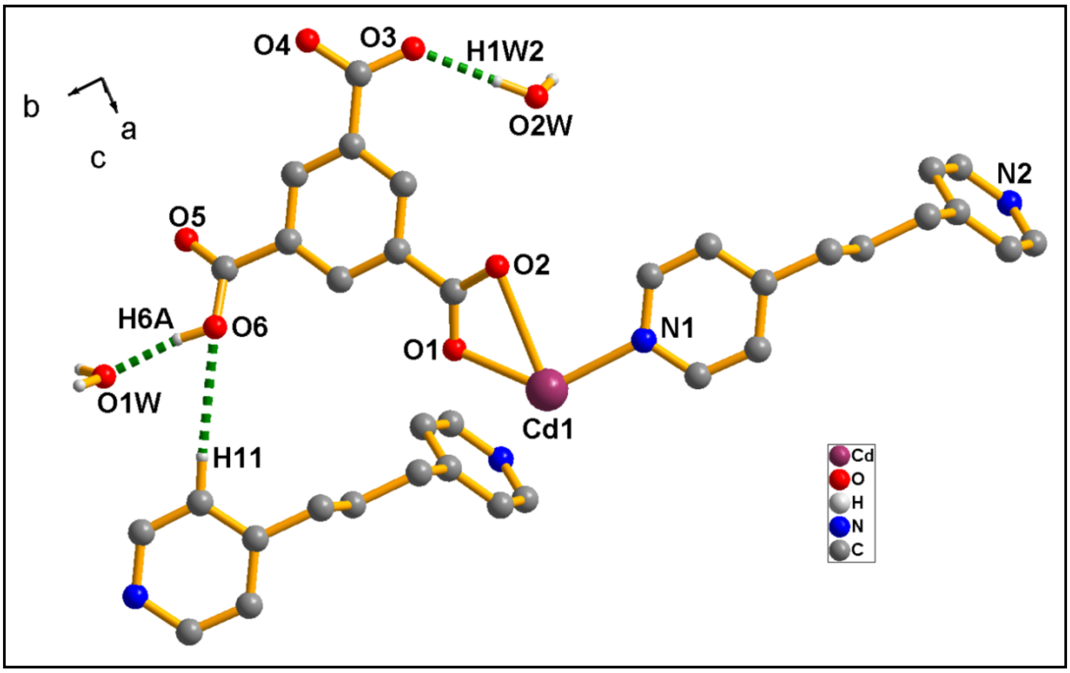

Figure S3. Diagram showing O–H···O and C–H···O hydrogen bonding interactions in **1**.

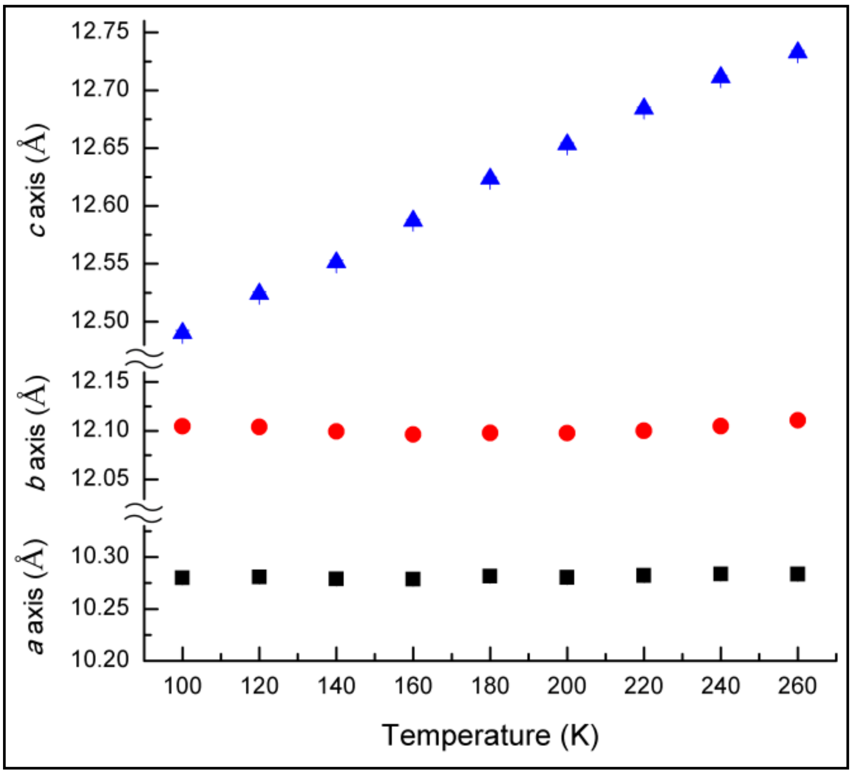

Figure S4. Variation of unit cell dimensions with temperature (estimated standard deviations are too small to visualize.

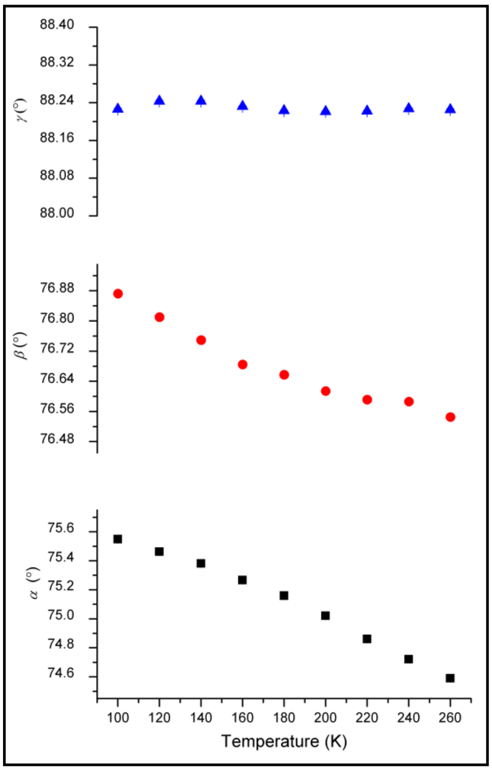

Figure S5. Variation of crystallographic angles (including standard deviations) with change in temperature (standard deviations are too small to visualize in the figure).

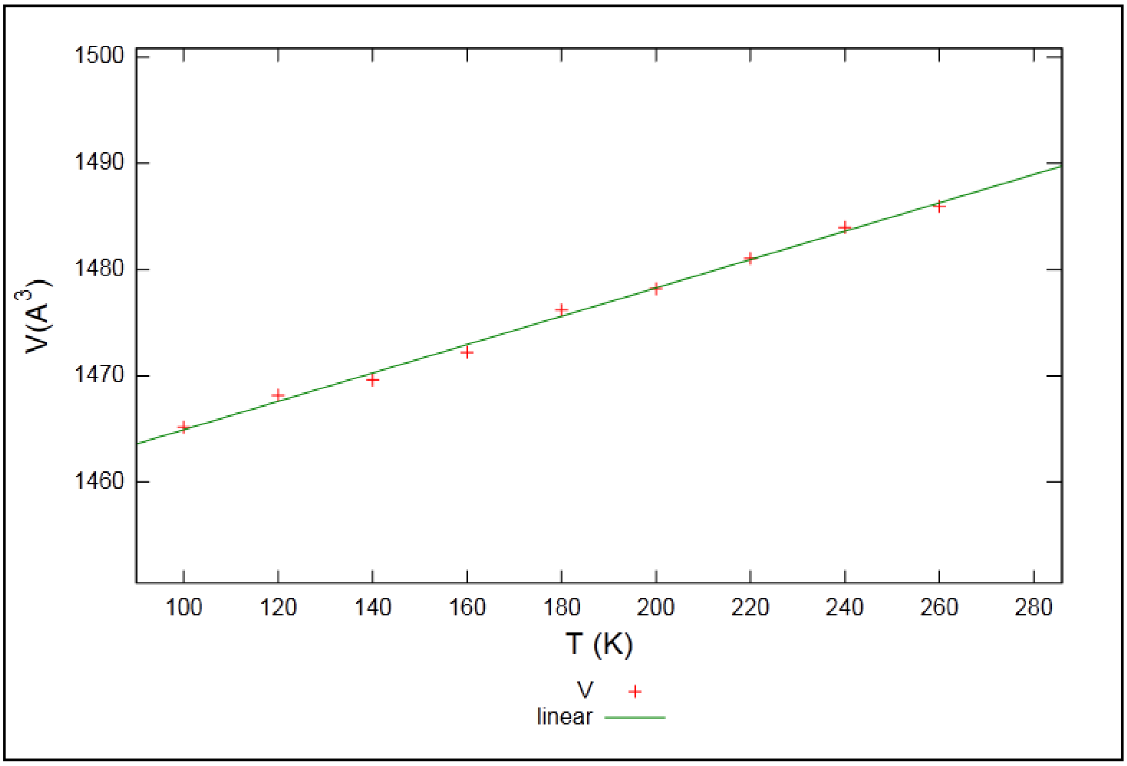

Figure S6. Variation of unit cell volume (including standard deviations) with change in temperature using PASCal method.

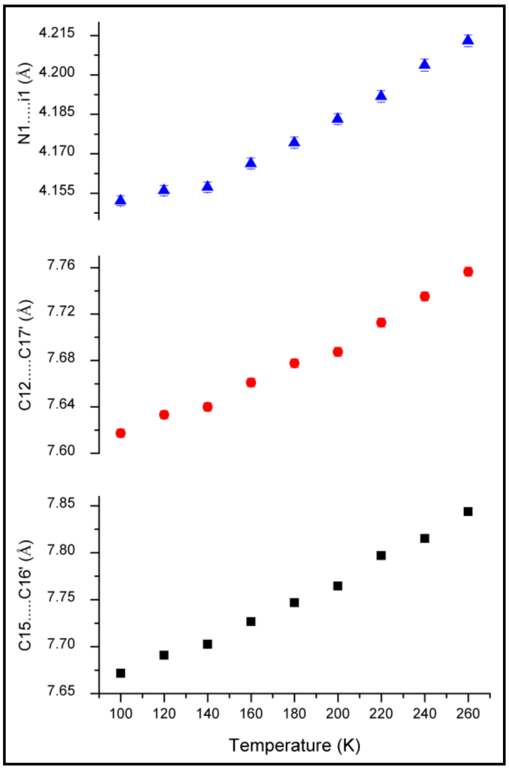

Figure S7. Variation of non-bonding distances (including standard deviations) upon change in temperature.

Single Crystal X-ray Diffraction (SCD)

Experimental

Single crystal X-ray diffraction data were collected on a Bruker APEX-II Quasar CCD area-detector diffractometer equipped with an Oxford Cryosystems Cryostream 700Plus cryostat. A multilayer monochromator with $\mathrm{Mo}_{K\alpha}$ radiation (λ = 0.71073 Å) from an Incoatec $I_{\mu S}$ microsource was used.

Data reduction was carried out by means of standard procedures using the Bruker software package SAINT[4] and absorption corrections and the correction of other systematic errors were performed using SADABS.[5] The structures were solved by direct methods using SHELXS-97 and refined using SHELXL-97.[6] X-Seed[5] was used as the graphical interface for the SHELX program suite. Hydrogen atoms were placed in calculated positions using riding models.

TableS1. Crystallographic details

Temperature (K)	**100**	**120**	**140**	**160**	**180**
Empirical formula	$C_{53}H_{58}N_7O_{19}Cd_2$	$C_{53}H_{58}N_7O_{19}Cd_2$	$C_{53}H_{58}N_7O_{19}Cd_2$	$C_{53}H_{58}N_7O_{19}Cd_2$	$C_{53}H_{58}N_7O_{19}Cd_2$
Formula weight	1321.86	1321.86	1321.86	1321.86	1321.86
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$

a, (Å)	10.2799(17)	10.2807(14)	10.2788(14)	10.2786(10)	10.2817(10)
b, (Å)	12.1045(14)	12.1039(16)	12.0994(16)	12.0962(12)	12.0978(12)
c, (Å)	12.4903(21)	12.5241(16)	12.5513(17)	12.5872(13)	12.6236(13)
α, (°)	75.549(2)	75.460(2)	75.381(2)	75.267(1)	75.159(1)
β, (°)	76.872(2)	76.810(2)	76.749(2)	76.684(1)	76.657(1)
γ, (°)	88.226(2)	88.243(2)	88.243(2)	88.232(1)	88.223(2)
Volume (Å^3)	1465.2(4)	1468.2(3)	1469.6(3)	1472.2(3)	1476.2(3)
Z	1	1	1	1	1
Calculated density (g cm^{-3})	1.498	1.495	1.494	1.491	1.487
Absorption coefficient (mm^{-1})	0.803	0.801	0.800	0.799	0.797
F_{000}	673	673	673	673	673
Approx. Crystal size (mm^3)	0.114×0.198×0.605	0.114×0.198×0.606	0.114×0.198×0.608	0.114×0.198×0.610	0.113×0.198×0.611
θ range for data collection (º)	1.73 to 26.10	1.73 to 26.09	1.72 to 26.08	1.72 to 26.09	1.72 to 26.08
Miller index ranges	$-12 \le h \le 12, -14 \le k \le 14, -14 \le l \le 15$	$-12 \le h \le 12, -14 \le k \le 14, -14 \le l \le 15$	$-12 \le h \le 12, -14 \le k \le 14, -14 \le l \le 15$	$-12 \le h \le 12, -14 \le k \le 14, -14 \le l \le 15$	$-12 \le h \le 12, -14 \le k \le 14, -14 \le l \le 15$
Reflections collected	12840	12959	12990	13075	13056
Independent reflections	5762 [R_{int} = 0.0289]	5793 [R_{int} = 0.0272]	5795 [R_{int} = 0.0262]	5821 [R_{int} = 0.0265]	5828 [R_{int} = 0.0268]
Completeness to $\theta_{\max}$ (%)	99.0	99.4	99.4	99.5	99.4
Max. and min. transmission	0.9141 and 0.6423	0.9142 and 0.6424	0.9143 and 0.6419	0.9144 and 0.6415	0.9144 and 0.6415
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5762 / 4 / 440	5793 / 4 / 441	5795 / 4 / 446	5821 / 4 / 441	5828 / 4 / 449
Goodness-of-fit on F^2	1.040	1.053	1.065	1.006	1.045
Final *R* indices [$I > 2\sigma(I)$]]	$R1$ = 0.0269, $wR2$ = 0.0692	$R1$ = 0.0264, $wR2$ = 0.0650	$R1$ = 0.0261, $wR2$ = 0.0643	$R1$ = 0.0272, $wR2$ = 0.0710	$R1$ = 0.0271, $wR2$ = 0.0658
R indices (all data)	$R1$ = 0.0291, $wR2$ = 0.0707	$R1$ = 0.0287, $wR2$ = 0.0664	$R1$ = 0.0284, $wR2$ = 0.0657	$R1$ = 0.0295, $wR2$ = 0.0727	$R1$ = 0.0296, $wR2$ = 0.0673
Largest diff. peak and hole (e Å^{-3})	0.651 and -0.507	0.580 and -0.470	0.565 and -0.562	0.596 and -0.610	0.577 and -0.404
CCDC number	984355	984356	984357	984358	984359

Temperature (K)	**200**	**220**	**240**	**260**	**100-R**
Empirical formula	$C_{53}H_{58}N_7O_{19}Cd_2$	$C_{53}H_{58}N_7O_{19}Cd_2$	$C_{53}H_{58}N_7O_{19}Cd_2$	$C_{53}H_{58}N_7O_{19}Cd_2$	$C_{53}H_{58}N_7O_{19}Cd_2$
Formula weight	1321.86	1321.86	1321.86	1321.86	1321.86
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, (Å)	10.2804(9)	10.2816(9)	10.2837(10)	10.2835(13)	10.2731(6)
b, (Å)	12.0976(11)	12.0994(10)	12.1048(12)	12.1107(15)	12.1111(7)
c, (Å)	12.6532(11)	12.6836(11)	12.7112(13)	12.7326(16)	12.4854(7)
α, (°)	75.021(1)	74.861(1)	74.721(1)	74.590(2)	75.519(1)
β, (°)	76.614(1)	76.591(1	76.586(2)	76.545(2)	76.822(1)
γ, (°)	88.221(1)	88.222(1)	88.227(2)	88.255(2)	88.265(1)
Volume (Å^3)	1478.2(2)	1480.8(2)	1484.0(3)	1485.9(3)	1463.9(2)
Z	1	1	1	1	1
Calculated density (g cm^{-3})	1.485	1.482	1.479	1.477	1.499
Absorption coefficient (mm^{-1})	0.796	0.794	0.792	0.791	0.803
F_{000}	673	673	673	673	673
Approx. Crystal size (mm^3)	0.113×0.198×0.612	0.113×0.199×0.614	0.112×0.199×0.615	0.112×0.199×0.617	0.114×0.198×0.605
θ range for data collection (º)	1.73 to 26.10	1.71 to 26.02	1.71 to 26.03	1.71 to 26.37	1.73 to 26.05
Miller index ranges	$-12 \le h \le 12, -14 \le k \le 14, -14 \le l \le 15$	$-12 \le h \le 12, -14 \le k \le 14, -14 \le l \le 15$	$-12 \le h \le 12, -14 \le k \le 14, -15 \le l \le 15$	$-12 \le h \le 12, -15 \le k \le 15, -15 \le l \le 15$	$-12 \le h \le 12, -14 \le k \le 14, -15 \le l \le 15$

Reflections collected	13055	13046	13102	13453	17032
Independent reflections	5817 [$R_{\mathrm{int}} = 0.0255$]	5808 [$R_{\mathrm{int}} = 0.0240$]	5822 [$R_{\mathrm{int}} = 0.0246$]	6028 [$R_{\mathrm{int}} = 0.0264$]	6028 [$R_{\mathrm{int}} = 0.0246$]
Completeness to θ_{max} (%)	99.5	99.4	99.4	99.4	99.9
Max. and min. transmission	0.9155 and 0.6417	0.9156 and 0.6413	0.9165 and 0.6414	0.9166 and 0.6409	0.9140 and 0.6421
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5817 / 4 / 441	5808 / 5 / 449	5822 / 5 / 443	6028 / 4 / 430	5791 / 4 / 440
Goodness-of-fit on F^2	1.007	1.043	1.067	1.037	1.070
Final R indices [$I > 2\sigma(I)$]]	$R1 = 0.0270$, $wR2 = 0.0702$	$R1 = 0.0270$, $wR2 = 0.0660$	$R1 = 0.0279$, $wR2 = 0.0681$	$R1 = 0.0300$, $wR2 = 0.0725$	$R1 = 0.0207$, $wR2 = 0.0522$
R indices (all data)	$R1 = 0.0297$, $wR2 = 0.0722$	$R1 = 0.0300$, $wR2 = 0.0679$	$R1 = 0.0311$, $wR2 = 0.0699$	$R1 = 0.0342$, $wR2 = 0.0752$	$R1 = 0.0219$, $wR2 = 0.0530$
Largest diff. peak and hole (e Å^{-3})	0.613 and -0.472	0.503 and -0.428	0.508 and -0.380	0.511 and -0.406	0.586 and -0.357
CCDC number	984360	984361	984362	984363	984364

Details about the refinement of the SCD structures:

For all structures the hydrogen atom of the water molecules were fixed using DFIX and DANG refinement. The disorder of the lattice DMF molecules was modelled in all of the structures.

Structural Analysis

All the non-bonding distances and angles were measured using the program X-Seed.[7]

TableS2. Unit cell axes and crystal volume at variable temperatures for **1**.

	Unit cell parameters								
T **(K)**	***a*** **(Å)**	**St. dev.***	***b*** **(Å)**	**St. dev.***	***c*** **(Å)**	**St. dev. ***	**Cell volume (Å^3)**	**St. dev. ***	**Crystal mosaicity**
100	10.2799	0.0017	12.1045	0.0021	12.4903	0.0021	1465.2	4	0.64
120	10.2807	0.0014	12.1039	0.0016	12.5241	0.0016	1468.2	3	0.63
140	10.2788	0.0014	12.0994	0.0016	12.5513	0.0017	1469.6	3	0.63
160	10.2786	0.0010	12.0962	0.0012	12.5872	0.0013	1472.2	3	0.63
180	10.2817	0.0010	12.0978	0.0012	12.6236	0.0013	1476.2	3	0.65
200	10.2804	0.0009	12.0976	0.0011	12.6532	0.0011	1478.2	2	0.66
220	10.2821	0.0009	12.0999	0.0010	12.6842	0.0011	1480.8	2	0.66
240	10.2837	0.0010	12.1048	0.0012	12.7112	0.0013	1484.0	3	0.68
260	10.2835	0.0013	12.1107	0.0015	12.7326	0.0016	1485.9	3	0.66
100-R	10.2731	0.0006	12.1111	0.0007	12.4854	0.0007	1463.9	2	0.64

*Standard deviation calculated from unit cell refinement using the Apex II software suite.

TableS3. Unit cell axes and crystal volume at variable temperatures for **1**.

	Unit cell parameters					
T **(K)**	***α*** **(°)**	**St. dev.***	***β*** **(°)**	**St. dev.***	***γ*** **(°)**	**St. dev. ***
100	75.549	0.002	76.872	0.002	88.226	0.002
120	75.462	0.002	76.81	0.002	88.243	0.002
140	75.381	0.002	76.749	0.002	88.243	0.002
160	75.267	0.001	76.684	0.001	88.232	0.001
180	75.159	0.001	76.657	0.001	88.223	0.001
200	75.021	0.002	76.614	0.001	88.221	0.001
220	74.861	0.001	76.591	0.001	88.222	0.001
240	74.721	0.001	76.586	0.002	88.227	0.002
260	74.590	0.002	76.545	0.002	88.225	0.002
100-R	75.519	0.001	76.822	0.001	88.265	0.001

*Standard deviation calculated from unit cell refinement using the Apex II Data collection software suite.

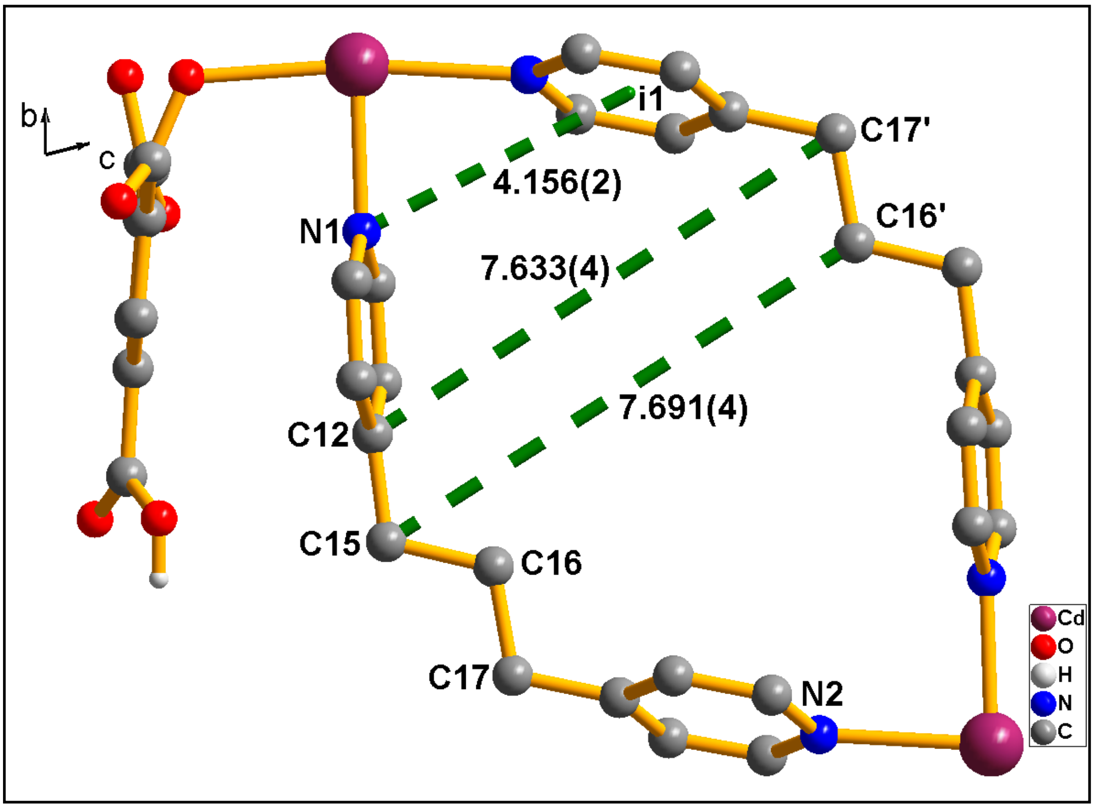

Figure S8. Diagram showing selected non-bonding distances within the macrocyclic unit in **1** at 120 K.

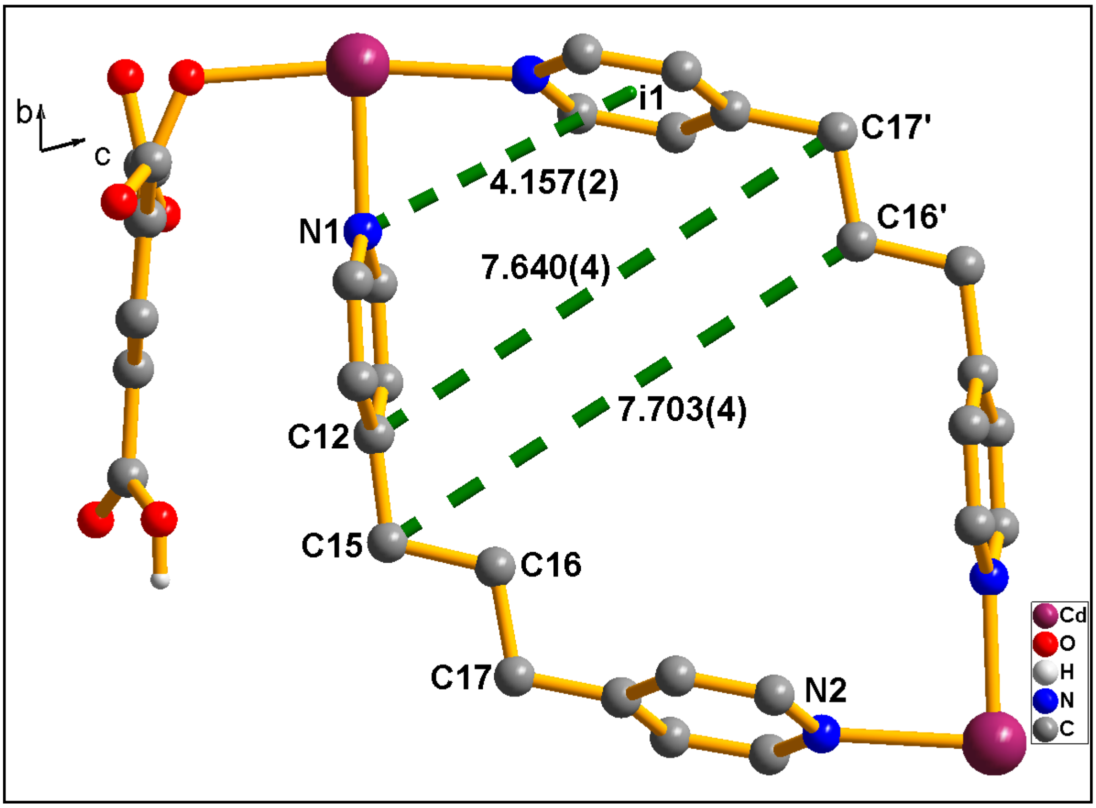

Figure S9. Diagram showing selected non-bonding distances within the macrocyclic unit in **1** at 140 K.

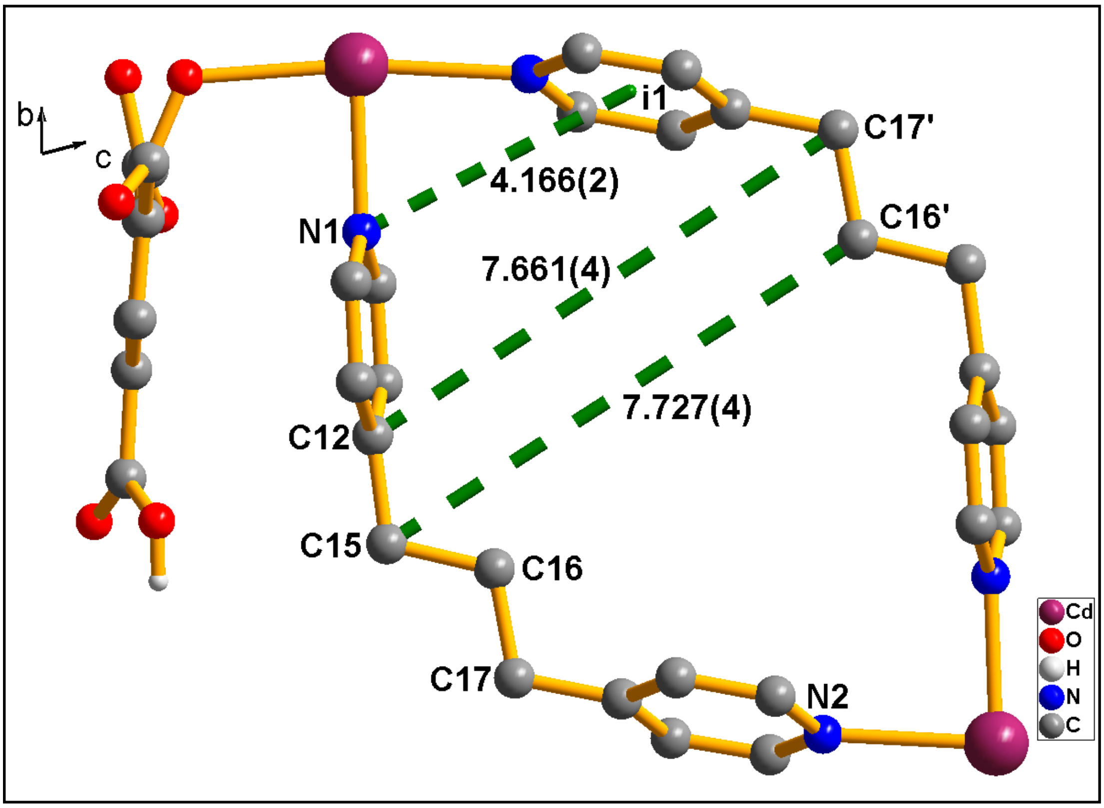

Figure S10. Diagram showing selected non-bonding distances within the macrocyclic unit in **1** at 160 K.

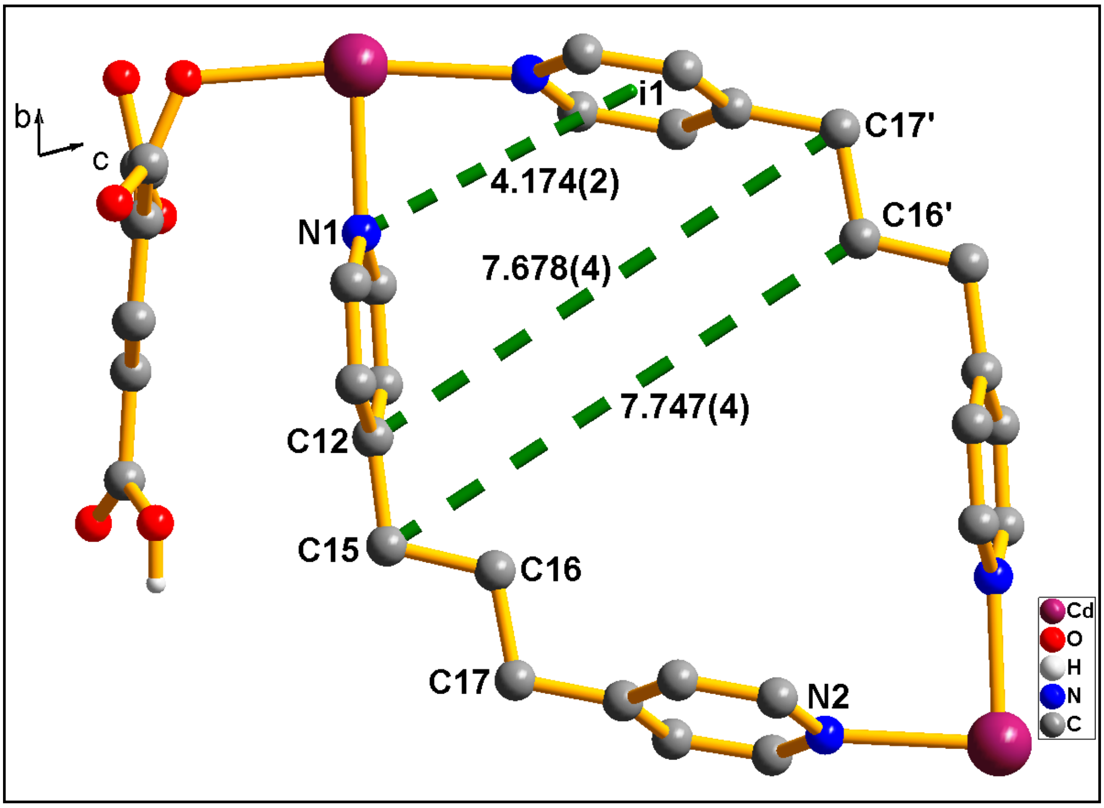

Figure S11. Diagram showing selected non-bonding distances within the macrocyclic unit in **1** at 180 K.

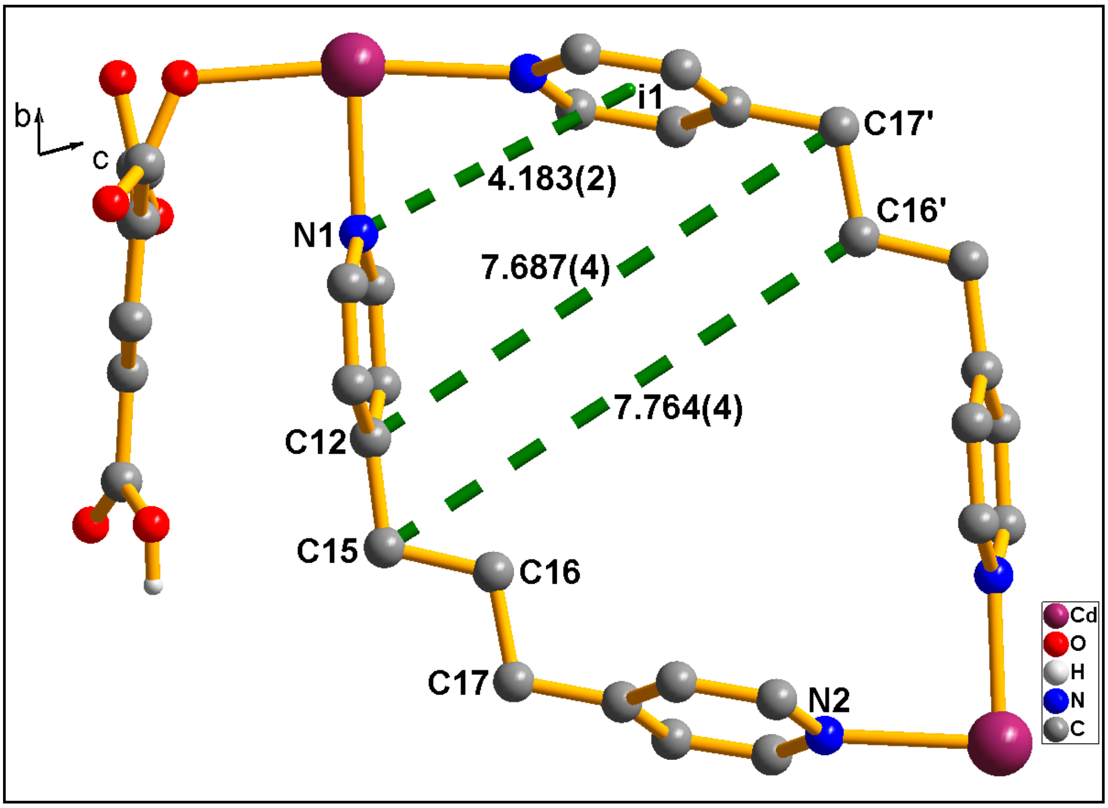

Figure S12. Diagram showing selected non-bonding distances within the macrocyclic unit in **1** at 200 K.

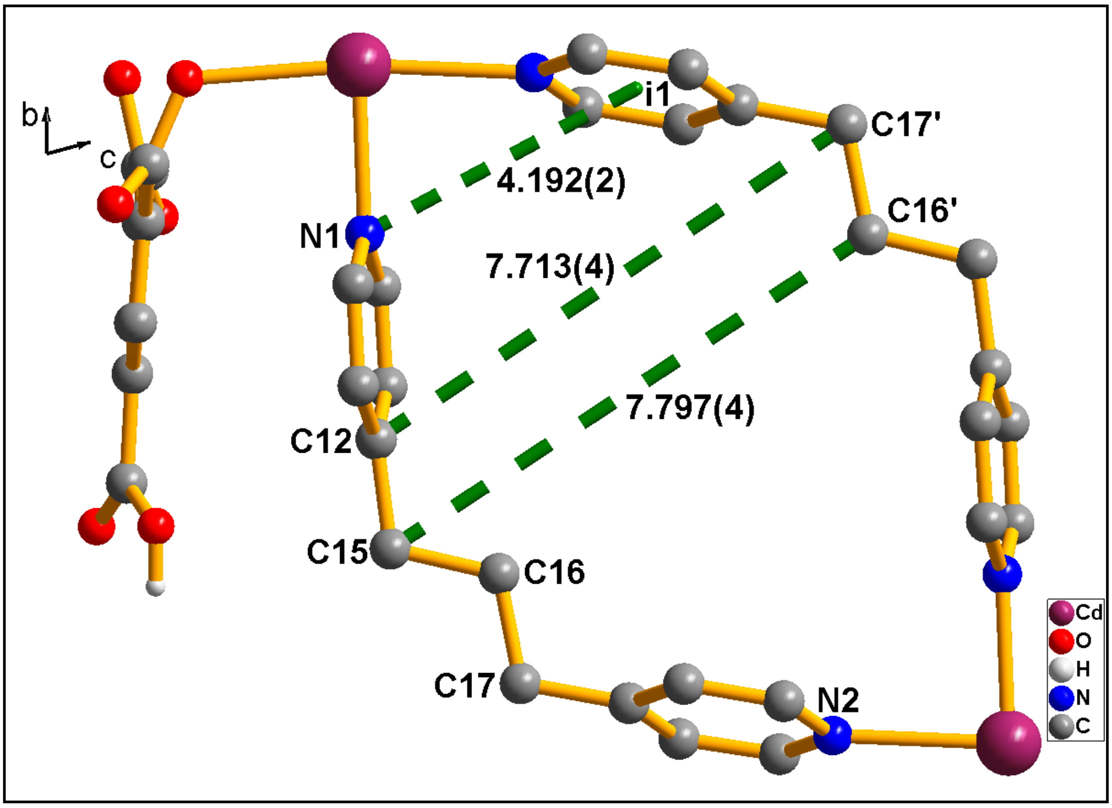

Figure S13. Diagram showing selected non-bonding distances within the macrocyclic unit in **1** at 220 K.

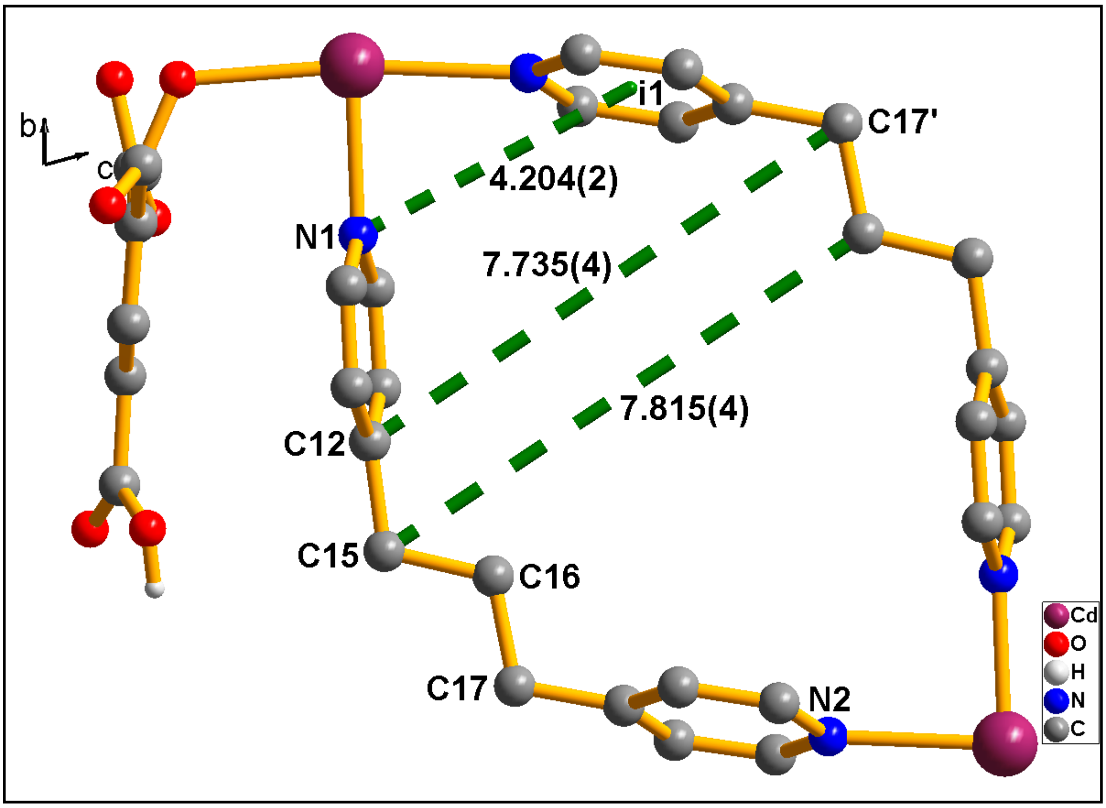

Figure S14. Diagram showing selected non-bonding distances within the macrocyclic unit in **1** at 240 K.

TableS4. List of hydrogen-bonding distances and angles between the lattice water molecules and carboxylate/carboxylic acid groups in **1** at 100 K and 260 K.

	O6-H6A… O1W		**O2W-H1W2… O3**	
	100 K	**260 K**	**100 K**	**260 K**
d(D-H)	0.840(2)	0.820(2)	0.899(2)	0.846(2)
d(H..A)	1.741(2)	1.772(2)	1.893(2)	1.982(2)
d(D..A)	2.572(2)	2.582(3)	2.792(2)	2.802(3)
<DHA	169.7(1)	169.0(2)	178.3(1)	163.2(2)

Powder X-ray Diffraction (PXRD)

To ascertain whether the anomalous thermal expansion observed in a single crystal also manifests in the bulk material, PXRD patterns of **1** were measured at various temperatures (Figures 6 and S16). Experiments were carried out on a PANalytical X'Pert PRO instrument with Bragg-Brentano geometry. Intensity data were collected using an X'Celerator detector and 2θ scans in the range of 5-40° were performed. During the experiment the powdered sample was exposed to Cu-K_α radiation (λ = 1.5418 Å). The sample was sealed within a glass capillary and the capillary spinner configuration (with focusing mirror) of the instrument was used since this setup allows for very accurate temperature control using an Oxford Cryostream Plus cryostat.

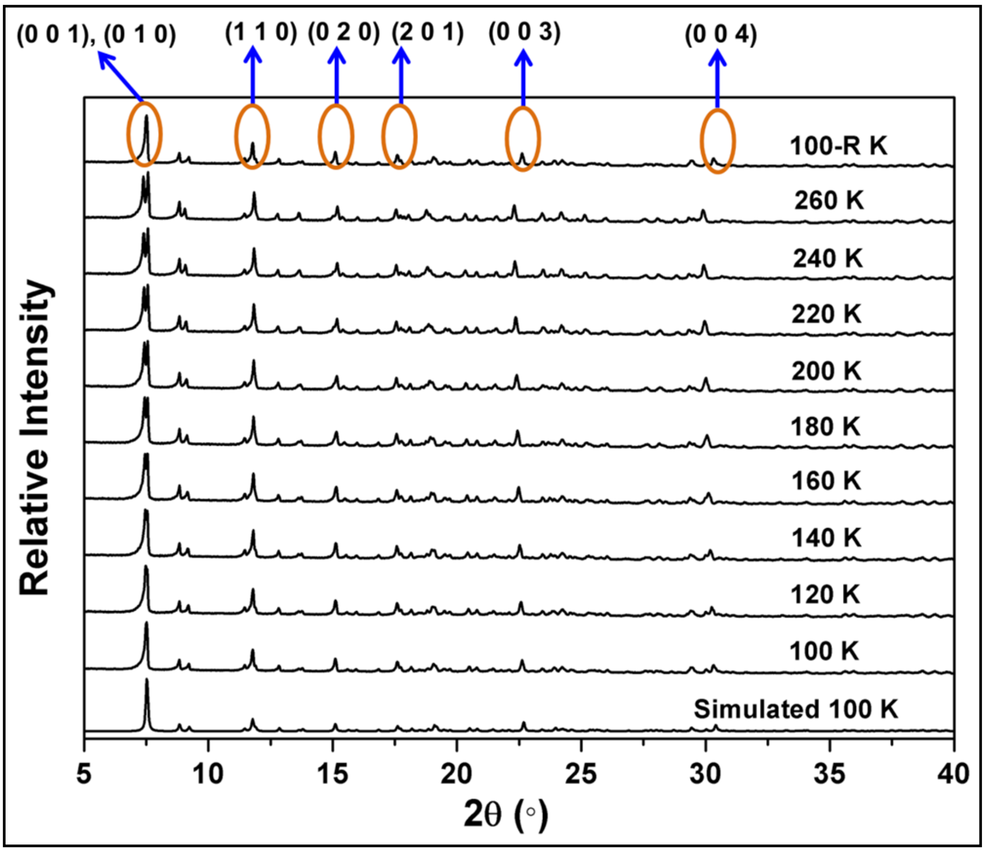

Figure S15. The simulated and measured PXRD patterns of **1** in the temperature range 100-260 K.

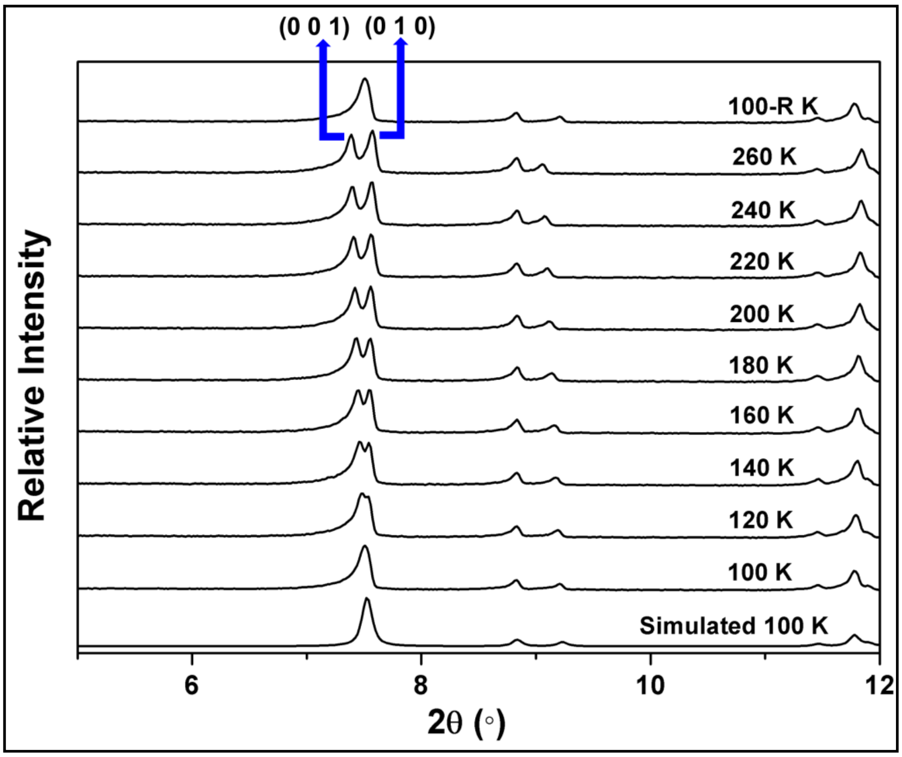

Figure S16. The simulated and measured PXRD patterns, magnified by plotting the range; 2θ = 5° to 12° only.

Differential scanning calorimetry analysis

Differential scanning calorimetry (DSC) measurement was carried out at the heating rate of 10 ^{o}C min^{-1} in the temperature range of 100-260 K, under nitrogen flow of 50 mL min^{-1} on a DSC Q100 instrument. 3.22 mg of sample was placed in an aluminum pan with a lid. An empty sealed pan was used as a reference.

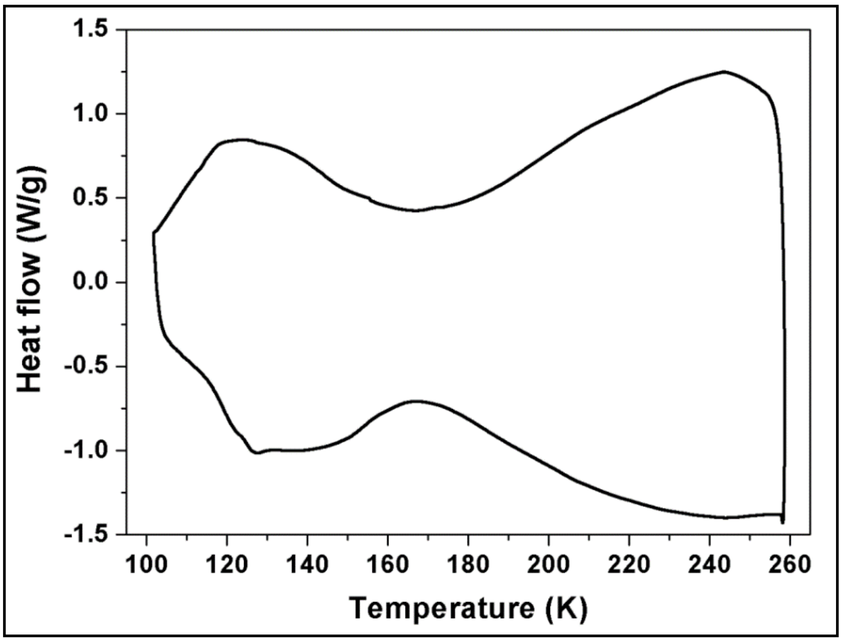

Figure S17. Differential scanning calorimetric thermogram of **1** in the temperature range 100-260 K.

Thermogravimetric analysis

The TGA trace was obtained using a TA Instruments Q500 thermogravimetric analyser. The sample was heated at 10 °C min^{-1}, Figure S17.

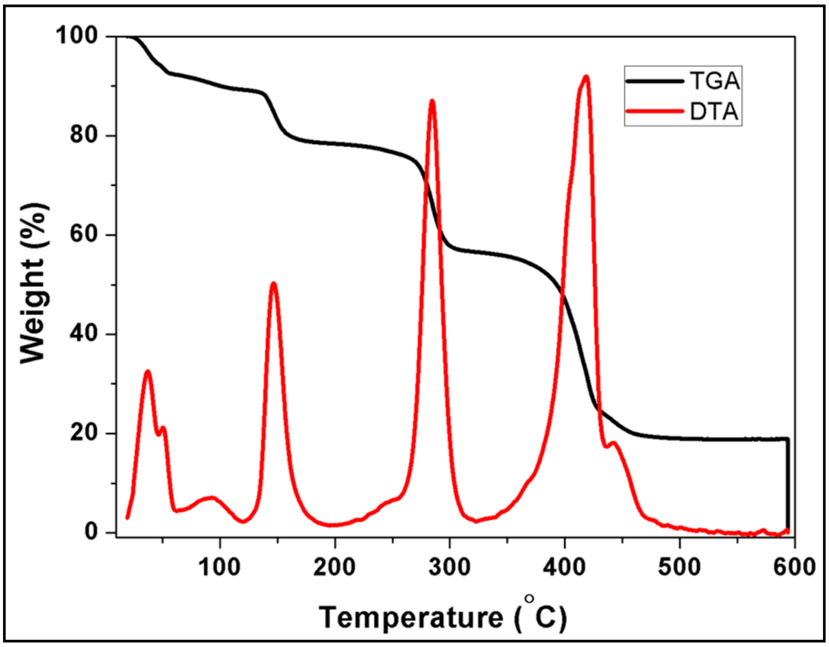

Figure S18. Thermogravimetric analysis of **1**.

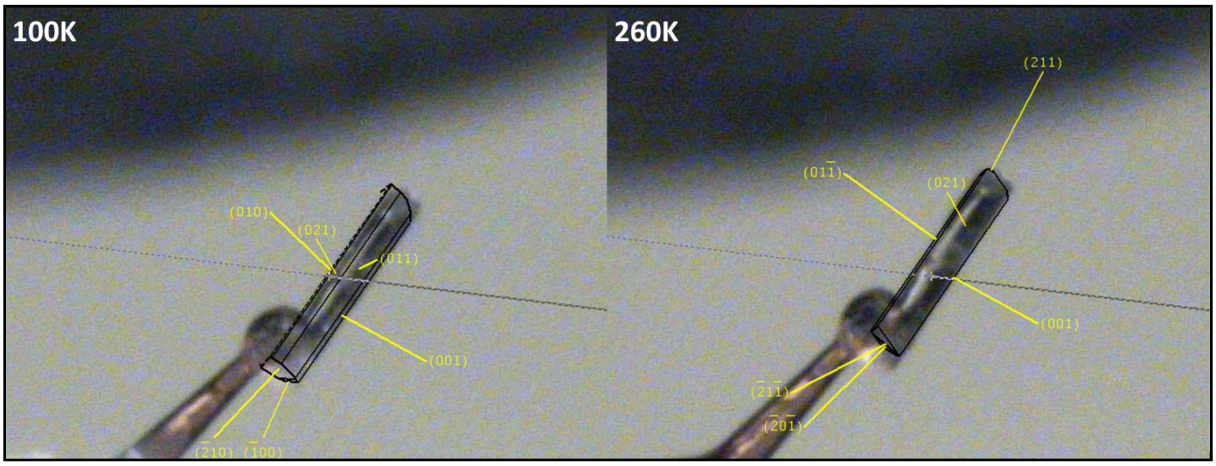

Figure S19. Face-indexing of **1** at 100 K and 260 K using the APEX II software suite. At 100 K and 260 K the crystal dimensions are 0.093 x 0.273 x 0.605 mm and 0.095 x 0.273 x 0.606 mm, respectively.

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*****************************************************************************************

                                STRAIN PROGRAM

                          VERSION 4.11 - RJA NOV 2011

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********************OUTPUT FROM CALCULATION NO.   1 ******************************


CELL PARAMETERS

BEFORE  10.27990  12.10450  12.49030  75.54900  76.87200  88.22600  AT P =   0.000 AND T =  100.00

ESD   0.00170   0.00210   0.00210   0.00200   0.00200   0.00200          0.000          2.00


AFTER   10.28350  12.11070  12.73260  74.59000  76.54500  88.22500  AT P =   0.000 AND T =  260.00

ESD   0.00130   0.00150   0.00160   0.00200   0.00200   0.00200          0.000          2.00


RECIPROCAL CELL PARAMETERS

BEFORE   0.09992   0.08534   0.08489 104.42712 103.10162  88.43700

AFTER    0.10004   0.08570   0.08377 105.42285 103.46980  88.11414


CARTESIAN AXES SET WITH X//A* AND Z//C: IRE CONVENTION

ANGLES BETWEEN XYZ AND ABC SYSTEMS

FOR LAGRANGIAN STRAINS TO CELL 1
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          +A      +B      +C

+X    13.22   90.00   90.00

+Y    91.52   14.45   90.00

+Z    76.87   75.55    0.00

FOR EULERIAN STRAINS TO CELL 2

          +A      +B      +C

+X    13.58   90.00   90.00

+Y    91.83   15.41   90.00

+Z    76.54   74.59    0.00

 S-MATRICES FOR INITIAL AND FINAL CELLS:

10.00751  -0.27307   2.33485          9.99583  -0.32913   2.39278

0.00000  11.72153   3.02070          0.00000  11.67531   3.21811

0.00000   0.00000  12.49030          0.00000   0.00000  12.73260


FINITE EULERIAN STRAIN TENSOR BASED ON XYZ          THERMAL EXPANSION TENSOR VALUES MULTIPLIED BY 10**1

      -0.001150     -0.002848      0.000828          -0.000072     -0.000178      0.000052

      -0.002848     -0.003883      0.005942          -0.000178     -0.000243      0.000371

       0.000828      0.005942      0.019211           0.000052      0.000371      0.001201


ESTIMATED STANDARD DEVIATIONS FROM UNIT CELL AND INTENSIVE VARIABLE ESDS

0.000207      0.000028      0.000044            0.000013      0.000004      0.000003

0.000028      0.000214      0.000046            0.000004      0.000014      0.000007

0.000044      0.000046      0.000210            0.000003      0.000007      0.000025


PRINCIPAL STRAIN    ESD   PROPERTY    ESD    ANGLES TO  +X        +Y          +Z          +A          +B          +C

-0.006860   0.000161  -0.000043   0.000001      62.6( 1.0)   30.4( 0.8)  102.2( 0.2)   68.2( 1.0)   39.2( 0.6)  102.2( 0.2)

0.000387    0.000174   0.000002  0.000001     152.6( 0.9)   63.3( 0.9)   95.9( 0.3)  154.3( 0.8)   66.1( 0.7)   95.9( 0.3)

0.020651    0.000187   0.000129  0.000003      89.6( 0.2)   76.4( 0.3)   13.6( 0.3)   77.0( 0.1)   61.0( 0.3)   13.6( 0.3)
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