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Supplementary information

Chains or grids of cadmium(II) helicates?

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S.1. Materials

All solvents, 1,3-diacetylbenzene, 4-N-methyl-thiosemicarbazone and the cadmium plate are commercially available and were used without further purification.

S.2 Physical Measurements

Elemental analyses of C, H and N were performed on a Carlo Erba EA 1108 analyser. ^{1}H NMR spectra were recorded on Bruker DPX-250 and Varian Inova 500 spectrometers, using DMSO-d_6 as solvent. ^{113}Cd NMR spectrum was recorded on a Bruker AMX-500 spectrometer, using DMSO-d_6 as solvent. Chemical shifts are expressed relative to tetramethylsilane (^{1}H NMR) and 0.1 M $Cd(ClO_4)_2$ (^{113}Cd NMR) as external reference. Infrared spectra were measured with KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000-600 cm^{-1}. Electrospray ionization (ESI) mass spectra were registered on an API4000 Applied Biosystems mass spectrometer. Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-TOF) mass spectra were registered on a Bruker Autoflex spectrometer using DCTB as matrix. Molar conductivity value was obtained at 25 °C from a 10^{-3} M solution in acetone on a Crison micro CM 2200.

S.3. Synthesis

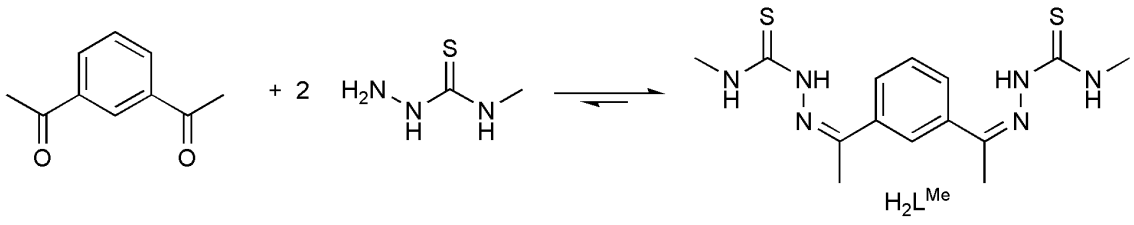

Chart S1

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S.3.1. Synthesis of H_2L^{Me}

The ligand *bis*(4-N-methylthiosemicarbazone)-1,3-diacetylbenzene (H_2L^{Me}), has been synthesized following the published procedure (Chart S1).[1]

S.3.2. Synthesis of $[Cd_2(L^{Me})_2]$ (**1**)

1 was obtained by means of an electrochemical methodology [2,3] An acetonitrile solution of the ligand H_2L^{Me}, in the presence of a supporting electrolyte, was electrolyzed using a platinum wire as cathode and a cadmium plate as anode. The cell can be summarised as: Pt(–)|H_2L^{Me} + MeCN|Cd(+).

A solution of the ligand (0.1 g, 0.19 mmol) in acetonitrile (80 cm^3), containing 10 mg of tetraethylammonium perchlorate (CAUTION: although no problem has been encountered in this work, all perchlorate compounds are potentially explosive, and should be handled in small quantities and with great care), was electrolyzed for 96 minutes using a current of 10 mA. The resulting pale yellow solid was filtered off, washed with diethyl ether and dried *in vacuo*.

The complex, $[Cd_2(L^{Me})_2]$ (**1**), was characterised by elemental analysis, mass spectrometry (ESI, MALDI-TOF), ^1H and ^{113}Cd NMR, infrared spectroscopy and magnetic and conductivity measurements. Recrystallization in DMSO allow us to obtain colourless crystals of $[Cd_2(L^{Me})_2]$·DMSO (**1**·DMSO) , studied by X-ray diffraction.

$Cd_2(L^{Me})_2$ (**1**): Yield: 0.12 g (95%). Anal. $Cd_2C_{28}H_{36}N_{12}S_4$ requires: C, 37.5; H, 4.4; N, 18.7; S, 14.2. Found: C, 37.2; H, 4.0; N, 18.6; S, 14.2. MS ESI (m/z) 445.2 $[ML+H]^+$, 785.1 $[ML_2+H]^+$, 894.0 $[M_2L_2]^+$; MS MALDI-TOF (m/z) 895.0 $[M_2L_2+ H]$;^1H NMR δ_H(DMSO-d_6): 8.30 (s, 1H), 7.57 (d, 2H, J= 7.9 Hz), 7.47 (m, 1H, J= 7.9 Hz), 6.74 (c, 1H, J= 4.4 Hz), 2.74 (d, 6H, J= 4.4 Hz), 2.42 (s, 6H); ^{113}Cd NMR (DMSO-d_6): δ 559.4 ppm; IR (KBr, cm^{-1}): ν(NH) 3339 (m), 3304 (m), ν(C=N+C-N) 1554 (w), 1497 (s), 1483 (s), ν(C=S) 1101 (w), 802 (w), ν(N-N) 1055 (w); Λ_M ($\mu S \cdot cm^2$)= 3.1.

S.4. X-Ray Crystallographic Studies

Crystals of **1**·DMSO**,** suitable for X-ray diffraction studies, were ground in DMSO. Crystallographic data were collected on a Bruker Appex-II CCD Diffractometer, using graphite-monocromated *Mo-*K_α radiation (λ = 0.71073 Å) from a fine focus sealed tube source. The structures were solved by direct methods[4] and finally refined by full-matrix,

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least-squares based on F^2 by SHELXL.[5] An empirical absorption correction was applied using SADABS.[6] All non-hydrogen atoms were anisotropically refined and the hydrogen atoms positions were included in the model by electronic density or were geometrically calculated and refined using a riding model.

Bond distances and angles are summarized in Tables S1 and S2, while hydrogen bond parameters are listed in Table S3.

CCDC 869388 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via ww.ccdc.cam.ac.uk/data_request.cif.

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Table S1 Bond lengths (Å) for $[Cd_2(L^{Me})_2]$·DMSO (**1**·DMSO)

Bond lengths (Å)			
C(1)-N(1)	1.454(3)	C(11)-H(11C)	0.98
C(1)-H(1A)	0.98	C(12)-N(4)	1.293(3)
C(1)-H(1B)	0.98	C(13)-N(5)	1.314(3)
C(1)-H(1C)	0.98	C(13)-N(6)	1.346(3)
C(2)-N(2)	1.310(3)	C(13)-S(2)	1.763(3)
C(2)-N(1)	1.347(3)	C(14)-N(6)	1.456(4)
C(2)-S(1)	1.755(3)	C(14)-H(14A)	0.98
C(3)-C(4)	1.500(3)	C(14)-H(14B)	0.98
C(3)-H(3A)	0.98	C(14)-H(14C)	0.98
C(3)-H(3B)	0.98	C(15)-S(3)	1.764(3)
C(3)-H(3C)	0.98	C(15)-H(15A)	0.98
C(4)-N(3)	1.301(3)	C(15)-H(15B)	0.98
C(4)-C(5)	1.479(3)	C(15)-H(15C)	0.98
C(5)-C(10)	1.388(3)	C(16)-S(3)	1.777(3)
C(5)-C(6)	1.400(3)	C(16)-H(16A)	0.98
C(6)-C(7)	1.389(4)	C(16)-H(16B)	0.98
C(6)-H(6)	0.95	C(16)-H(16C)	0.98
C(7)-C(8)	1.384(4)	N(1)-H(1N)	0.77(3)
C(7)-H(7)	0.95	N(2)-N(3)	1.391(3)
C(8)-C(9)	1.396(3)	N(3)-Cd(1)	2.320(2)
C(8)-H(8)	0.95	N(4)-N(5)	1.387(3)
C(9)-C(10)	1.390(3)	N(4)-Cd(1)#1	2.298(2)
C(9)-C(12)	1.485(3)	N(6)-H(6N)	0.81(3)
C(10)-H(10)	0.95	S(1)-Cd(1)	2.4430(7)
C(11)-C(12)	1.496(3)	S(2)-Cd(1)#1	2.4694(7)
C(11)-H(11A)	0.98	S(3)-O(1)	1.500(2)
C(11)-H(11B)	0.98	Cd(1)-N(4)#1	2.298(2)
		Cd(1)-S(2)#1	2.4694(7)
Symmetry transformations: #1 -x+3/2,y,-z+1			

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Table S2 Bond angles (°) for $[Cd_2(L^{Me})_2]$·DMSO (**1**·DMSO)

Bond Angles (º)			
N(1)-C(1)-H(1A)	109.5	N(5)-C(13)-S(2)	129.79(19)
N(1)-C(1)-H(1B)	109.5	N(6)-C(13)-S(2)	114.3(2)
H(1A)-C(1)-H(1B)	109.5	N(6)-C(14)-H(14A)	109.5
N(1)-C(1)-H(1C)	109.5	N(6)-C(14)-H(14B)	109.5
H(1A)-C(1)-H(1C)	109.5	H(14A)-C(14)-H(14B)	109.5
H(1B)-C(1)-H(1C)	109.5	N(6)-C(14)-H(14C)	109.5
N(2)-C(2)-N(1)	115.4(2)	H(14A)-C(14)-H(14C)	109.5
N(2)-C(2)-S(1)	130.7(2)	H(14B)-C(14)-H(14C)	109.5
N(1)-C(2)-S(1)	113.9(2)	S(3)-C(15)-H(15A)	109.5
C(4)-C(3)-H(3A)	109.5	S(3)-C(15)-H(15B)	109.5
C(4)-C(3)-H(3B)	109.5	H(15A)-C(15)-H(15B)	109.5
H(3A)-C(3)-H(3B)	109.5	S(3)-C(15)-H(15C)	109.5
C(4)-C(3)-H(3C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(3A)-C(3)-H(3C)	109.5	H(15B)-C(15)-H(15C)	109.5
H(3B)-C(3)-H(3C)	109.5	S(3)-C(16)-H(16A)	109.5
N(3)-C(4)-C(5)	119.6(2)	S(3)-C(16)-H(16B)	109.5
N(3)-C(4)-C(3)	122.2(2)	H(16A)-C(16)-H(16B)	109.5
C(5)-C(4)-C(3)	118.2(2)	S(3)-C(16)-H(16C)	109.5
C(10)-C(5)-C(6)	117.2(2)	H(16A)-C(16)-H(16C)	109.5
C(10)-C(5)-C(4)	121.5(2)	H(16B)-C(16)-H(16C)	109.5
C(6)-C(5)-C(4)	121.2(2)	C(2)-N(1)-C(1)	122.7(2)
C(7)-C(6)-C(5)	120.6(2)	C(2)-N(1)-H(1N)	117(2)
C(7)-C(6)-H(6)	119.7	C(1)-N(1)-H(1N)	118(2)
C(5)-C(6)-H(6)	119.7	C(2)-N(2)-N(3)	117.6(2)
C(8)-C(7)-C(6)	121.0(2)	C(4)-N(3)-N(2)	113.5(2)
C(8)-C(7)-H(7)	119.5	C(4)-N(3)-Cd(1)	131.03(17)
C(6)-C(7)-H(7)	119.5	N(2)-N(3)-Cd(1)	114.74(15)
C(7)-C(8)-C(9)	119.5(2)	C(12)-N(4)-N(5)	115.9(2)
C(7)-C(8)-H(8)	120.3	C(12)-N(4)-Cd(1)#1	123.42(17)
C(9)-C(8)-H(8)	120.3	N(5)-N(4)-Cd(1)#1	118.61(15)
C(10)-C(9)-C(8)	118.6(2)	C(13)-N(5)-N(4)	115.8(2)
C(10)-C(9)-C(12)	117.9(2)	C(13)-N(6)-C(14)	122.8(2)
C(8)-C(9)-C(12)	123.5(2)	C(13)-N(6)-H(6N)	120(2)
C(5)-C(10)-C(9)	123.0(2)	C(14)-N(6)-H(6N)	116(2)
C(5)-C(10)-H(10)	118.5	C(2)-S(1)-Cd(1)	94.61(9)
C(9)-C(10)-H(10)	118.5	C(13)-S(2)-Cd(1)#1	95.87(9)
C(12)-C(11)-H(11A)	109.5	O(1)-S(3)-C(15)	105.75(14)
C(12)-C(11)-H(11B)	109.5	O(1)-S(3)-C(16)	106.25(15)
H(11A)-C(11)-H(11B)	109.5	C(15)-S(3)-C(16)	97.59(18)
C(12)-C(11)-H(11C)	109.5	N(4)#1-Cd(1)-N(3)	127.85(7)
H(11A)-C(11)-H(11C)	109.5	N(4)#1-Cd(1)-S(1)	119.33(5)
H(11B)-C(11)-H(11C)	109.5	N(3)-Cd(1)-S(1)	81.24(5)

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N(4)-C(12)-C(9)	115.9(2)	N(4)#1-Cd(1)-S(2)#1	79.46(5)
N(4)-C(12)-C(11)	125.1(2)	N(3)-Cd(1)-S(2)#1	125.78(5)
C(9)-C(12)-C(11)	118.9(2)	S(1)-Cd(1)-S(2)#1	129.89(3)
N(5)-C(13)-N(6)	115.9(2)		
Symmetry transformations: #1 -x+3/2,y,-z+1			

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Table S3 Hydrogen bond parameters [Å] for $[Cd_2(L^{Me})_2]$·DMSO (**1**·DMSO)

Parameter	**D–H···A**	**D–H**	**H···A**	**∠DHA**
N6—H6N···O1	3.047(3)	0.81(3)	2.30(3)	154(3)
N1—H1N···O1^{i}	2.867(3)	0.77(3)	2.22(3)	142(3)

Symmetry transformations: (i) x+1/2,+y+1/2,+z+1/2

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S.5 Additional figures

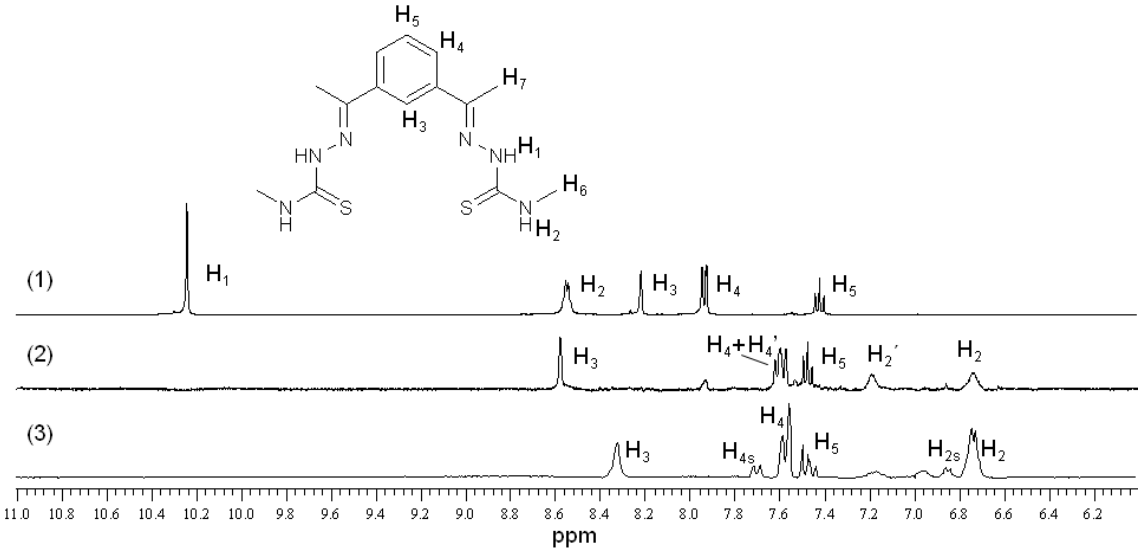

Figure S1 Overlapped aromatic regions of ^{1}H NMR spectra of (1) H_2L^{Me}, (2) $Zn_2(L^{Me})_2$[1] and (3) $Cd_2(L^{Me})_2$ (**1**)

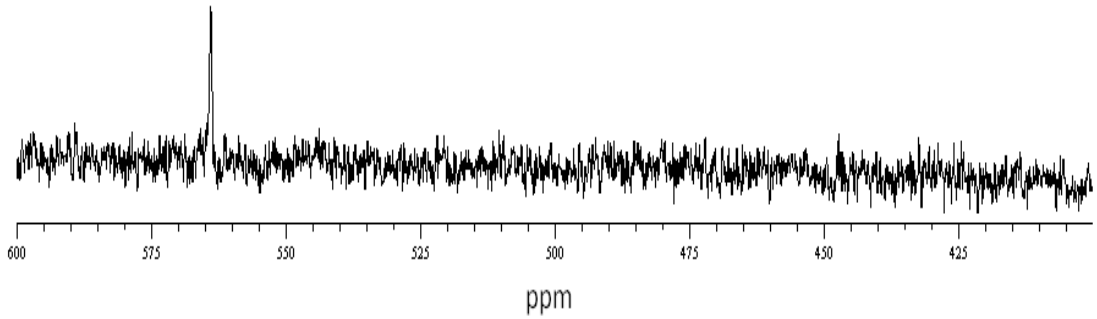

Figure S2. ^{113}Cd NMR (DMSO-d_6) spectrum of complex $Cd_2(L^{Me})_2$ (**1**)

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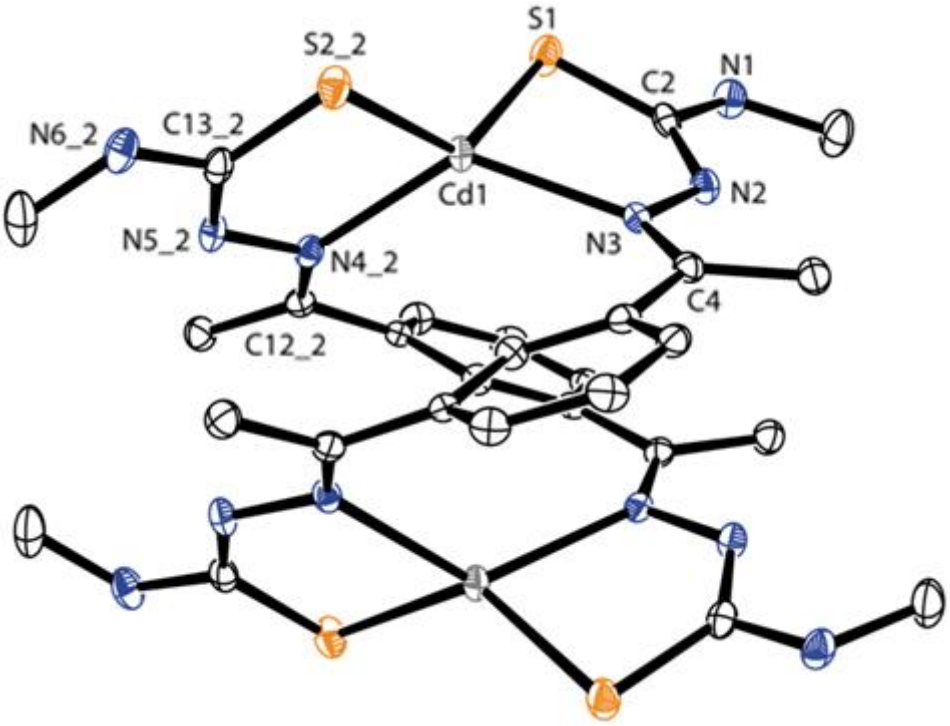

Figure S3 ORTEP representation of $Cd_2(L^{Me})_2$·DMSO (**1**·DMSO)

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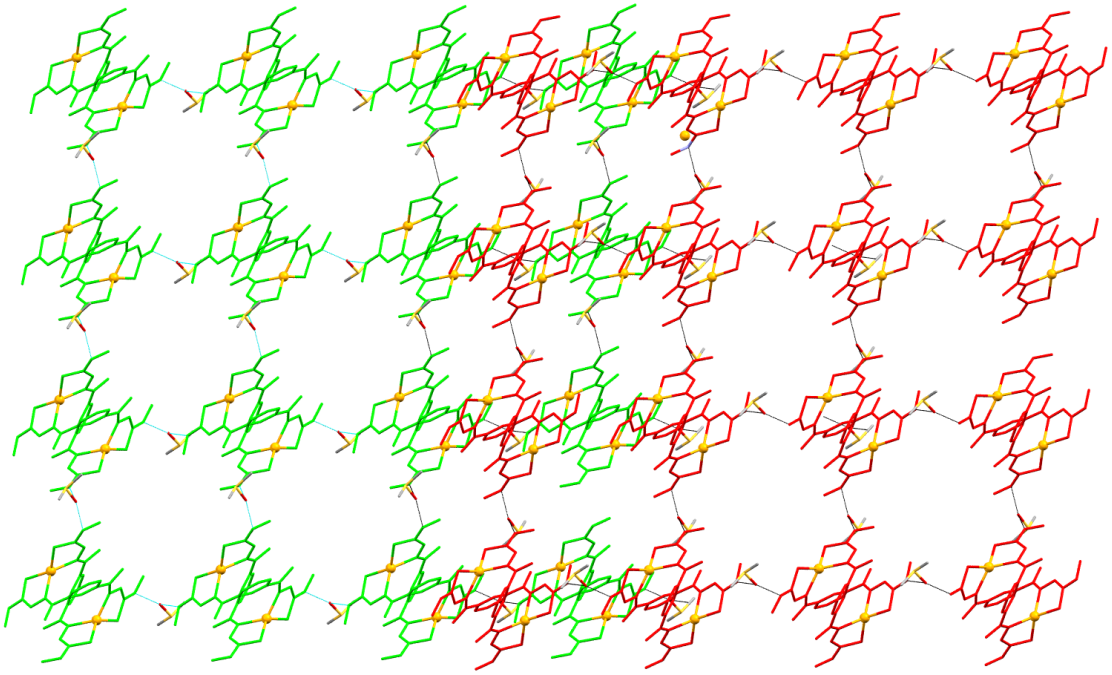

Figure S4 Parallel homochiral layers of grid-of helicates assembled by $Cd_2(L^{Me})_2$·DMSO (**1**·DMSO)

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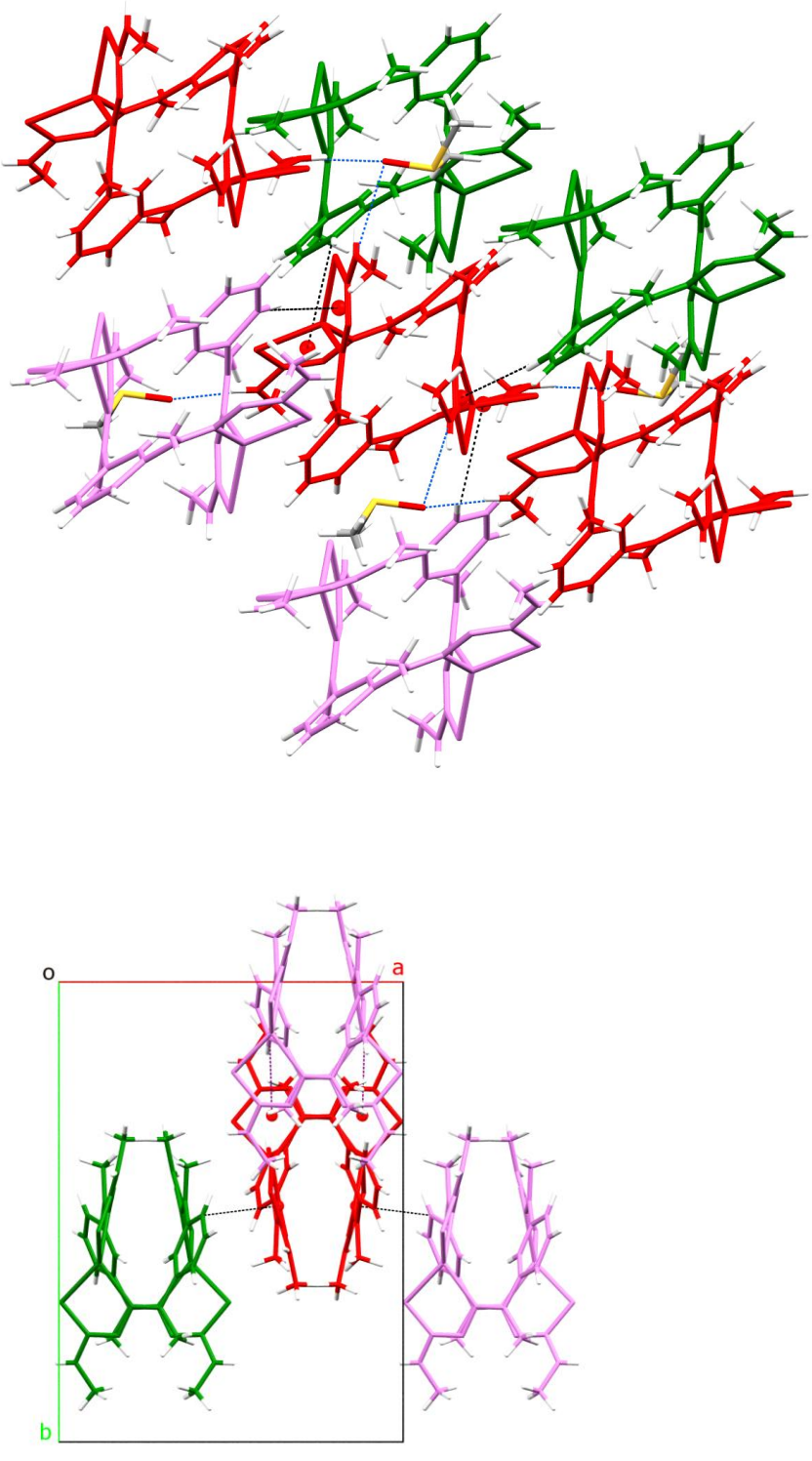

Figure S5 Details of the of the C-H···(CdNNSC) metallacycle interlayer interactions (in green, red and magenta colors) of the grid-of helicates assembled by $Cd_2(L^{Me})_2$·DMSO (**1**·DMSO)

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