Electronic Supplementary Information (ESI)

Spontaneous symmetry breaking of Co(II) metal-organic frameworks from achiral precursors *via* asymmetrical crystallization

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S1. Experimental Section

S1.1. Materials

The ligand 2H-imidazole-4-carboxylic acid (H_2**L**) was purchased from J&K Scientific Ltd. Metal salts, and organic solvents were commercially available and were used as received. The solvents used for synthesis were of analytical grade.

S1.2. Physical measurements

Infrared spectra were obtained as KBr disks on a Nicolet Avatar 360 FTIR spectrometer in the range of 4000−400 cm^{-1}(abbreviations used for the IR bands are w = weak, m = medium, b = broad, and vs = very strong). Elemental analyses (C, H, and N) were carried out with Elementar Vario EL Cube equipment. Thermogravimetric measurements were performed on a TA Instruments Q50 Thermogravimetric Analyzer under a nitrogen flow of 40 mL^{-1} min at a typical heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) experiments were performed on a D8 Advance X-ray diffractometer CuKα radiation. UV−vis diffused reflectance spectra were recorded with an Agilent 8453 UV−vis spectrophotometer (Agilent Technologies Co. Ltd.). Single crystal structures were determined using an Oxford Diffraction Gemini E instrument equipped with a graphite monochromator and ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd.). The circular dichroism spectrum (CD) was recorded on a MOS 450 AF/CD device (Bio-Logic, Claix, France) spectropolarimeter with KCl pellets. Low pressure (up to 1 bar) gas adsorption isotherms of CO_2 were measured on the Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. In one typical run, about 150 mg as-synthesis samples were activated at 180 °C for 15 hours by using the “outgas” function of the surface area analyzer before measurements. Magnetic data were collected using crushed crystals of the sample on a Quantum Design MPMS XL-7 SQUID magnetometer. Chiral separation experiments were recorded by using gas chromatography (GC). Conditions Column: CHIRALDEX G-TA by ASTEC Company (30 m × 0.25 mm I.D.). Column temperature: 26 °C. Carrier gas: N_2 0.5 mL/min, H_2 0.5 mL/min.

S1.3. X-ray crystallography

Summary of crystallographic data and details of data collection for **1P**-NH_3, **1M**-NH_3 and **1P**-H_2O are given in **Table S1**. Single crystals with suitable dimensions were chosen under an optical microscope and mounted on a glass fiber for data collection. Intensity data for all crystals were collected using MoKα (λ = 0.71073 Å) radiation on an Oxford Diffraction Gemini E instrument equipped with a graphite monochromator and ATLAS CCD detector under the room temperature (293 K). Structures were solved by direct methods (SHELXTL-97) and refined on F^2 using full-matrix least squares (SHELXTL-97).[1,2] All non-hydrogen atoms were refined with anisotropic thermal parameters, and All non-hydrogen atoms were refined anisotropically till convergence is reached. Hydrogen atoms attached to the organic moieties present in all compounds are either located from the difference Fourier map or stereochemically fixed. After refining the coordination polymeric network in all three

compounds, some of the diffused peaks very close to each other with residual electron density ranging from 1.1Å^{-3} to 1.9 Å^{-3} were observed in the difference Fourier map which can be attributed to disordered solvent molecules present in the crystal lattice. Attempts made to model these disordered peaks were unsuccessful since residual electron density of the peaks obtained was diffused and there was no obvious major site occupations for the solvent molecules. PLATON/SQUEEZE[3] was used to correct the diffraction data for the contribution from disordered lattice solvent molecule. Final cycles of least-squares refinements improved the R-values with the modified data set after subtracting the contribution from the disordered solvent molecules using SQUEEZ program

S1.4. Synthesis of metal-organic frameworks

Synthesis of Conglomerate 1 (1P-NH_3 + **1M**-NH_3**):**

The mixture $Co(Ac)_2{\cdot}4H_2O$ (0.4 mmol, 0.10 mg), H_2**L** (0.3 mmol, 0.034 g), and mixed solvents EtOH/THF/$NH_3{\cdot}H_2O$ (*v*/*v*/*v* = 4/1/1, 6 mL) were loaded into a 15-mL Teflon-lined reactor, stirred for 30 minutes at room temperature, then heated to 160 °C in a programmable oven for 72 h, followed by slow cooling (4 °C/h) to room temperature. After washing with ethanol, both irregular and triangular crystals with blackish-purple colors were obtained. Yield: 80% (based on ligand). IR (KBr pellet, cm^{-1}): 3400 (b), 1590 (s), 1550 (s), 1400 (s), 1230 (m), 1200 (w), 1100 (w), 830 (w), 800 (w), 670 (w). Elemental analysis (%) Calcd for ($[Co_6(C_4H_2N_2O_2)_6(NH_3)]{\cdot}(H_2O)_6$): C, 25.31; H, 2.37; N, 15.99. Found: C, 25.52; H, 2.20; N, 15.86.

Synthesis of 1M-NH_3

The mixture $Co(Ac)_2{\cdot}4H_2O$ (0.4 mmol, 0.10 mg), H_2**L** (0.3 mmol, 0.034 g), and mixed solvents CH_3CN/DMF/$NH_3{\cdot}H_2O$ (*v*/*v*/*v* = 4/1/1, 6 mL) were loaded into a 15-mL Teflon-lined reactor, stirred for 30 minutes at room temperature, then heated to 160 °C in a programmable oven for 72 h, followed by slow cooling (4 °C/h) to room temperature. After washing with ethanol, irregular crystals with blackish-purple colors were obtained. Yield: 85% (based on ligand). IR (KBr pellet, cm^{-1}): 3400 (b), 1590 (s), 1550 (s), 1400 (s), 1230 (m), 1200 (w), 1100 (w), 830 (w), 800 (w), 670 (w). Elemental analysis (%) Calcd for ($[Co_6(C_4H_2N_2O_2)_6(NH_3)]{\cdot}(H_2O)_6$): C, 25.31; H, 2.37; N, 15.99. Found: C, 25.22; H, 2.39; N, 16.12.

Synthesis of 1P-H_2O

The mixture $Co(Ac)_2{\cdot}4H_2O$ (0.4 mmol, 0.10 mg), H_2**L** (0.3 mmol, 0.034 g), and mixed solvents DMF/$NH_3{\cdot}H_2O$ (*v*/*v* = 4/1, 10 mL) were loaded into a 15-mL Teflon-lined reactor, stirred for 30 minutes at room temperature, then heated to 140 °C in a programmable oven for 72 h, followed by slow cooling (3 °C/h) to room temperature. After washing with ethanol, triangular crystals with reddish-purple colors were obtained. Yield: 55% (based on ligand). IR (KBr pellet, cm^{-1}): 3400 (b), 1590 (s), 1550 (s), 1400 (s), 1230 (m), 1200 (w), 1100 (w), 830 (w), 800 (w), 670 (w). Elemental analysis (%) Calcd for ($[Co_6(C_4H_2N_2O_2)_6(H_2O)]{\cdot}(H_2O)_6$): C, 25.28; H, 2.28; N, 14.75. Found: C, 25.14; H, 2.45; N, 14.96.

Fig. S2 ORTEP diagrams for MOFs **1P**-NH_3, **1M**-NH_3, **1P**-H_2O

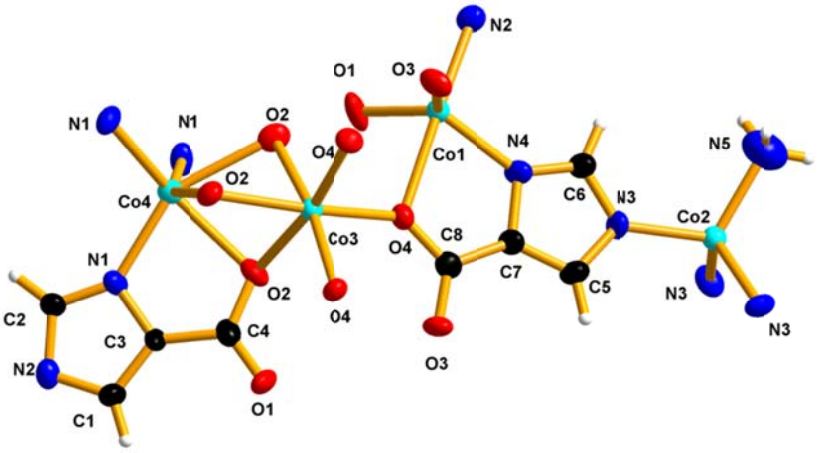

Fig. S2.1: ORTEP diagram depicting the coordination sphere with atom numbering scheme for **1P**-NH_3 (50% probability factor for the thermal ellipsoids).

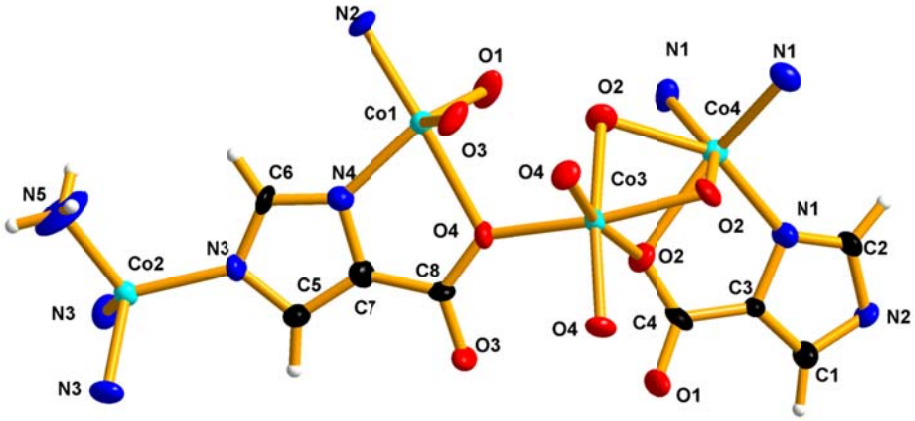

Fig. S2.2: ORTEP diagram depicting the coordination sphere with atom numbering scheme for **1M**-NH_3 (50% probability factor for the thermal ellipsoids).

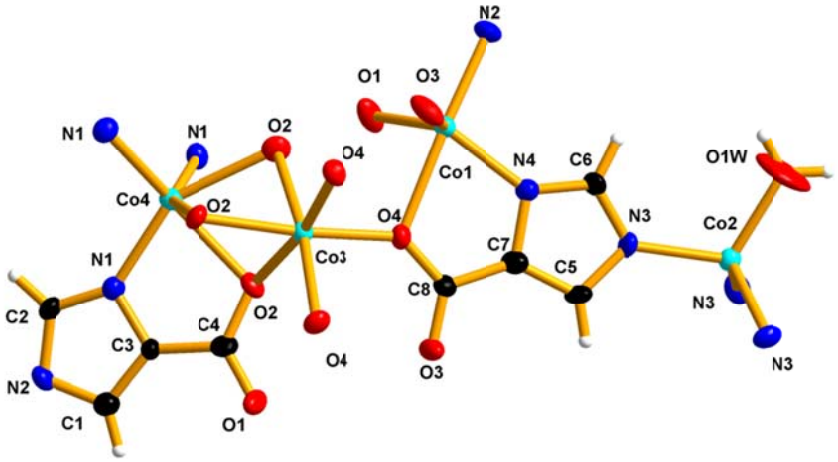

Fig. S2.3: ORTEP diagram depicting the coordination sphere with atom numbering scheme for **1P**-H_2O (50% probability factor for the thermal ellipsoids).

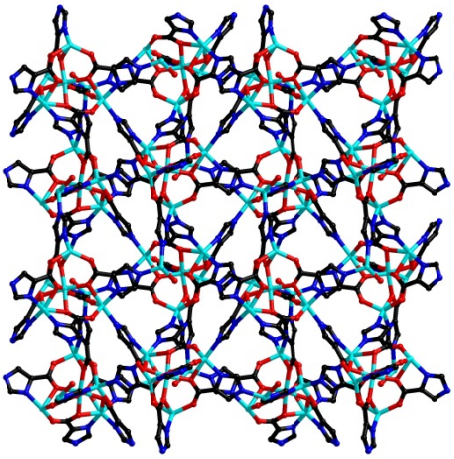

Fig. S3 Portion of the crystal structure of **1P**-H_2O as viewed along the *b*-axis. Turquoise, black, blue and red spheres represent Co, C, N and O atoms, respectively; H atoms have been omitted for clarity.

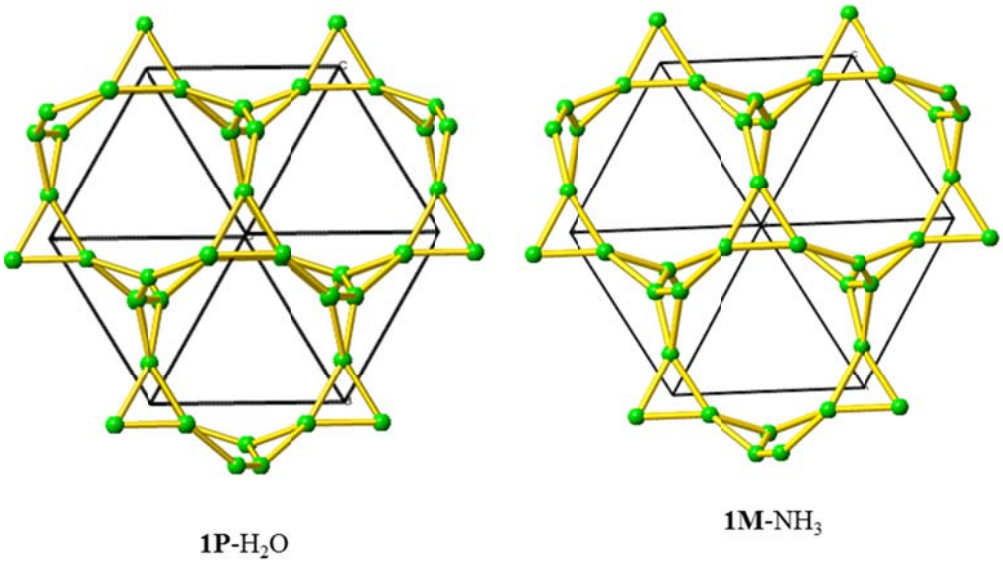

Figure S4. The underlying net **lcv** of **1P**-H_2O and **1M**-NH_3 (the identification of the nets and computation of their ideal symmetry are performed through the program *Systre*.[4] Note **lcv** is known to RSCR.[5])

Table S1 Selected bond length and bond angle for MOFs **1P**-NH_3, **1M**-NH_3 and **1P-**H_2O

1P-NH_3			
Co(1)-O(1)#1	1.997(6)	Co(3)-O(4)#1	2.036(5)
Co(1)-O(3)#2	1.997(6)	Co(3)-O(2)	2.088(6)
Co(1)-N(4)	2.019(7)	Co(3)-O(2)#1	2.088(6)
Co(1)-N(2)#3	2.043(8)	Co(3)-O(2)#2	2.088(6)
Co(1)-O(4)	2.262(6)	Co(4)-N(1)	2.064(7)
Co(2)-N(5)	1.97(3)	Co(4)-N(1)#2	2.064(7)
Co(2)-N(3)	2.003(7)	Co(4)-N(1)#1	2.064(7)

Co(2)-N(3)#4	2.003(7)	Co(4)-O(2)#2	2.262(6)
Co(2)-N(3)#5	2.003(7)	Co(4)-O(2)#1	2.262(6)
Co(3)-O(4)#2	2.036(5)	Co(4)-O(2)	2.262(6)
Co(3)-O(4)	2.036(5)		
O(1)#1-Co(1)-O(3)#2	125.9(3)	O(4)-Co(3)-O(2)#1	92.3(2)
O(1)#1-Co(1)-N(4)	118.1(3)	O(4)#1-Co(3)-O(2)#1	170.5(3)
O(3)#2-Co(1)-N(4)	112.1(3)	O(2)-Co(3)-O(2)#1	78.5(3)
O(1)#1-Co(1)-N(2)#3	91.1(3)	O(4)#2-Co(3)-O(2)#2	170.5(3)
O(3)#2-Co(1)-N(2)#3	98.0(3)	O(4)-Co(3)-O(2)#2	97.3(2)
N(4)-Co(1)-N(2)#3	101.2(3)	O(4)#1-Co(3)-O(2)#2	92.3(2)
O(1)#1-Co(1)-O(4)	86.0(3)	O(2)-Co(3)-O(2)#2	78.5(3)
O(3)#2-Co(1)-O(4)	88.2(2)	O(2)#1-Co(3)-O(2)#2	78.5(3)
N(4)-Co(1)-O(4)	75.4(2)	N(1)-Co(4)-N(1)#2	106.7(2)
N(2)#3-Co(1)-O(4)	173.7(3)	N(1)-Co(4)-N(1)#1	106.7(2)
N(5)-Co(2)-N(3)	111.4(2)	N(1)#2-Co(4)-N(1)#1	106.7(2)
N(5)-Co(2)-N(3)#4	111.4(2)	N(1)-Co(4)-O(2)#2	149.0(3)
N(3)-Co(2)-N(3)#4	107.5(2)	N(1)#2-Co(4)-O(2)#2	77.6(3)
N(5)-Co(2)-N(3)#5	111.4(2)	N(1)#1-Co(4)-O(2)#2	101.1(3)
N(3)-Co(2)-N(3)#5	107.5(2)	N(1)-Co(4)-O(2)#1	101.1(3)
N(3)#4-Co(2)-N(3)#5	107.5(2)	N(1)#2-Co(4)-O(2)#1	149.0(3)
O(4)#2-Co(3)-O(4)	91.4(3)	N(1)#1-Co(4)-O(2)#1	77.6(3)
O(4)#2-Co(3)-O(4)#1	91.4(3)	O(2)#2-Co(4)-O(2)#1	71.5(2)
O(4)-Co(3)-O(4)#1	91.4(3)	N(1)-Co(4)-O(2)	77.6(3)
O(4)#2-Co(3)-O(2)	92.3(2)	N(1)#2-Co(4)-O(2)	101.1(3)
O(4)-Co(3)-O(2)	170.5(3)	N(1)#1-Co(4)-O(2)	149.0(3)
O(4)#1-Co(3)-O(2)	97.3(2)	O(2)#2-Co(4)-O(2)	71.5(2)
O(4)#2-Co(3)-O(2)#1	97.3(2)	O(2)#1-Co(4)-O(2)	71.5(2)
Symmetry transformations: #1 -z-1,x-1/2,-y-3/2; #2 y+1/2,-z-3/2,-x-1; #3 x+1/2,-y-3/2,-z-2; #4 -z-1/2,-x,y-1/2; #5 -y,z+1/2,-x-1/2			
1M-NH_3			
Co(1)-O(3)	1.987(3)	Co(3)-O(4)#2	2.041(3)
Co(1)-O(1)#1	2.011(3)	Co(3)-O(2)#6	2.099(3)
Co(1)-N(4)#2	2.016(4)	Co(3)-O(2)#7	2.099(3)
Co(1)-N(2)	2.038(4)	Co(3)-O(2)#1	2.099(3)
Co(1)-O(4)#2	2.273(3)	Co(4)-N(1)#3	2.063(4)
Co(2)-N(5)	1.947(16)	Co(4)-N(1)	2.063(4)
Co(2)-N(3)#3	2.018(4)	Co(4)-N(1)#4	2.063(4)
Co(2)-N(3)	2.018(4)	Co(4)-O(2)	2.273(4)
Co(2)-N(3)#4	2.018(4)	Co(4)-O(2)#4	2.273(3)
Co(3)-O(4)#5	2.041(3)	Co(4)-O(2)#3	2.273(4)
Co(3)-O(4)	2.041(3)		
O(3)-Co(1)-O(1)#1	125.10(16)	O(4)-Co(3)-O(2)#7	170.32(14)
O(3)-Co(1)-N(4)#2	112.85(18)	O(4)#2-Co(3)-O(2)#7	96.81(13)
O(1)#1-Co(1)-N(4)#2	118.02(18)	O(2)#6-Co(3)-O(2)#7	78.88(15)

O(3)-Co(1)-N(2)	98.26(16)	O(4)#5-Co(3)-O(2)#1	170.32(14)
O(1)#1-Co(1)-N(2)	91.43(16)	O(4)-Co(3)-O(2)#1	96.81(13)
N(4)#2-Co(1)-N(2)	100.87(17)	O(4)#2-Co(3)-O(2)#1	91.83(14)
O(3)-Co(1)-O(4)#2	88.68(13)	O(2)#6-Co(3)-O(2)#1	78.88(15)
O(1)#1-Co(1)-O(4)#2	85.34(14)	O(2)#7-Co(3)-O(2)#1	78.88(15)
N(4)#2-Co(1)-O(4)#2	75.31(14)	N(1)#3-Co(4)-N(1)	107.00(12)
N(2)-Co(1)-O(4)#2	172.98(15)	N(1)#3-Co(4)-N(1)#4	107.00(12)
N(5)-Co(2)-N(3)#3	111.05(13)	N(1)-Co(4)-N(1)#4	107.00(12)
N(5)-Co(2)-N(3)	111.05(12)	N(1)#3-Co(4)-O(2)	149.13(15)
N(3)#3-Co(2)-N(3)	107.84(13)	N(1)-Co(4)-O(2)	77.36(14)
N(5)-Co(2)-N(3)#4	111.05(13)	N(1)#4-Co(4)-O(2)	100.46(15)
N(3)#3-Co(2)-N(3)#4	107.84(13)	N(1)#3-Co(4)-O(2)#4	100.46(15)
N(3)-Co(2)-N(3)#4	107.84(13)	N(1)-Co(4)-O(2)#4	149.13(14)
O(4)#5-Co(3)-O(4)	91.96(14)	N(1)#4-Co(4)-O(2)#4	77.36(14)
O(4)#5-Co(3)-O(4)#2	91.96(14)	O(2)-Co(4)-O(2)#4	71.83(13)
O(4)-Co(3)-O(4)#2	91.96(14)	N(1)#3-Co(4)-O(2)#3	77.36(14)
O(4)#5-Co(3)-O(2)#6	96.81(13)	N(1)-Co(4)-O(2)#3	100.46(15)
O(4)-Co(3)-O(2)#6	91.83(14)	N(1)#4-Co(4)-O(2)#3	149.13(14)
O(4)#2-Co(3)-O(2)#6	170.32(14)	O(2)-Co(4)-O(2)#3	71.83(13)
O(4)#5-Co(3)-O(2)#7	91.83(14)	O(2)#4-Co(4)-O(2)#3	71.83(13)
Symmetry transformations: #1 -z,x+1/2,-y+1/2; #2 z-1,x+1,y; #3 -z+1/2,-x,y+1/2; #4 -y,z-1/2,-x+1/2; #5 y-1,z,x+1; #6 x-1/2,-y+1/2,-z+1; #7 -y-1/2,-z+1,x+1/2			
1P-H_2O			
Co(1)-O(3)#1	1.989(3)	Co(3)-O(4)#5	2.041(3)
Co(1)-O(1)#1	2.010(3)	Co(3)-O(2)#1	2.097(3)
Co(1)-N(4)	2.025(4)	Co(3)-O(2)#5	2.097(3)
Co(1)-N(2)#2	2.042(4)	Co(3)-O(2)	2.097(3)
Co(1)-O(4)	2.278(3)	Co(4)-N(1)#5	2.057(4)
Co(2)-O(1W)	1.983(15)	Co(4)-N(1)#1	2.057(4)
Co(2)-N(3)	2.015(4)	Co(4)-N(1)	2.057(4)
Co(2)-N(3)#3	2.015(4)	Co(4)-O(2)	2.267(3)
Co(2)-N(3)#4	2.015(4)	Co(4)-O(2)#5	2.267(3)
Co(3)-O(4)#1	2.041(3)	Co(4)-O(2)#1	2.267(3)
Co(3)-O(4)	2.041(3)		
O(3)#1-Co(1)-O(1)#1	123.76(16)	O(4)-Co(3)-O(2)#5	170.20(14)
O(3)#1-Co(1)-N(4)	113.25(17)	O(4)#5-Co(3)-O(2)#5	96.93(12)
O(1)#1-Co(1)-N(4)	119.05(17)	O(2)#1-Co(3)-O(2)#5	78.80(14)
O(3)#1-Co(1)-N(2)#2	98.45(15)	O(4)#1-Co(3)-O(2)	170.20(14)
O(1)#1-Co(1)-N(2)#2	91.44(15)	O(4)-Co(3)-O(2)	96.93(12)
N(4)-Co(1)-N(2)#2	100.38(16)	O(4)#5-Co(3)-O(2)	91.76(13)
O(3)#1-Co(1)-O(4)	88.52(13)	O(2)#1-Co(3)-O(2)	78.80(14)
O(1)#1-Co(1)-O(4)	85.85(13)	O(2)#5-Co(3)-O(2)	78.80(14)
N(4)-Co(1)-O(4)	75.33(13)	N(1)#5-Co(4)-N(1)#1	107.29(12)
N(2)#2-Co(1)-O(4)	172.88(14)	N(1)#5-Co(4)-N(1)	107.29(12)

O(1W)-Co(2)-N(3)	110.38(12)	N(1)#1-Co(4)-N(1)	107.29(12)
O(1W)-Co(2)-N(3)#3	110.38(12)	N(1)#5-Co(4)-O(2)	149.11(14)
N(3)-Co(2)-N(3)#3	108.55(12)	N(1)#1-Co(4)-O(2)	99.98(14)
O(1W)-Co(2)-N(3)#4	110.38(12)	N(1)-Co(4)-O(2)	77.25(13)
N(3)-Co(2)-N(3)#4	108.55(12)	N(1)#5-Co(4)-O(2)#5	77.25(13)
N(3)#3-Co(2)-N(3)#4	108.55(12)	N(1)#1-Co(4)-O(2)#5	149.11(14)
O(4)#1-Co(3)-O(4)	91.99(13)	N(1)-Co(4)-O(2)#5	99.98(14)
O(4)#1-Co(3)-O(4)#5	91.99(13)	O(2)-Co(4)-O(2)#5	71.90(12)
O(4)-Co(3)-O(4)#5	91.99(13)	N(1)#5-Co(4)-O(2)#1	99.99(14)
O(4)#1-Co(3)-O(2)#1	96.93(12)	N(1)#1-Co(4)-O(2)#1	77.25(13)
O(4)-Co(3)-O(2)#1	91.76(13)	N(1)-Co(4)-O(2)#1	149.11(14)
O(4)#5-Co(3)-O(2)#1	170.20(14)	O(2)-Co(4)-O(2)#1	71.90(12)
O(4)#1-Co(3)-O(2)#5	91.76(13)	O(2)#5-Co(4)-O(2)#1	71.90(12)
Symmetry transformations: #1 -z-1,x-1/2,-y-3/2; #2 -y-1/2,-z-2,x-1/2; #3 z+1/2,-x-3/2,-y-2; #4 -y-3/2,-z-2,x-1/2; #5 y+1/2,-z-3/2,-x-1			

Table S2 A summary of structure determinations of ten randomly selected reddish-purple and triangular crystals of **1P**-H_2O: Cell parameters, *R* factors, Flack absolute structure parameters for each refinement in $P2_13$ space group and observed helicity are given.

SN	a	Vol.	*R*1	*wR*2	Flack parameter	Helicity
1	17.465(2)	5326.9(12)	0.0538	0.1545	0.98(4)	M
2	17.49820(10)	5357.72(5)	0.0394	0.1436	0.03(3)	P
3	17.5204(2)	5378.14(11)	0.0656	0.1964	0.04(6)	P
4	17.4524(8)	5315.8(4)	0.0549	0.1618	0.00(5)	P
5	17.5332(5)	5389.9(3)	0.0509	0.1755	0.03(4)	P
6	17.43180(10)	5296.96(5)	0.0657	0.1952	-0.011(10)	P
7	17.4907(2)	5350.83(11)	0.0656	0.2045	-0.03(5)	P
8	17.45850(10)	5321.34(5)	0.0581	0.1828	0.01(4)	P
9	17.46890(10)	5330.85(5)	0.0583	0.1861	0.03(4)	P
10	17.46840(10)	5330.40(5)	0.0441	0.1308	0.01(3)	P

Table S3 A summary of structure determinations of ten randomly selected blackish-purple and irregular crystals of **1M**-NH_3: Cell parameters, *R* factors, Flack absolute structure parameters for each refinement in $P2_13$ space group and observed helicity are given.

SN	a	Vol.	*R*1	*wR*2	Flack parameter	Helicity
1	17.47050(10)	5332.32(5)	0.0418	0.1457	0.00(4)	M
2	17.46870(10)	5330.67(5)	0.0449	0.1453	0.02(4)	M
3	17.50350(10)	5362.59(5)	0.0395	0.1323	0.00(3)	M
4	17.4779(3)	5339.10(16)	0.0770	0.1688	0.94(7)	P
5	17.50570(10)	5364.61(5)	0.0490	0.1521	0.01(3)	M
6	17.51450(10)	5372.71(5)	0.0531	0.1704	-0.05(4)	M
7	17.51760(10)	5375.56(5)	0.0561	0.1873	-0.07(4)	M
8	17.48820(10)	5348.54(5)	0.0520	0.1733	0.03(4)	M
9	17.48450(10)	5345.15(5)	0.0550	0.1824	0.05(4)	M
10	17.50280(10)	5361.95(5)	0.0491	0.1669	0.00(4)	M

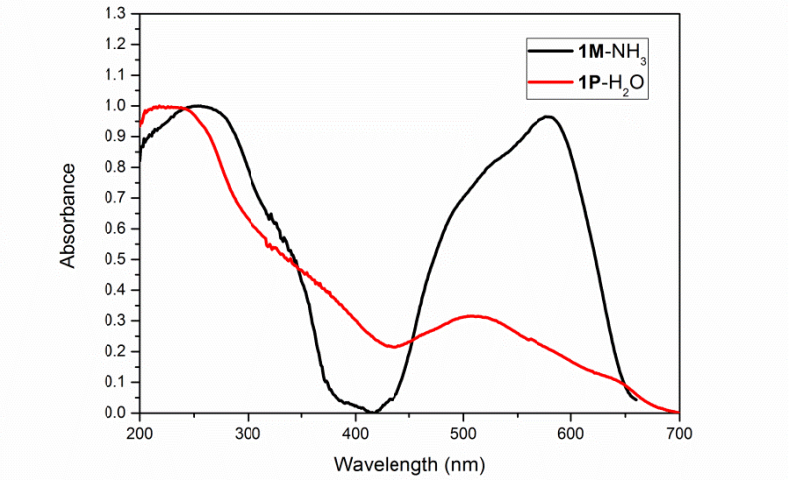

Fig. S5 Solid state UV-vis diffused reflectance spectra of **1M**-NH_3 and **1P-**H_2O (using $BaSO_4$ as substrate).

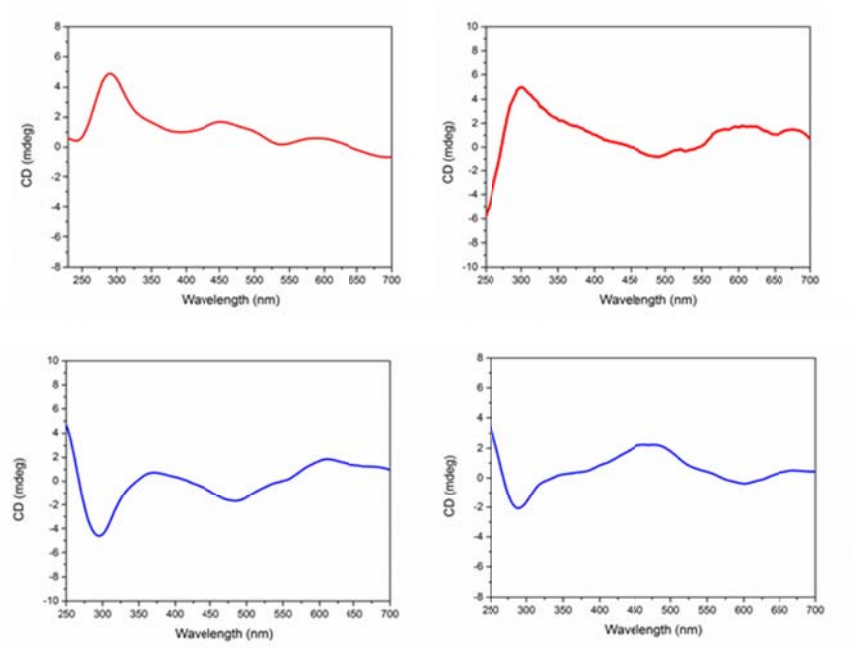

Fig. S6 Solid state CD spectra recorded for four blackish-purple and triangular single crystals of racemic conglomerate (**1P**-NH_3 + **1M**-NH_3). Two of them show positive dichroic signal approximately at 300 nm (top), the other two show the opposite signals (bottom).

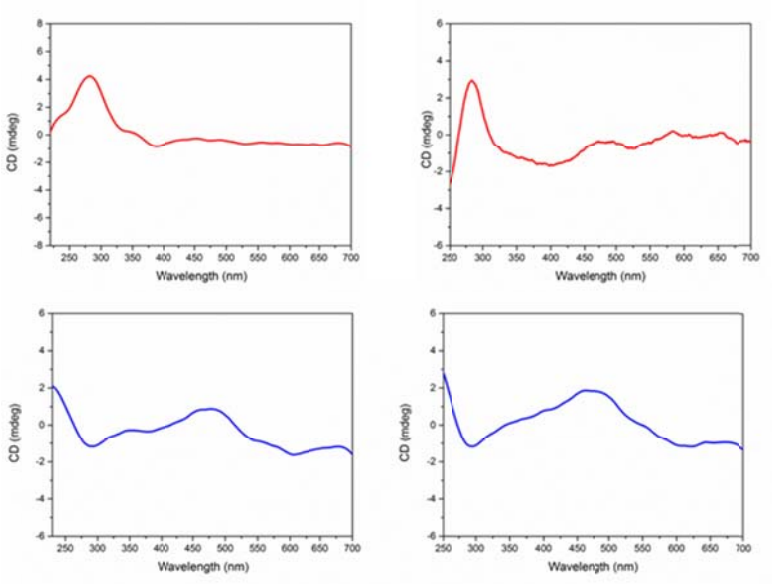

Fig. S7 Solid state CD spectra recorded for four blackish-purple and irregular single crystals of racemic conglomerate (**1P**-NH_3 + **1M**-NH_3). Two of them show positive dichroic signal approximately at 300 nm (top), the other two shows the opposite signal (bottom)

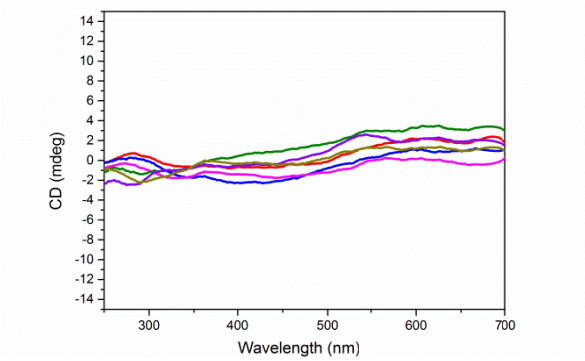

Fig. S8 Solid state CD spectra of bulk samples of **1** (containing both **1P**-NH_3 and **1M**-NH_3) from six batches. All of them are almost CD silent, which show the formation of racemic conglomerate.

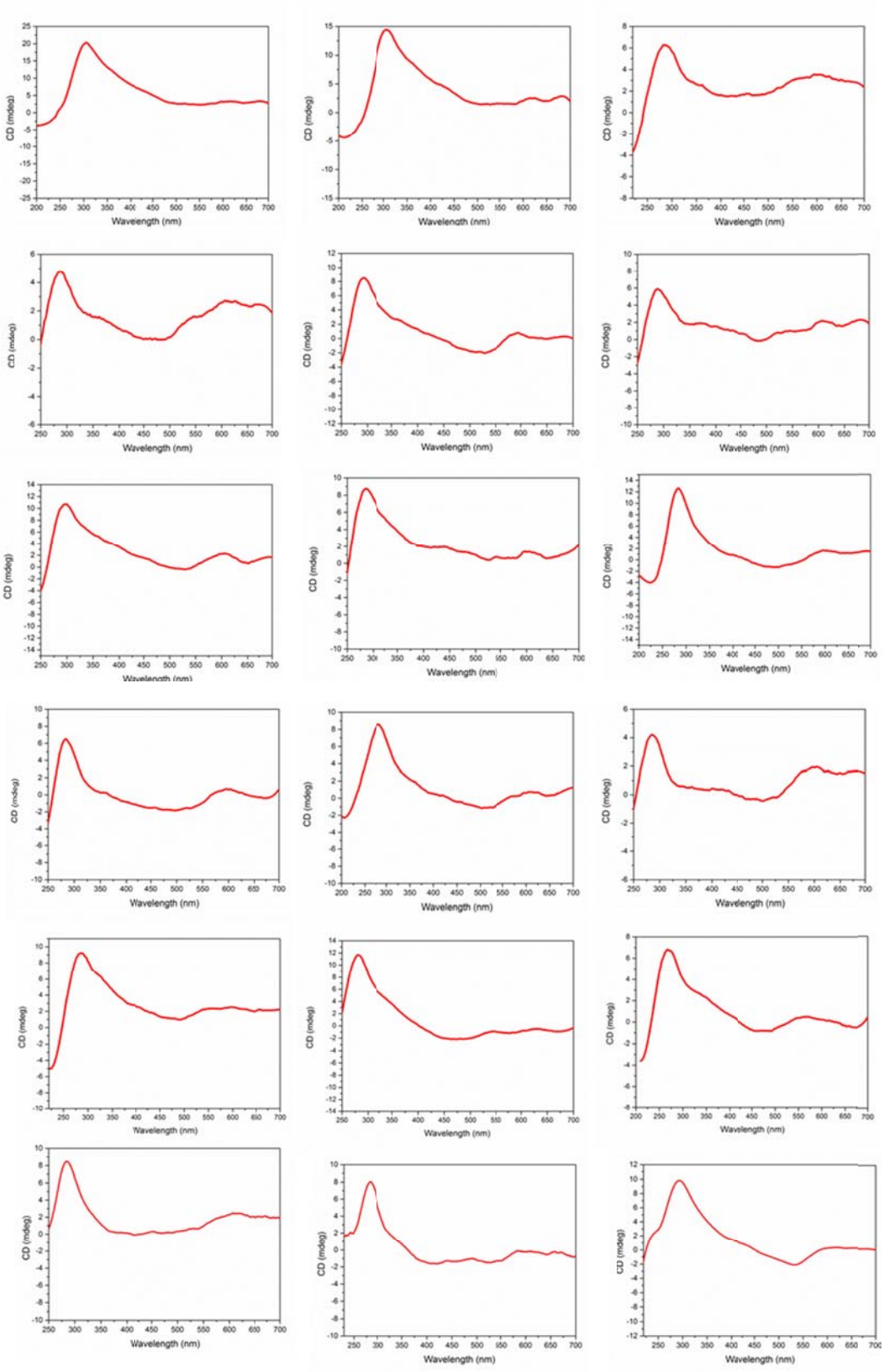

Fig. S9 Solid state CD spectra of bulk samples of **1P**-H_2O from eighteen batches. Positive dichroic signal approximately at 300 nm for all samples indicate the bulk homochirality nature of **1P**-H_2O.

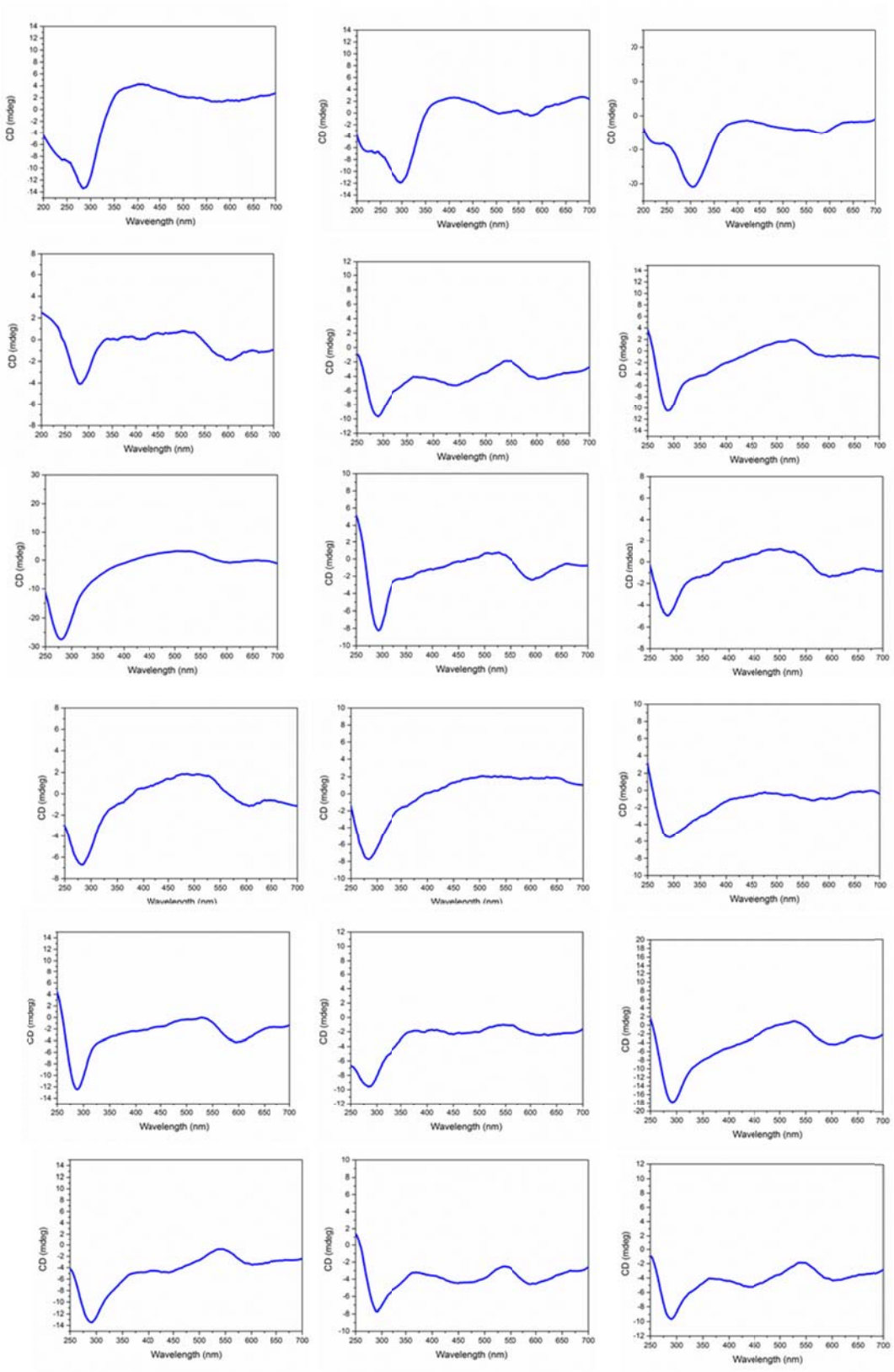

Fig. S10 Solid state CD spectra of bulk samples of **1M**-H_2O from eighteen batches. Negative dichroic signal approximately at 300 nm for all samples indicate the bulk homochirality nature of **1M**-H_2O.

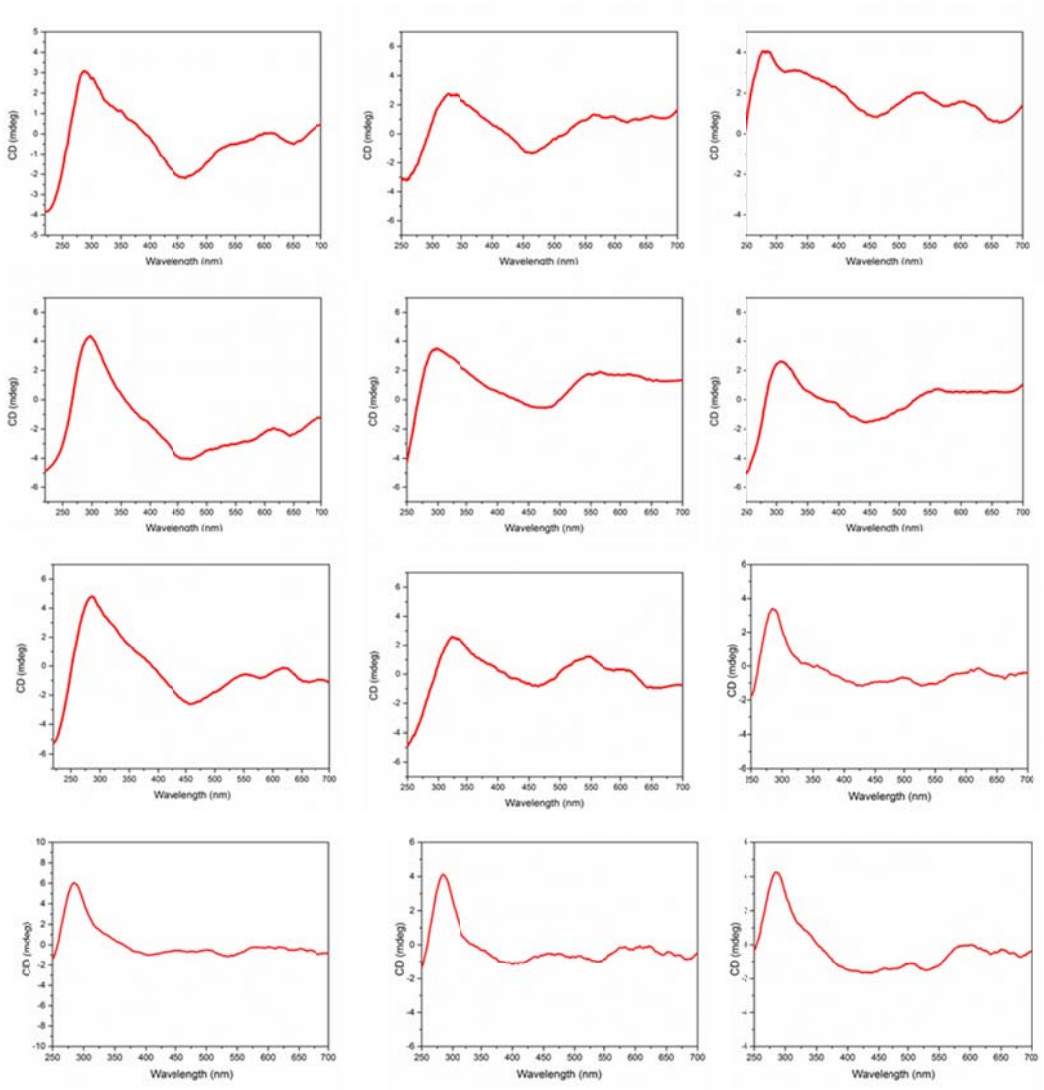

Fig. S11 Solid state CD spectra recorded for twelve reddish-purple and triangular single crystals of **1P**-H_2O. Positive dichroic signal approximately at 300 nm for all samples indicate the exclusive formation of enantiomorph **1P**-H_2O.

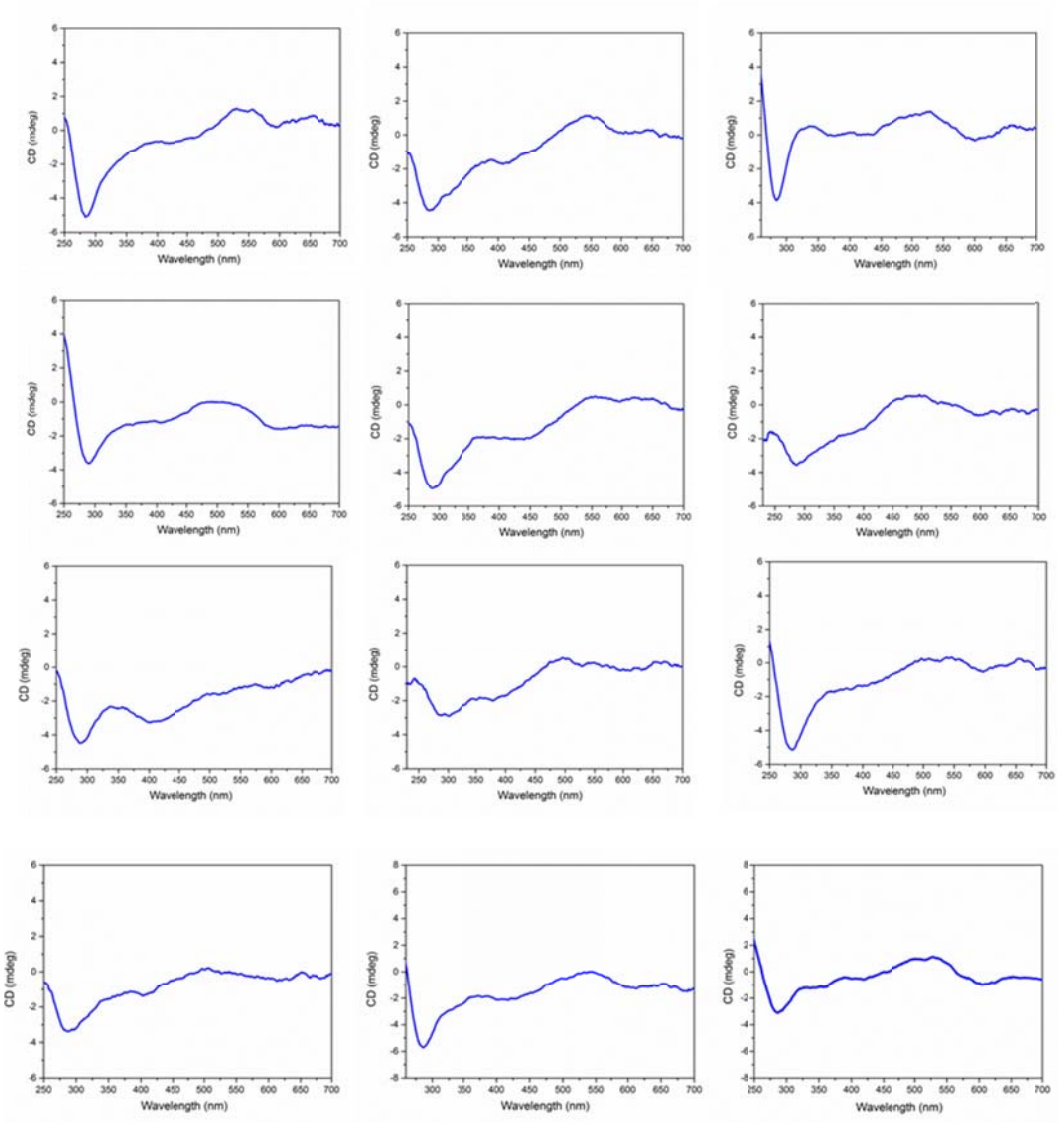

Fig. S12 Solid state CD spectra recorded for twelve blackish-purple and irregular single crystals of **1M**-NH_3. Negative dichroic signal approximately at 300 nm for all samples indicate the exclusive formation of enantiomorph **1M**-NH_3.

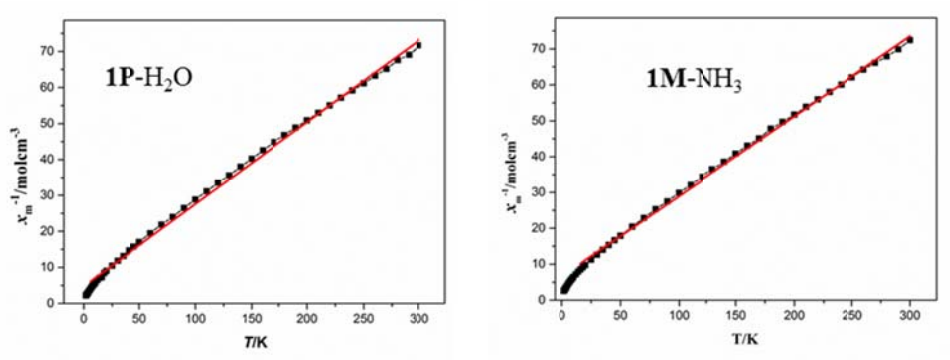

Fig. S13 Curie plot for **1P**-H_2O and **1M**-NH_3.The solid line is the best fit to the Curie-Weiss law.

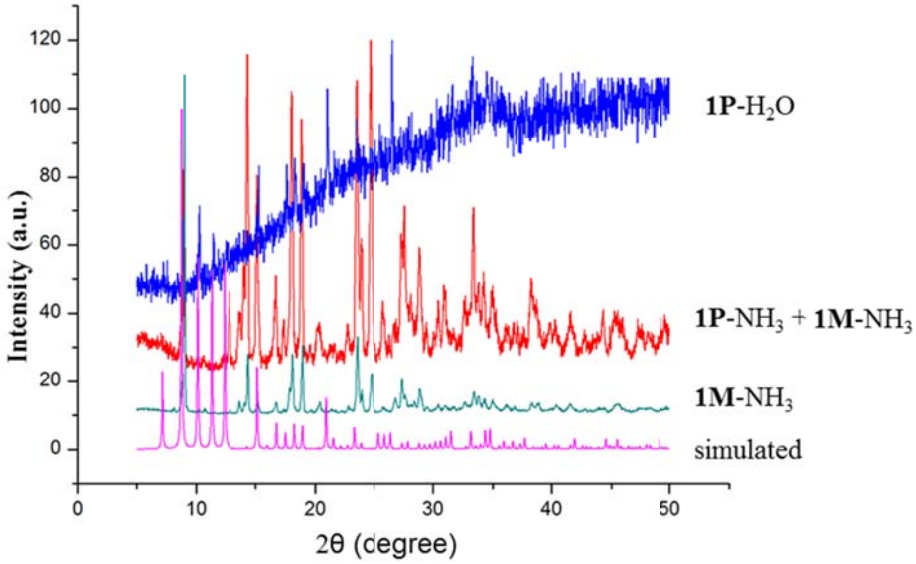

Fig. S14 Comparison of the experimental PXRD patterns of **1M**-NH_3, conglomerate **1P**-NH_3 + **1M**-NH_3 and **1P**-H_2O with the simulated patterns.

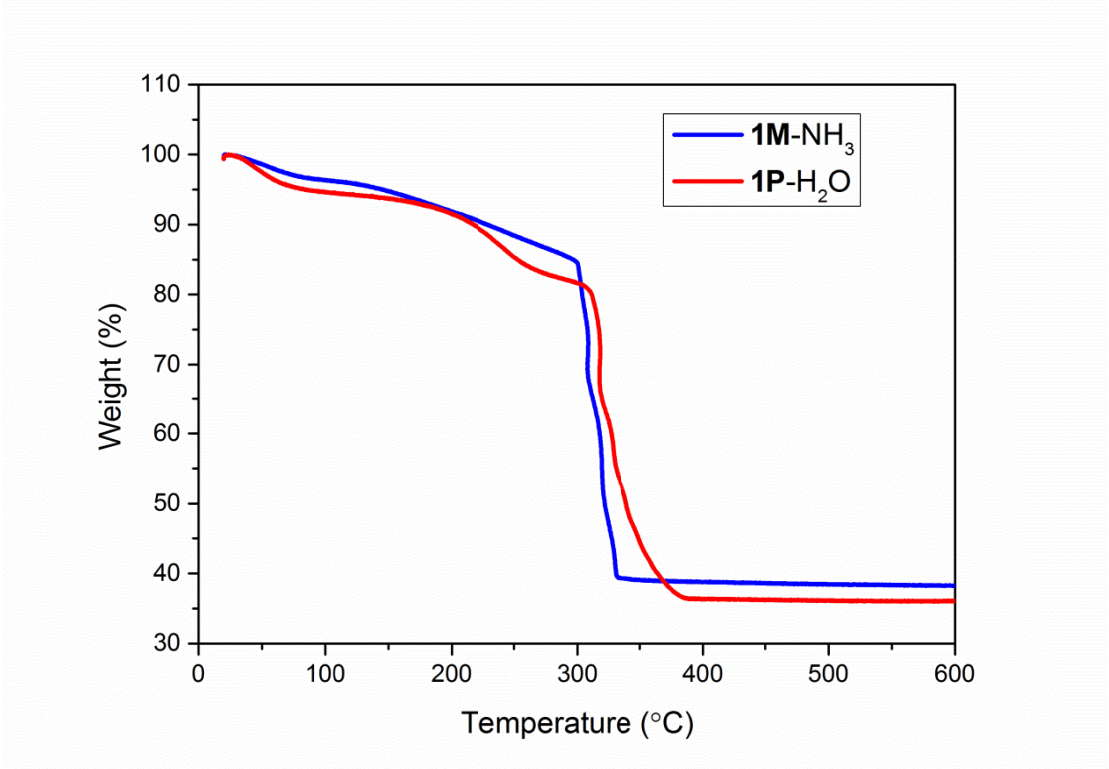

Fig. S15 TGA plots of **1P**-H_2O and **1M**-NH_3 at the temperature range of 30-600 °C. The Y-axis is the percentages of residual weight.

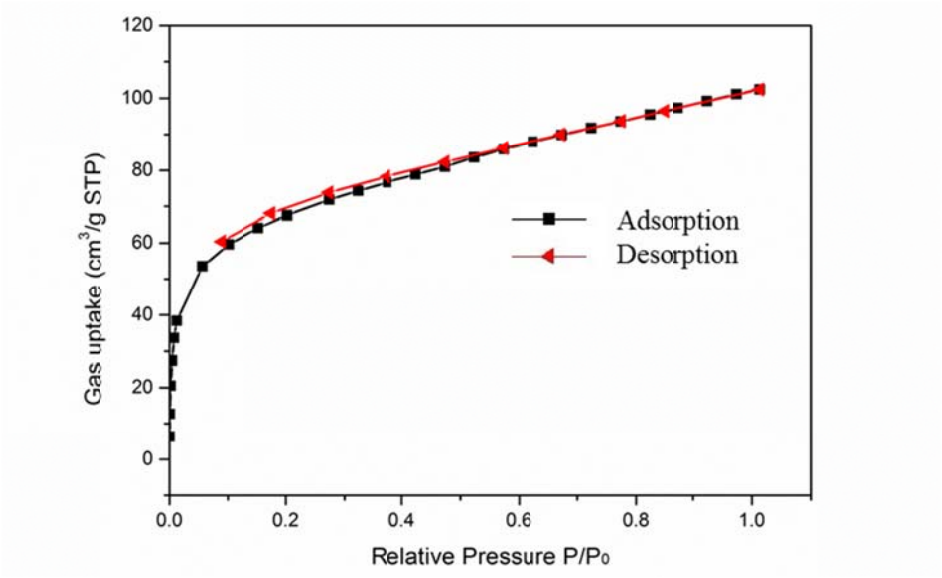

Fig. S16 CO_2 sorption isotherm of **1P**-H_2O at 195 K. P/P_0 is the ratio of gas pressure (P) to saturation pressure (P_0), with P_0 = 1.0 bar.

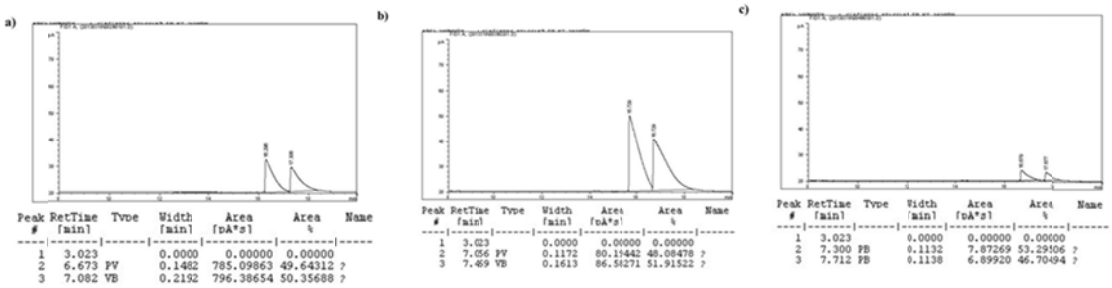

Fig. S17 Chiral GC results of the a) **b**lank racemic 2-butanol; b) racemic 2-butanol with **1M**-NH_3; c) racemic 2-butanol with **1P**-H_2O.

Table S3 Chiral GC results (*ee* = (|(R) - (S)|/|(R) + (S)|) × 100%).

Sample	Area (%)		ee (%)
racemic 2- butanol	49.6	50.7	1.1
1M-NH_3 + racemic 2- butanol	48.1	51.9	3.8
1P-H_2O + racemic 2- butanol	53.3	46.7	6.6

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