

## Electronic Supplementary Information

### Helix-based Supramolecular Isomerism of Metal-Organic Framework

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**Table S1** Selected Bond Lengths (Å) and Bond Angles (deg) of **1-4<sup>a</sup>**

#### Complex 1

Cd(1)-O(3B)	2.27(5)	Cd(1)-O(3A)	2.33(3)	Cd(1)-O(2)	2.409(7)
Cd(1)-N(1)#2	2.358(5)	Cd(1)-O(1)	2.543(11)		
O(3B)-Cd(1)-N(1)#2	77.61(12)	O(3A)-Cd(1)-N(1)#2	81.2(5)	O(3A)#1-Cd(1)-N(1)#2	74.4(5)
N(1)#2-Cd(1)-N(1)#3	155.2(2)	O(3B)-Cd(1)-O(2)	92.41(16)	O(2)#1-Cd(1)-O(1)	125.7(3)
O(1)-Cd(1)-O(1)#1	76.8(4)	O(3A)#1-Cd(1)-O(2)	103.2(6)	O(2)-Cd(1)-O(2)#1	175.2(3)
N(1)#2-Cd(1)-O(2)	96.6(2)	N(1)#3-Cd(1)-O(2)	84.42(19)	N(1)#3-Cd(1)-O(1)	91.7(2)
O(3B)-Cd(1)-O(1)	141.6(2)	O(3A)-Cd(1)-O(1)	130.6(6)	O(2)-Cd(1)-O(1)	49.5(3)
O(3A)#1-Cd(1)-O(1)	152.6(6)	N(1)#2-Cd(1)-O(1)	107.9(2)	O(3A)-Cd(1)-O(2)	81.6(6)

#### Complex 2

Cd(1)-O(1)	2.333(4)	Cd(1)-O(2)	2.405(3)	Cd(1)-O(3)#1	2.245(3)
Cd(1)-N(1)#3	2.301(3)	Cd(1)-N(3)#2	2.251(3)	Cd(1)-O(4)#1	2.512(4)
O(1)-Cd(1)-O(2)	54.74(11)	O(3)#1-Cd(1)-O(1)	146.97(13)	O(3)#1-Cd(1)-N(3)#2	118.89(13)
O(1)-Cd(1)-O(4)#1	108.05(14)	N(3)#2-Cd(1)-O(1)	88.80(12)	O(3)#1-Cd(1)-N(1)#3	85.81(12)
O(2)-Cd(1)-O(4)#1	87.55(13)	N(1)#3-Cd(1)-O(1)	100.88(13)	N(3)#2-Cd(1)-N(1)#3	111.98(12)
O(3)#1-Cd(1)-O(2)	94.23(12)	N(1)#3-Cd(1)-O(2)	85.40(12)	N(3)#2-Cd(1)-O(4)#1	98.05(12)
N(3)#2-Cd(1)-O(2)	142.68(11)	O(3)#1-Cd(1)-O(4)#1	53.95(12)	N(1)#3-Cd(1)-O(4)#1	138.44(11)

#### Complex 3

Cd(1)-O(1)	2.336(2)	Cd(1)-O(2)	2.347(2)	Cd(1)-O(3)#3	2.526(2)
Cd(1)-N(1)#1	2.275(2)	Cd(1)-N(4)#2	2.283(2)	Cd(1)-O(4)#3	2.290(2)
N(1)#1-Cd(1)-O(1)	110.69(8)	N(4)#2-Cd(1)-O(1)	102.32(8)	N(1)#1-Cd(1)-N(4)#2	101.76(9)
O(4)#3-Cd(1)-O(1)	151.50(8)	N(1)#1-Cd(1)-O(2)	96.90(8)	N(1)#1-Cd(1)-O(4)#3	91.23(8)
N(4)#2-Cd(1)-O(2)	155.48(8)	O(4)#3-Cd(1)-O(3)#3	53.96(7)	N(4)#2-Cd(1)-O(4)#3	90.18(8)
O(1)-Cd(1)-O(2)	55.69(8)	N(4)#2-Cd(1)-O(3)#3	85.47(7)	N(1)#1-Cd(1)-O(3)#3	144.74(8)
O(2)-Cd(1)-O(3)#3	88.42(7)	O(1)-Cd(1)-O(3)#3	101.09(8)	O(4)#3-Cd(1)-O(2)	105.27(8)

#### Complex 4

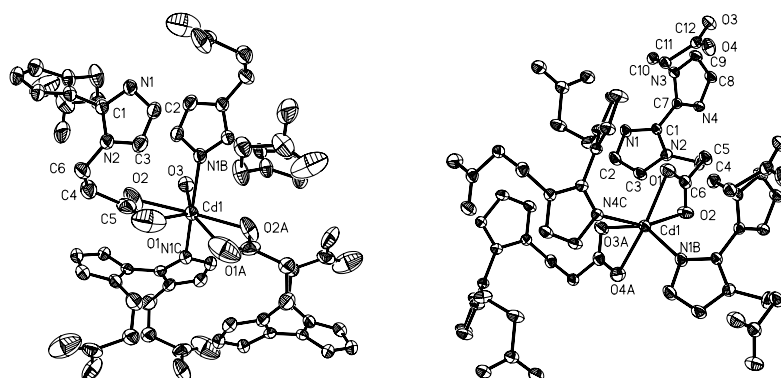
Cd(1)-O(1)#1	2.273(3)	Cd(1)-N(1)	2.307(3)	Cd(1)-O(3)	2.404(3)
O(1)#1-Cd(1)-N(1)	97.97(12)	O(1)#2-Cd(1)-N(1)	97.01(12)	N(1)#3-Cd(1)-N(1)	98.42(16)
N(1)-Cd(1)-O(3)	85.11(13)	O(1)#1-Cd(1)-O(3)	78.85(13)	O(1)#2-Cd(1)-O(3)	85.13(12)

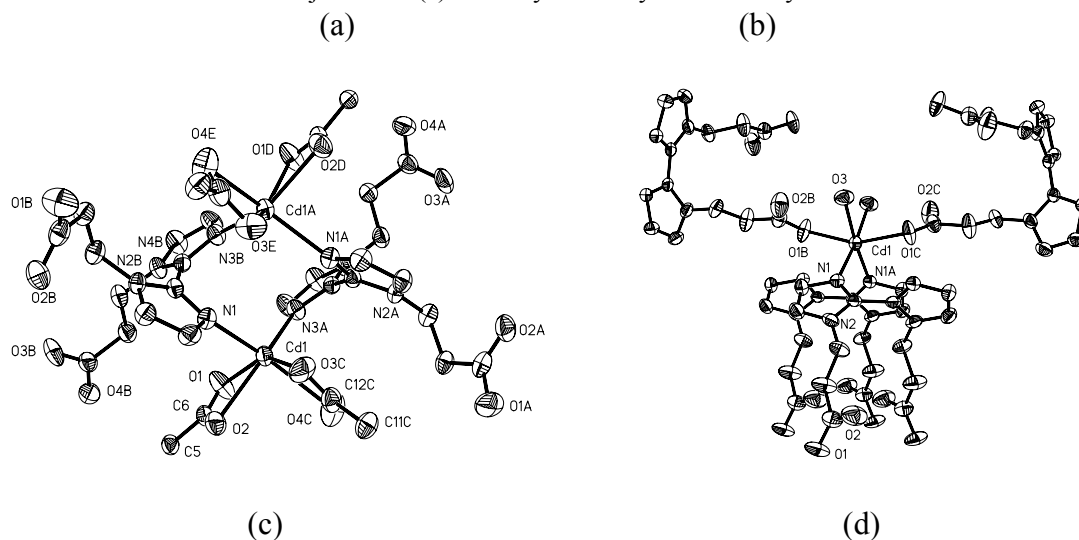
O(1)#1-Cd(1)-O(1)#2 157.0(2) N(1)-Cd(1)-O(3)#3 174.94(11) O(3)-Cd(1)-O(3)#3 91.60(16)

<sup>a</sup> Symmetry code: for **2**: #1:  $x + 1, y, z$ ; #2:  $-x + 1, y + 1/2, -z + 3/2$ ; #3:  $x + 1, -y + 3/2, z + 1/2$ . For **3**: #1:  $-x, y - 1/2, -z + 1/4$ ; #2:  $y - 1/2, x, z - 1/4$ ; #3:  $y - 1/2, -x + 1/2, -z + 1/2$ ; For **4**: #1:  $x + 1/2, -y + 1/2, -z + 1$ ; #2:  $-y + 1/2, x + 1/2, z - 1$ ; #3:  $y, x, -z$ .

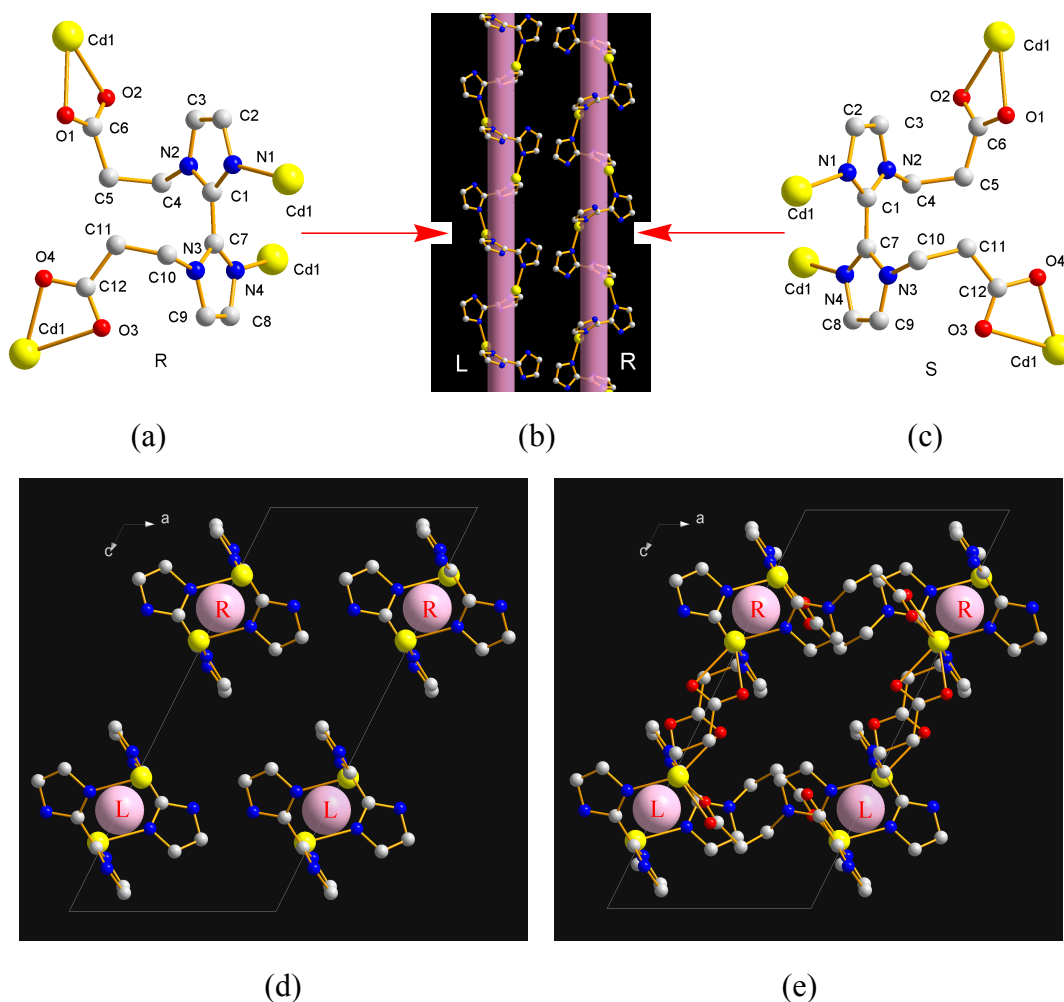
**Table S2** H-Bond lengths (Å) and angles (°) in **1–4**.

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)	symmetry code
<b>Complex 1</b>					
O(1W)–H(1W)⋯O(2W)	0.97	1.76	2.733(19)	172.3	$y, -x+y+1, -z+1$
O(2W)–H(2W)⋯O(1)	0.83	2.49	2.978(18)	118.7	
O(3A)–H(3W)⋯O(2)	0.82	1.81	2.574(6)	155.9	$x-y+1/3, -y+2/3, -z+7/6$
<b>Complex 2</b>					
O(1W)–H(1WB)⋯O(4)	0.86	2.03	2.822(4)	152.5	$-x+1, y-1/2, -z+3/2$
O(1W)–H(1WA)⋯O(1)	0.87	2.24	2.899(4)	132.4	$-x+1, y-1/2, -z+3/2$
<b>Complex 3</b>					
O(1W)–H(1WA)⋯O(4)	0.93	2.15	2.970(6)	146.6	$x+1, y, z$
O(1W)–H(1WB)⋯O(1W)	0.91	2.26	2.850(11)	122.4	$-x+3/2, y, -z+3/4$
O(2W)–H(2WA)⋯O(2W)	0.87	1.96	2.826(19)	174.8	$-x+1, -y+2, z$
O(2W)–H(2WB)⋯O(1W)	0.80	2.11	2.901(13)	175.8	
<b>Complex 4</b>					
O(2)–H(2A)⋯O(3)#5	0.82	1.78	2.588(5)	166.8	$y-1/2, -x+1/2, z+1$
O(3)–H(3C)⋯O(3)#9	0.89	2.16	2.915(7)	142.4	$-x+1, -y+1, z$
O(3)–H(3D)⋯O(1)#10	0.85	2.23	2.985(5)	147.6	$-y+1/2, x+1/2, z$
O(3)–H(3D)⋯O(3)#4	0.85	2.48	3.126(6)	133.2	$y, x, -z+1$

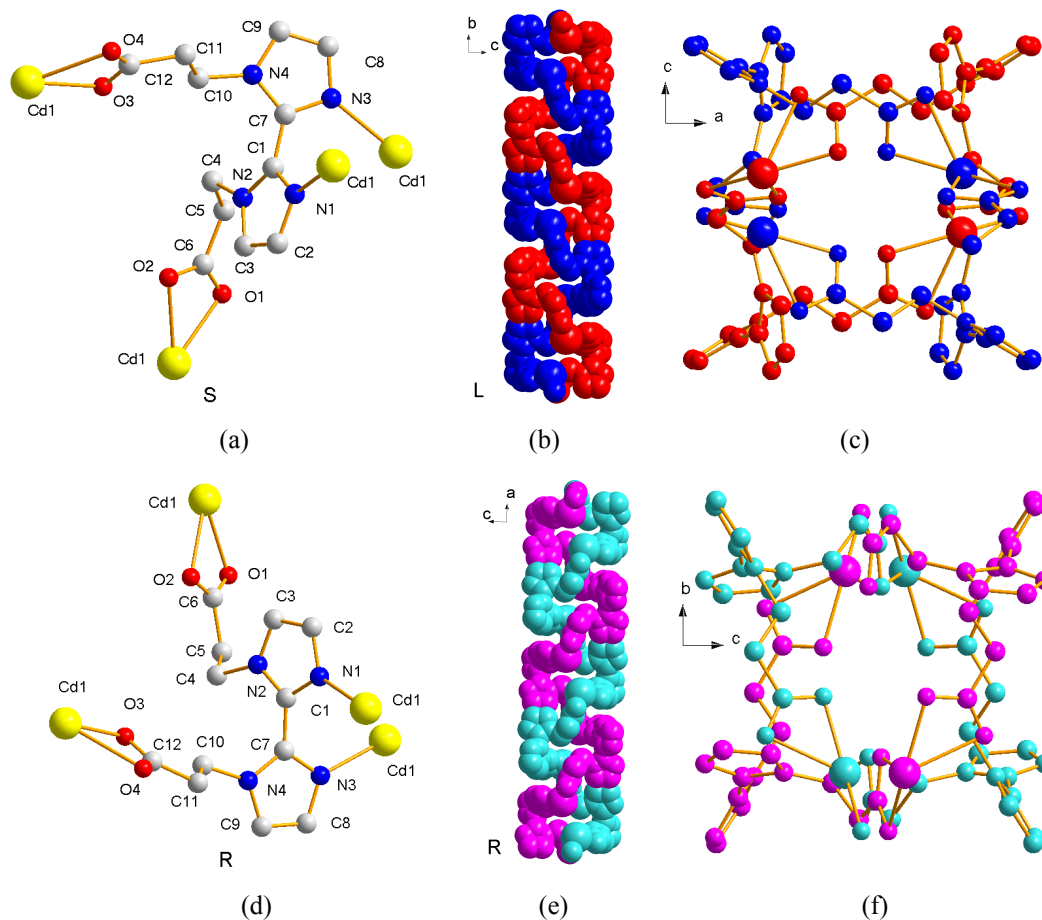




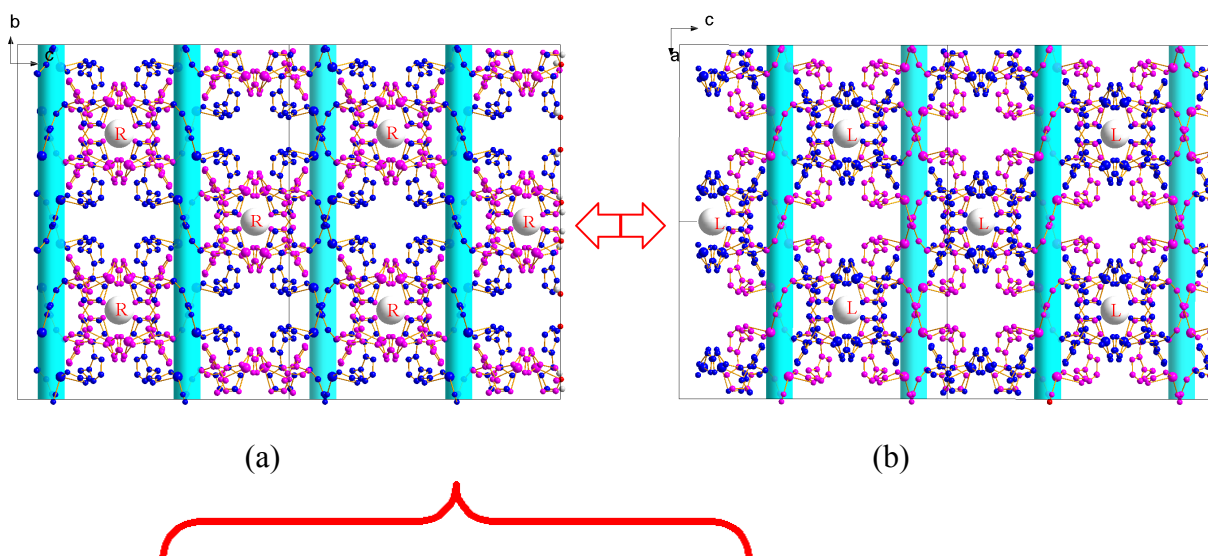
**Fig. S1.** The ORTEP drawing of the coordination environments of Cd(II) of **1-4** (a-d) with 50% probability thermal ellipsoids.



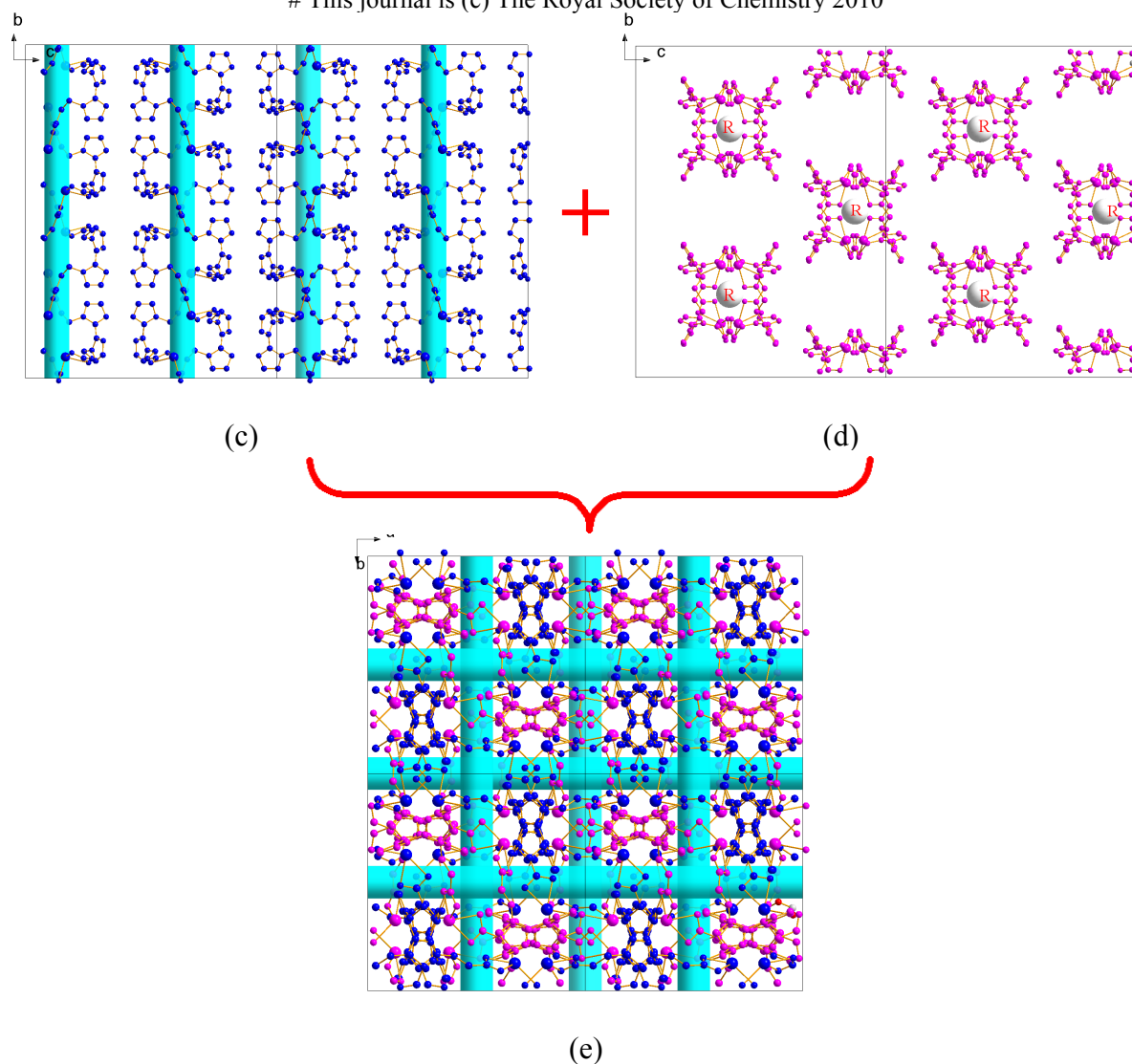
**Fig. S2.** (a), (c): Coordination modes of two chiral conformations (R-Prä<sub>2</sub>biim and S-Prä<sub>2</sub>biim ligand), (b) view of the two types of helical chains along the *a* direction, (d) along the *b* direction and (e) showing the connection of these helical chains, in compound **2**. Color code: yellow, Cd; red, O; blue, N; white, C atoms.



**Fig. S3.** View of the helices in compound **3**: (a), (d) coordination modes of two chiral conformations (S-Pra<sub>2</sub>biim and R-Pra<sub>2</sub>biim ligand) (b) space-filling diagrams of two intertwined left-handed helices along the *b* direction, (c) ball-and stick diagram two intertwined left-handed helices along the *b* direction, (d) space-filling diagrams of two intertwined right-handed helices along the *a* direction, and (e) ball-and stick diagram two intertwined right-handed helices along the *a* direction.

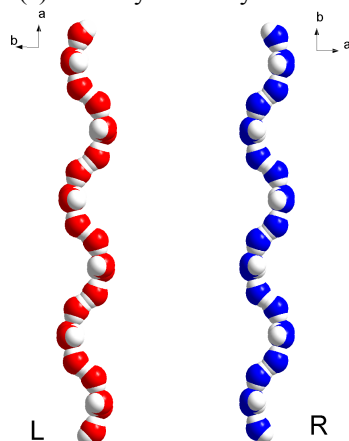




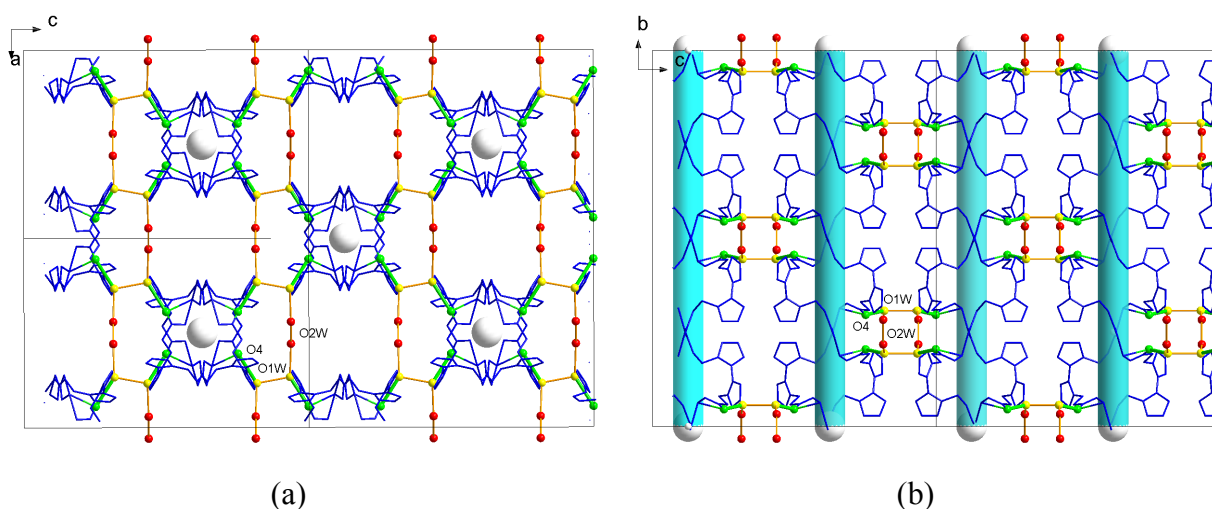


**Fig. S4.** View of the diagrammatic sketch of the construction of the structure of **3**. (a) The open-framework structure, showing the intertwined helices along  $a$  direction. (b) Along  $b$  direction. (c) Two intertwined right-handed helices along the  $a$  direction. (d) Two intertwined left-handed helices along the  $b$  direction. (e) The open-framework structure, showing the intertwined helices along along  $c$  direction.

The left-handed double stranded helices along  $b$  direction: blue sticks. The right-handed double stranded helices along  $a$  direction: pink sticks. Similarly hereinafter.



**Fig. S5.** Space-filling diagram of the helical water chains. L/R: left/right-handed helical chains, respectively.

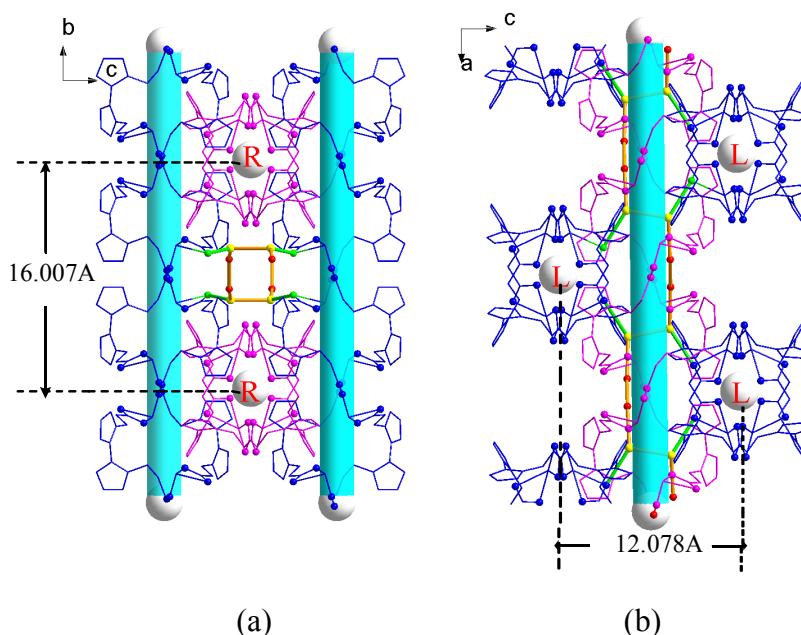


**Fig. S6.** View of the H-bond between the left-handed helical water chains along *a* direction and the left-handed double stranded helices along *b* direction in the structure of **3**. View along *b* direction (a); View along *a* direction (b); the right-handed helical water chains along *b* direction, the right-handed double stranded helices along *a* direction and H atoms are omitted.

The coordinated carboxylic oxygen atom O4: bright green ball. The left-handed helical water chains along *a* direction filled in the channels is formed by two independent lattice water molecules [O1W (yellow ball), O2W (red ball)]. The H-bond (bright green stick) between the coordinated carboxylic oxygen atom O4 and the left-handed helical water chains [O(1W)-H(1WA)...O(4): 2.970(6) Å]. The H-bond (orange stick) in the helical water chains [O(1W)-H(1WB)...O(1W) 2.850(11); O(2W)-H(2WA)...O(2W) 2.826(19); O(2W)-H(2WB)...O(1W) 2.901(13) Å].

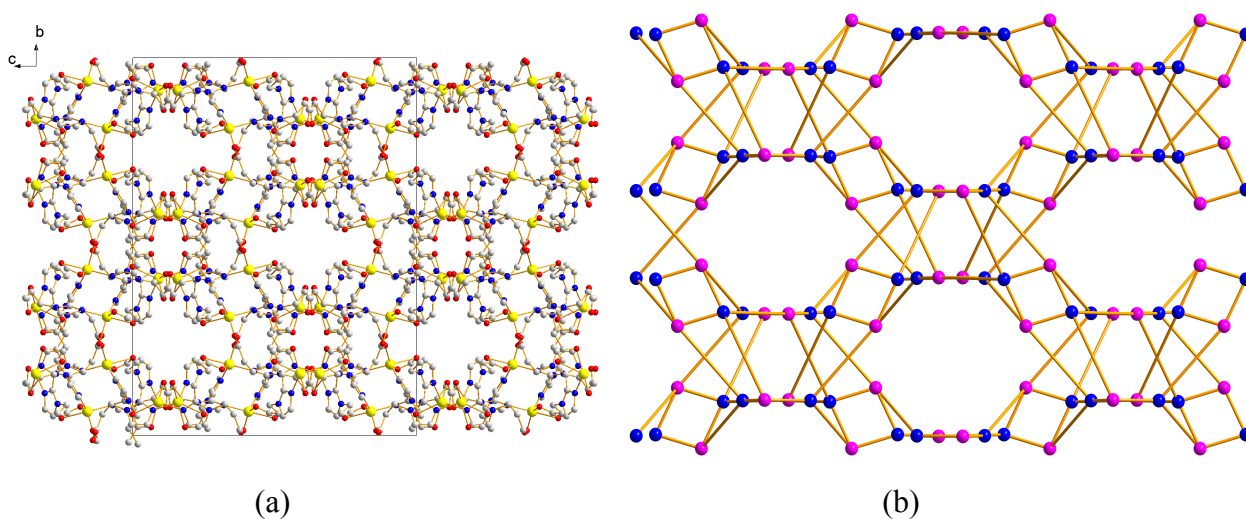
As shown in Fig. S6, two independent lattice water molecules (O1W, O2W) within channels along *a* direction are hydrogen bonded to each other [O(1W)-H(1WB)...O(1W) 2.850(11); O(2W)-H(2WA)...O(2W) 2.826(19); O(2W)-H(2WB)...O(1W) 2.901(13) Å] forming left-handed helical water chains along *a* axis, and there are hydrogen bonds between the left-handed helical water chains along *a* direction and the left-handed double stranded helices along *b* direction [O(1W)-H(1WA)...O(4): 2.970(6) Å]. Similarly, two independent lattice water molecules (O1W,

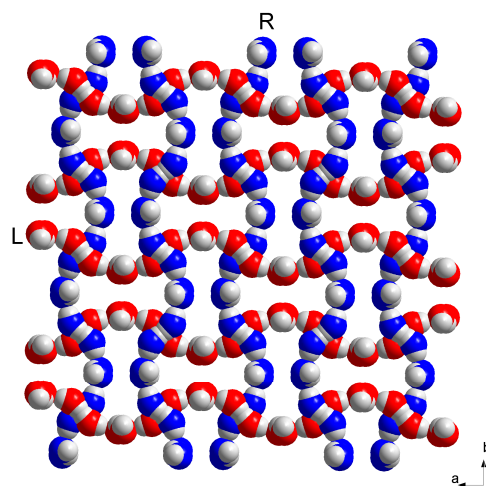
O2W) within channels along *b* direction are hydrogen bonded to each other forming right-handed helical water chains along *b* axis, and there are hydrogen bonds between the right-handed helical water chains along *b* direction and the right-handed double stranded helices along *a* direction.



**Fig. S7.** View of the chiral channel built from the left-handed double stranded helices along *b* direction and two right-handed double stranded helices along *a* direction, and the left-handed helical water chains along *a* direction. View along *a* direction (a); View along *b* direction (b).

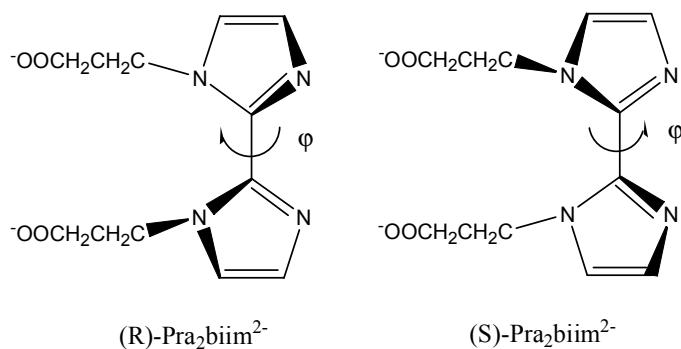
As shown in Fig. S7, the chiral channel are built from the left-handed double stranded helices along *b* direction and two right-handed double stranded helices along *a* direction, and there is the left-handed helical water chain along *a* axis within this channel. The distance between the center of two right-handed double stranded helices in *b* direction is 16.007 Å and that between the plane define the the left-handed double stranded helices in *c* direction is 12.078 Å.





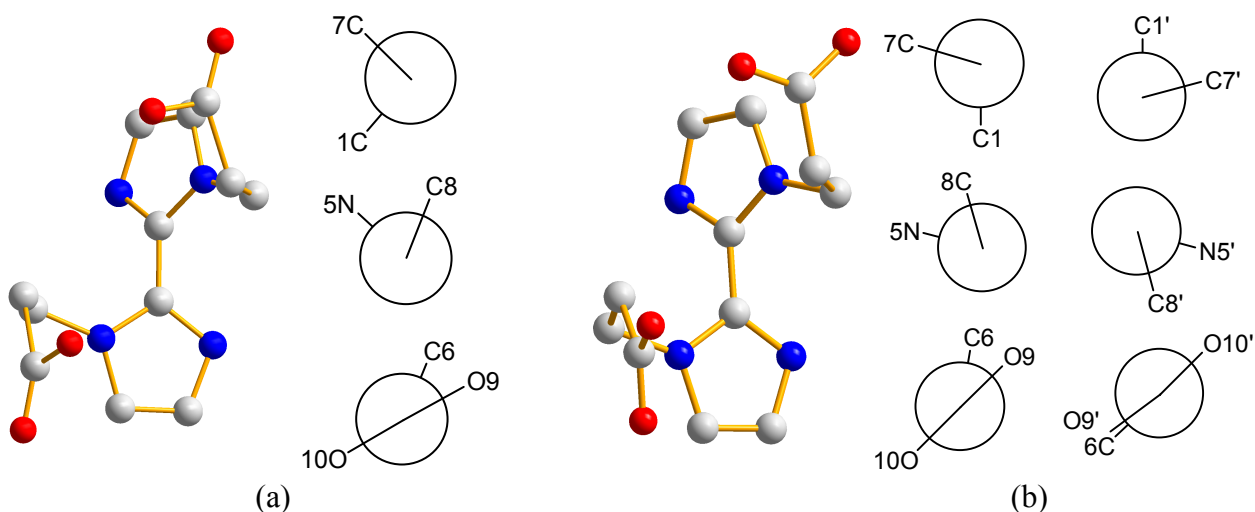
(c)

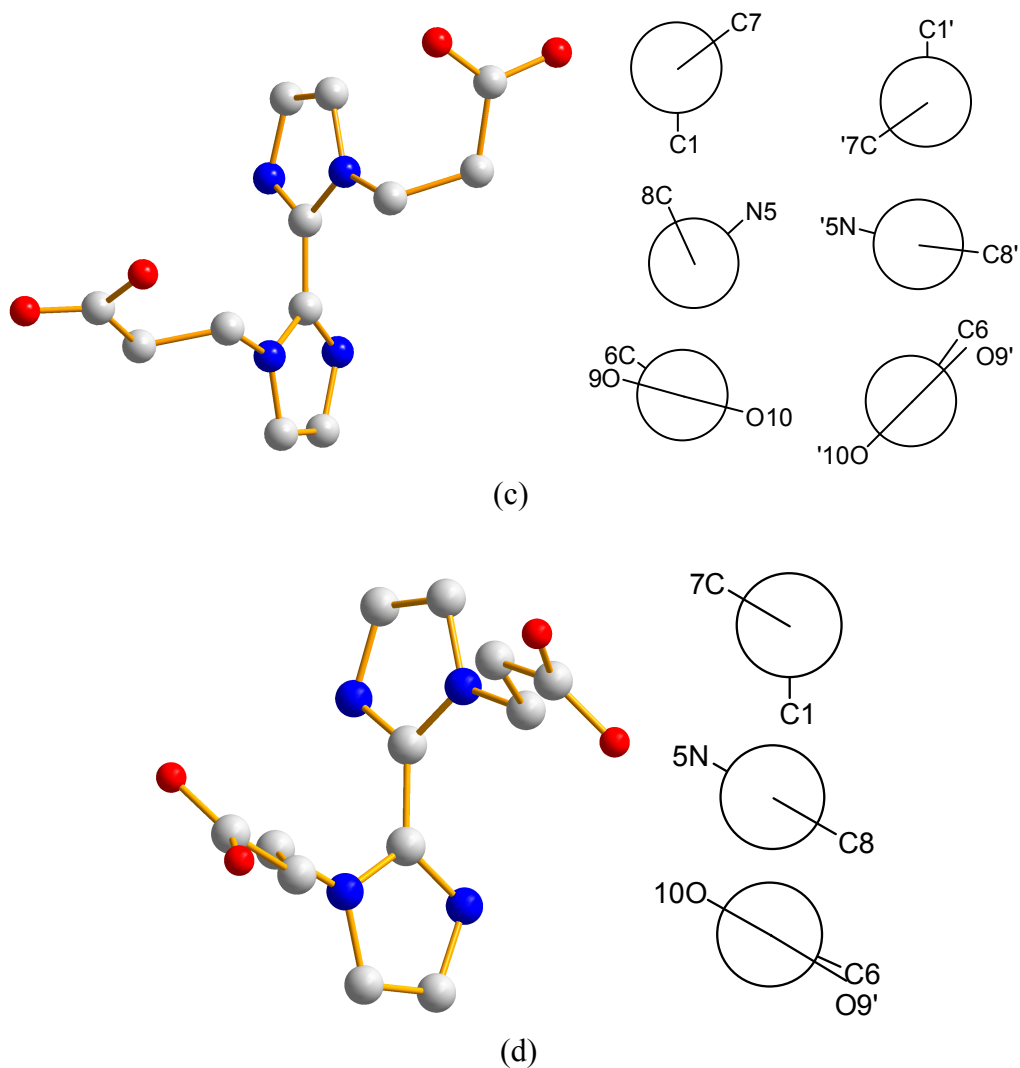
**Fig. S8.** The 3D structure of **3**, (a) the ball-and-stick representation, showing the channels, (b) schematic representation of 3D network with  $(4^3 \cdot 12^3)$  topology, (c) view of a pair of helical water chains (blue and red) along  $c$  direction, L/R: left/right-handed helical tube, respectively.



Achiral, when  $\varphi = 0^\circ$  or  $90^\circ$ ; Chiral, when  $0^\circ < \varphi < 90^\circ$  and  $90^\circ < \varphi < 180^\circ$

**Scheme 1** The configuration of Pra<sub>2</sub>biim<sup>2-</sup>.





**Fig. S9.** The conformation of Pra<sub>2</sub>biim<sup>2-</sup> and the schematic representation of the conformations of the propionate arms. (a) **1**; (b) **2**; (c) **3**; (d) **4**.