Supporting Information for

Host–guest key–lock hydrogen-bonding interactions: A rare case in the design of a V-shaped polycarboxylate Ni(II)-based chiral coordination polymer

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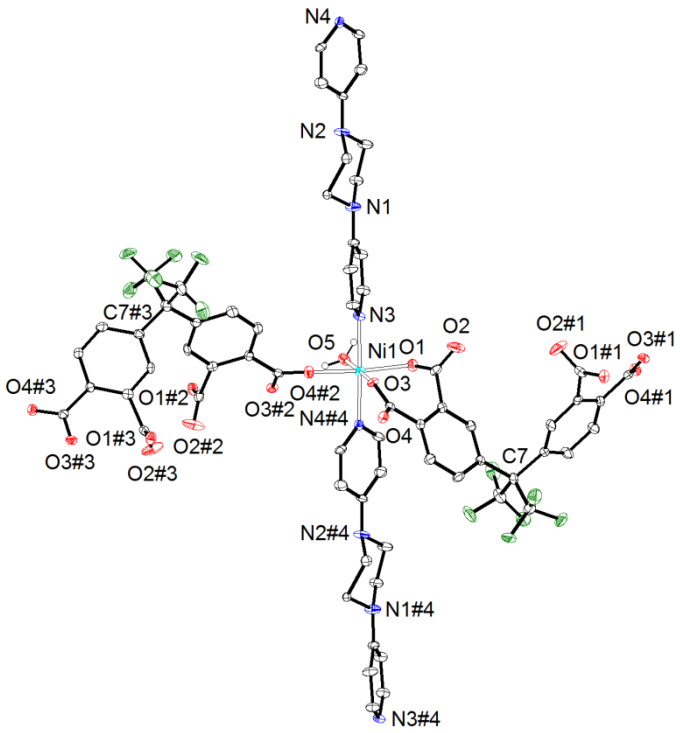
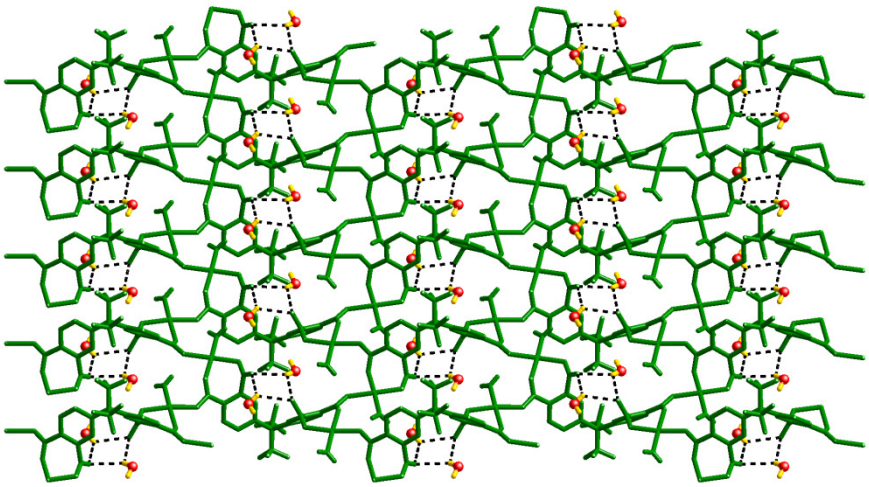
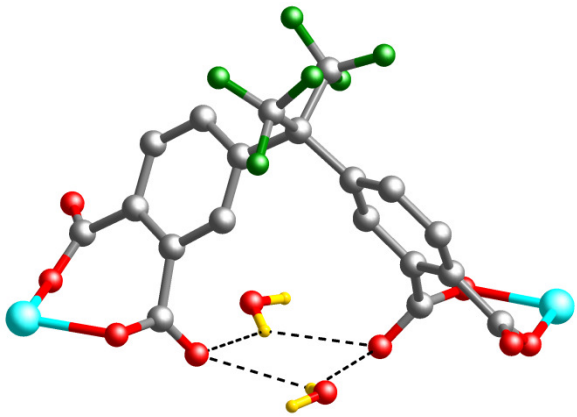


Fig. S1 ORTEP diagram with the atomic numbering scheme, showing the coordination environment for the Ni atom in **1**. Displacement ellipsoids are drawn at the 50% probability level. Disordered minor-occupied atoms, hydrogen atoms and lattice water molecules are omitted for clarity. Selected bond length (Å): Ni1–O3 = 2.052(5), Ni1–O1 = 2.066(4), Ni1–O4#2 = 2.067(4), Ni1–O5 = 2.068(5), Ni1–N4#4 = 2.087(5), Ni1–N3 = 2.106(5). Symmetry codes: #1, $-x + 2$, $-y + 2$, z; #2, $-x + 3/2$, $y - 1/2$, $-z + 2$; #3, $x - 1/2$, $-y + 3/2$, $-z + 2$; #4, x, y, $z + 1$.



(a)



(b)

Fig. S2 (a) View of the hydrogen-bonding interactions between the V-shaped hfdpa ligands and the locked lattice water molecules in **1**. (b) Highlightling the hydrogen-bonding interactions between a single V-shaped hfdpa ligand and two locked lattice water molecules.

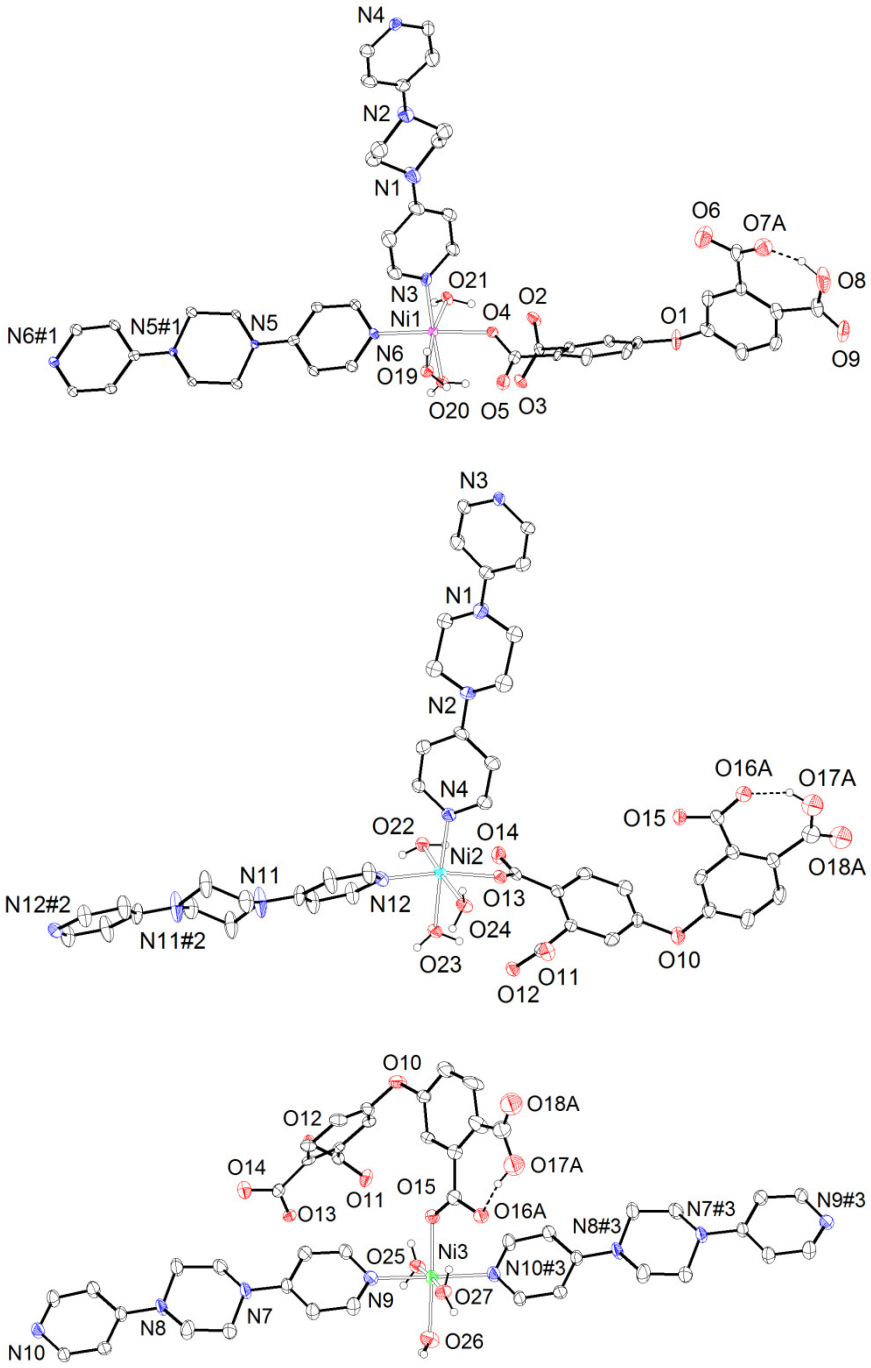


Fig. S3 ORTEP diagrams with the atomic numbering scheme, showing the coordination environments for the crystallographically independent Ni atoms in **2**. Displacement ellipsoids are drawn at the 30% probability level. Disordered minor-occupied atoms, hydrogen atoms and lattice water molecules are omitted for clarity. Selected bond length (Å): Ni1–O4 = 2.034(5), Ni1–O20 = 2.053(4), Ni1–N3 = 2.054(6), Ni1–N6 = 2.064(6), Ni1–O21 = 2.131(5), Ni1–O19 = 2.184(5), Ni2–O13 = 2.035(5), Ni2–N12 = 2.049(7), Ni2–N4 = 2.079(6), Ni2–O22 = 2.097(5), Ni2–O23 = 2.107(5), Ni2–O24 = 2.147(5), Ni3–O27 = 2.071(5), Ni3–O15 = 2.075(6), Ni3–O25 = 2.078(5), Ni3–N9 = 2.086(6), Ni3–N10#3 = 2.101(6), Ni3–O26 = 2.119(6). Symmetry codes: #1, $-x + 2$, $-y$, $-z + 3$; #2, $-x$, $-y + 1$, $-z + 1$; #3, x, $y + 1$, z.

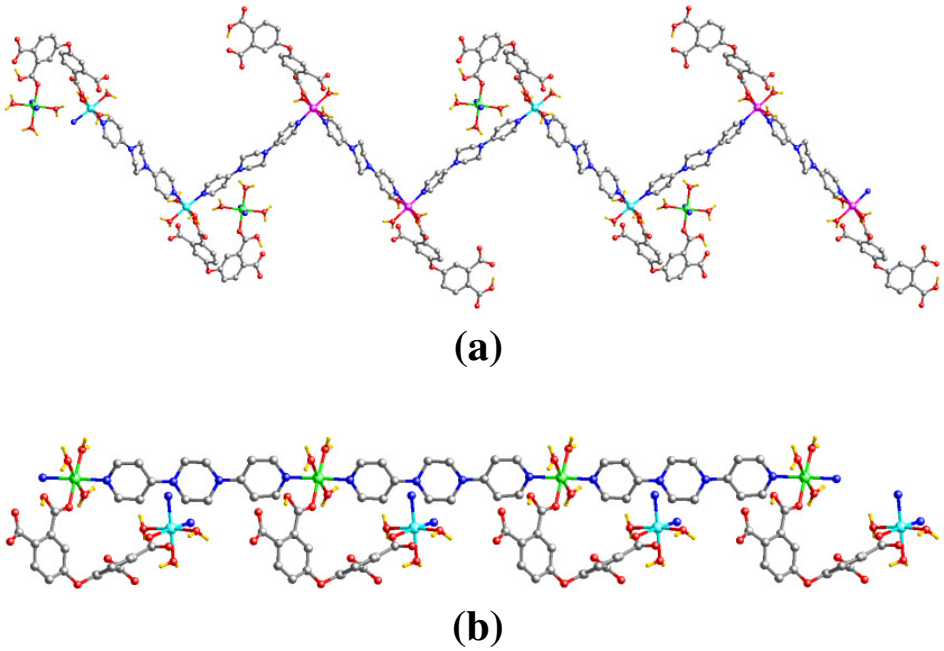


Fig. S4 The two types of infinite one-dimensional Ni–bpypip chain structures in **2**, together with the Ni(1) atoms (pink) bound Hodpa^{L1} arms, the bridged Hodpa^{L2} ligands connected to Ni(2) (cyan) and Ni(3) atoms (green), and the aqua ligands: (a) the zigzag manner of Ni–bpypip chain; (b) the linear manner of Ni–bpypip chain.

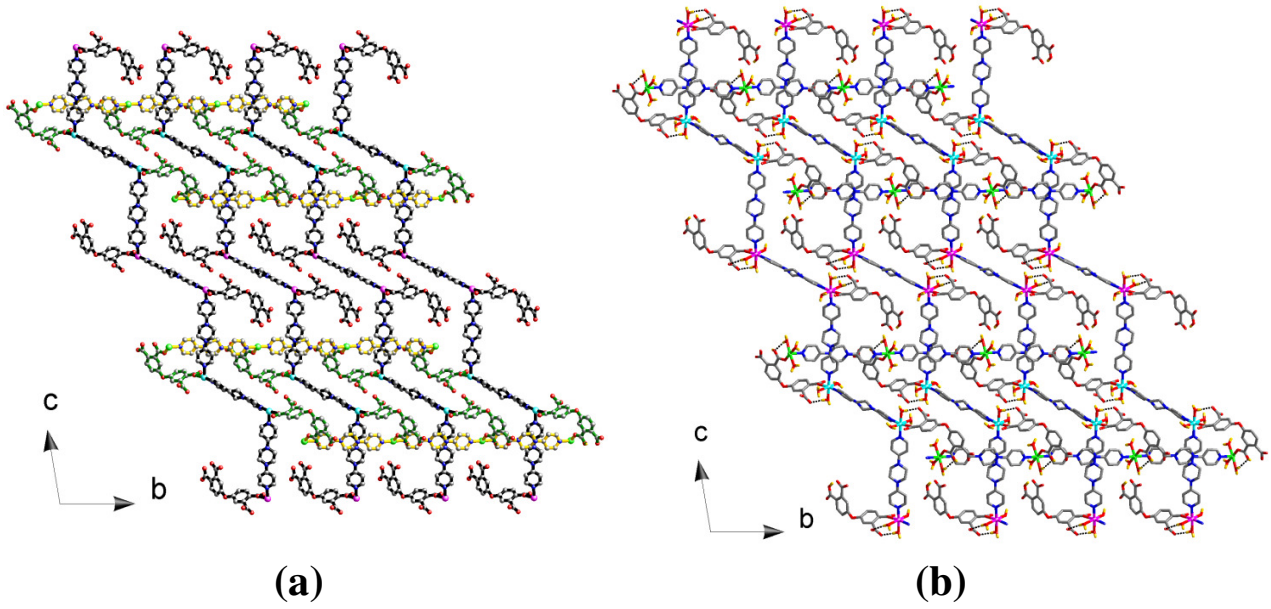
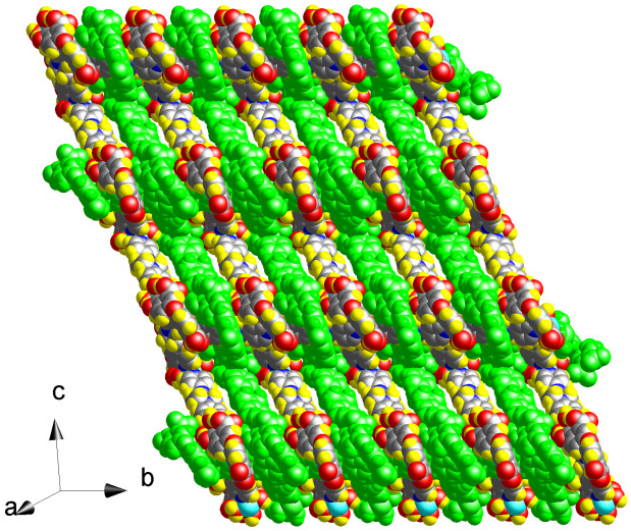
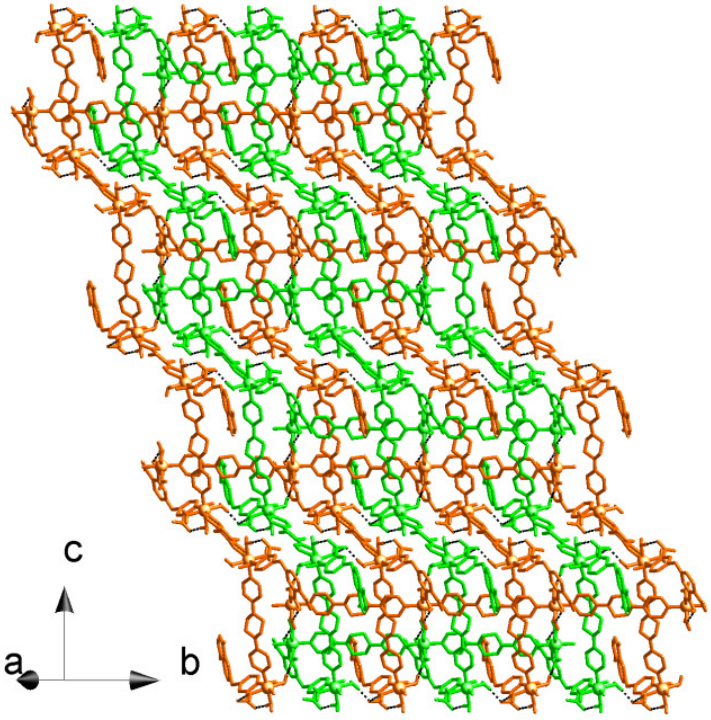


Fig. S5 (a) Perspective view of the two-dimensional sheet structure in **2**, showing that the one-dimnesional Ni–bpypip zigzag (black lines) and linear (yellow lines) chains are interconnected by Hodpa^{L2} bridging ligands (green lines). The aqua ligands and hydrogen atoms are omitted for clarity. (a) Space-filling representation of the two-dimensional sheet structure, showing large obliquely shaped cavities in **2**. (a) Hydrogen-bonding interactions (dashed lines) within a single sheet structure in **2**. Color scheme: pink, Ni(1); cyan, Ni(2); green, Ni(3); red, O; blue, N; gray, C; yellow, H.



(a)



(b)

Fig. S6 (b) Space-filling representation of the 2D + 2D → 2D interwoven sheet structures in **2**. (b) Intra- and inter-sheet hydrogen-bonding interactions (dashed lines) within a set of 2D + 2D → 2D interwoven sheets in **2**.

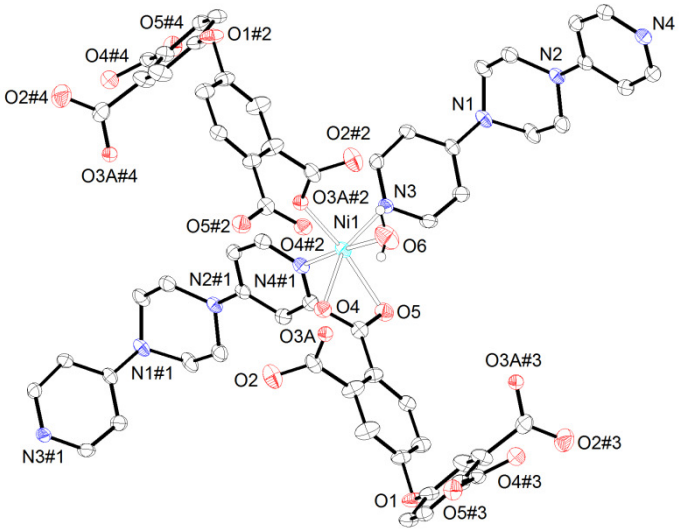


Fig. S7 ORTEP diagram with the atomic numbering scheme, showing the coordination environment for the Ni atom in **3**. Displacement ellipsoids are drawn at the 20% probability level. Disordered minor-occupied atoms, hydrogen atoms and lattice water molecules are omitted for clarity. Selected bond length (Å): Ni1–N3 = 2.036(4), Ni1–N4#1 = 2.076(5), Ni1–O3A#2 = 1.987(6), Ni1–O4 = 2.132(4), Ni1–O5 = 2.144(5), Ni1–O6 = 2.228(6). Symmetry codes: #1, $x + 1/2$, $y - 1/2$, z; #2, $-x + 1/2$, $-y + 3/2$, $-z$; #3, $-x$, y, $-z - 1/2$; #4, $x + 1/2$, $-y + 3/2$, $z + 1/2$.

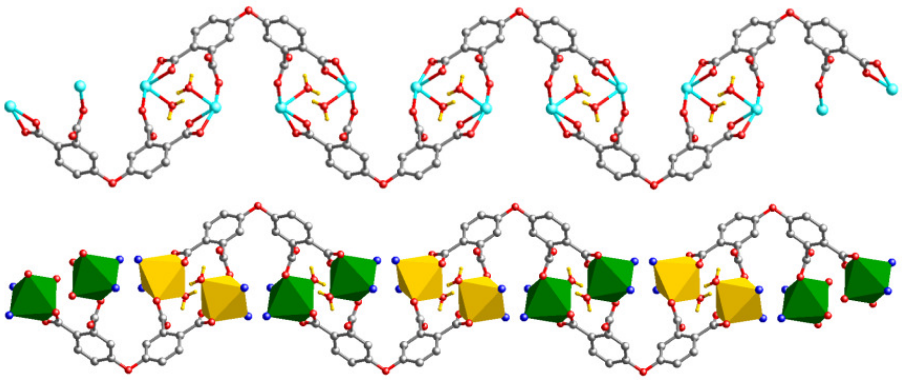


Fig. S8 Perspective views of the one-dimensional wavelike Ni–odpa chain structure in **3**.

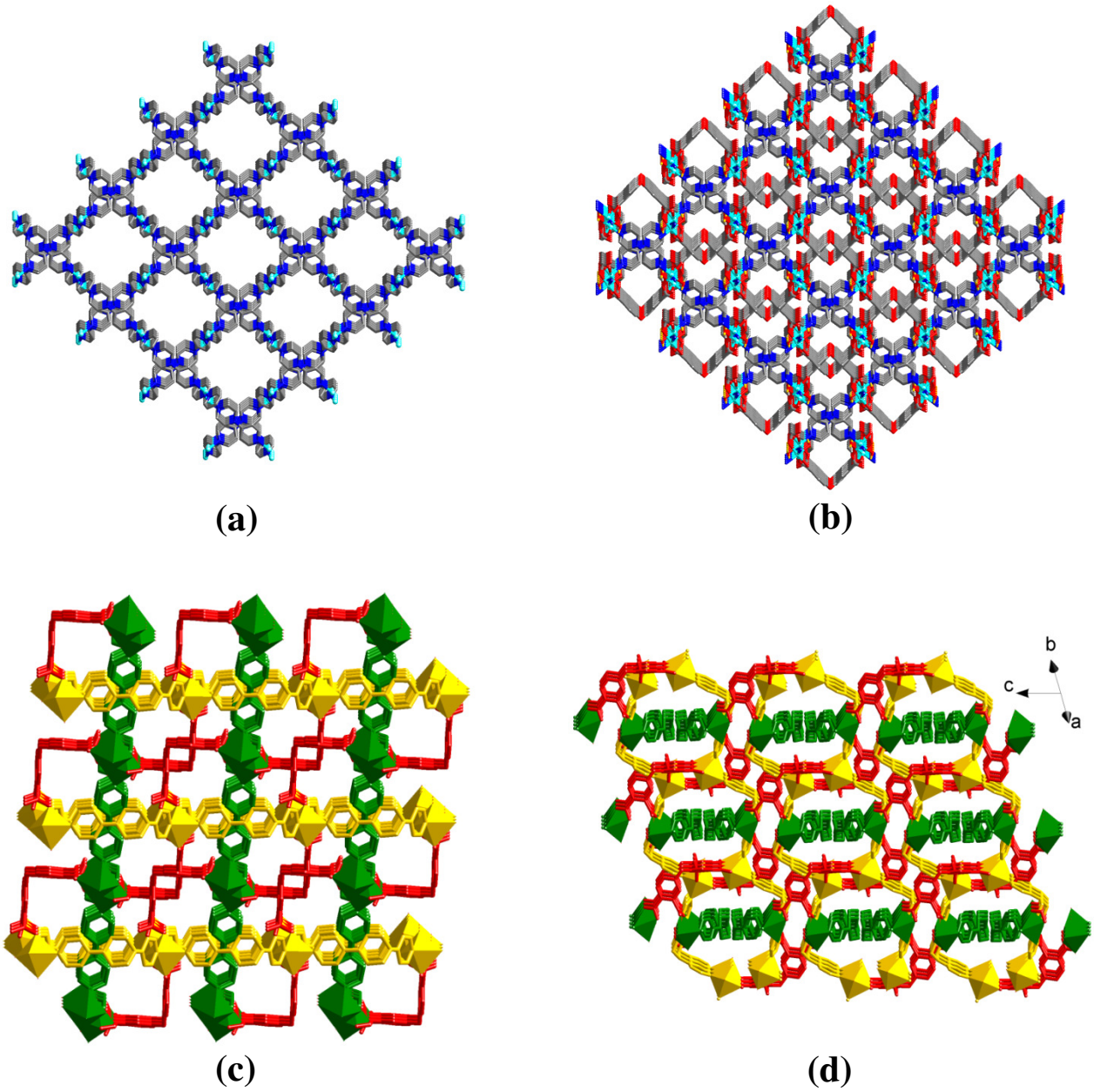


Fig. S9 (a) Packing arrangement of the wavelike Ni–bpypip chains in **3**, showing the open channels along the crystallographic [001] direction. (b) The complicated three-dimensional framework in **3** viewed down and slightly off the crystallographic [001] direction; the open channels are occupied by the odpa ligands. (c) The complicated three-dimensional framework in **3** viewed down the crystallographic [001] direction. (d) The complicated three-dimensional framework in **3** viewed down the crystallographic [110] direction.

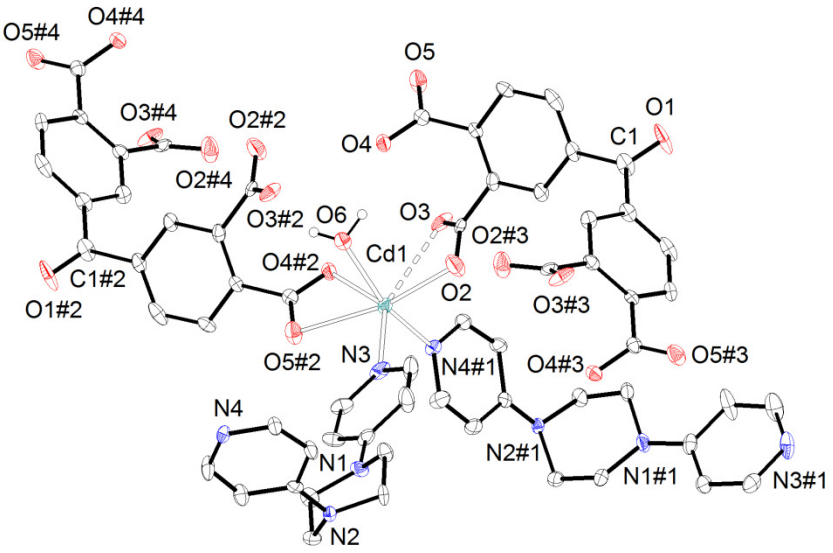


Fig. S10 ORTEP diagram with the atomic numbering scheme, showing the coordination environment for the Cd atom in **4**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms and lattice water molecules are omitted for clarity. Selected bond length (Å): Cd1–N4#1 = 2.258(7), Cd1–N3 = 2.309(7), Cd1–O6 = 2.348(6), Cd1–O2 = 2.376(7), Cd1–O4#2 = 2.400(6), Cd1–O5#2 = 2.481(6). Weak coordination of Cd1–O3 (2.708 Å) is drawn with empty dashed bond. Symmetry codes: #1, $x - 1/2$, $y - 1/2$, $-z + 1/2$; #2, $-x + 2$, $-y$, $-z$; #3, $2 - x$, y, $-z + 1/2$; #4, x, $-y$, $z - 1/2$.

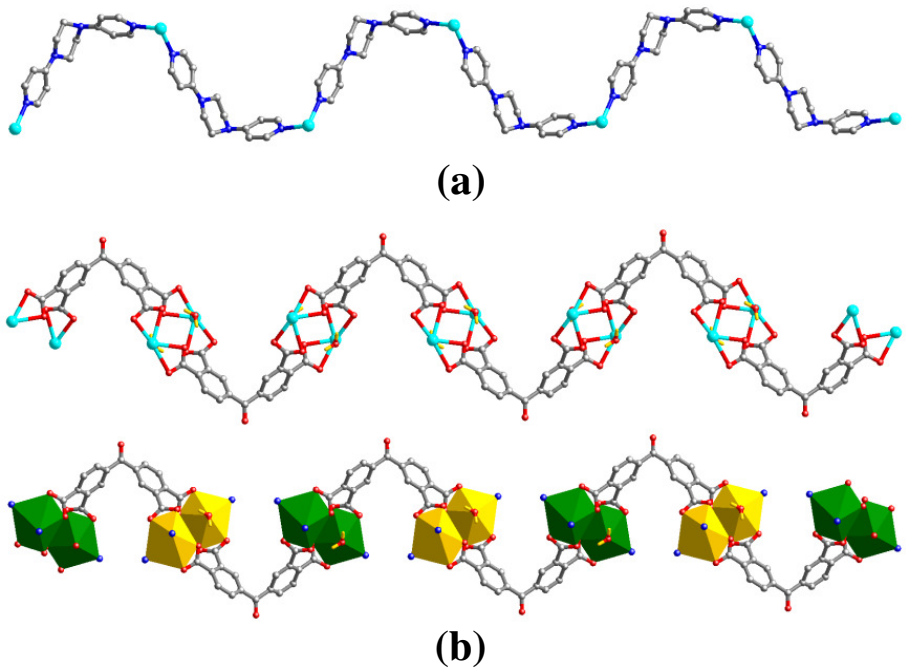
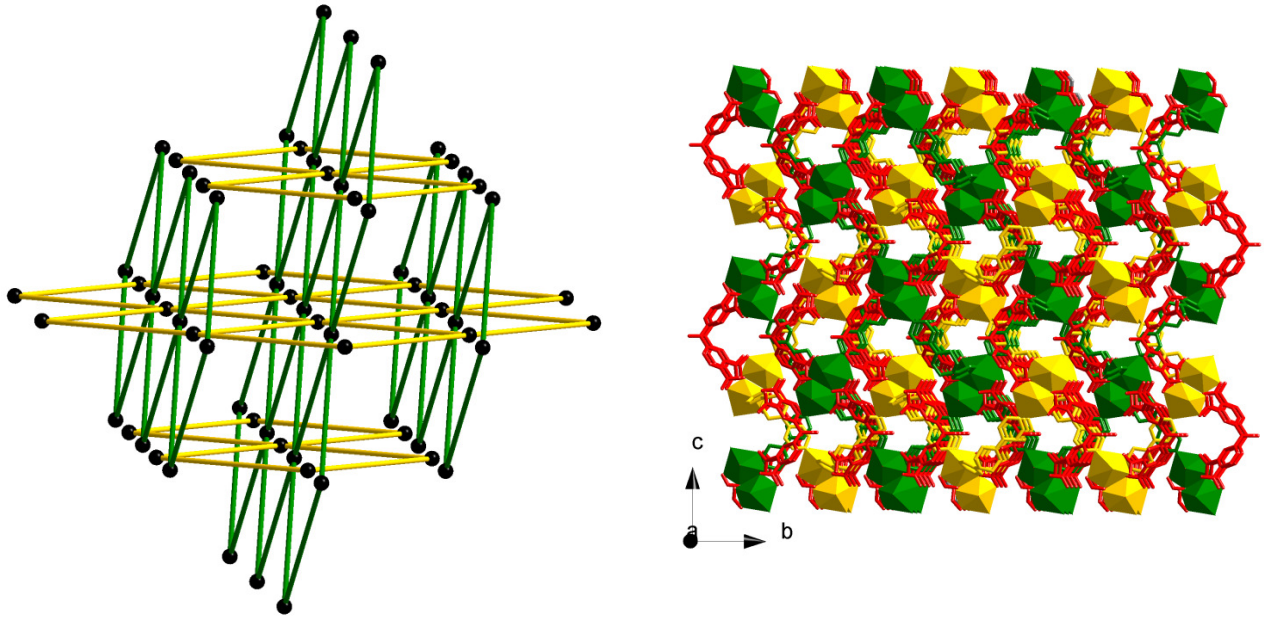


Fig. S11 (a) Perspective view of the one-dimensional wavelike Cd–bpypip chain structure in **4**. (b) Perspective views of the one-dimensional wavelike Cd–bptc chain structure in **4**.



(a) **(b)**

Fig. S12 (a) Schematic representation of the 2D + 2D → 3D interpenetrating coordination polymer entanglement in **4**. (b) The complicated three-dimensional framework in **4** viewed down slight off the crystallographic [100] direction.

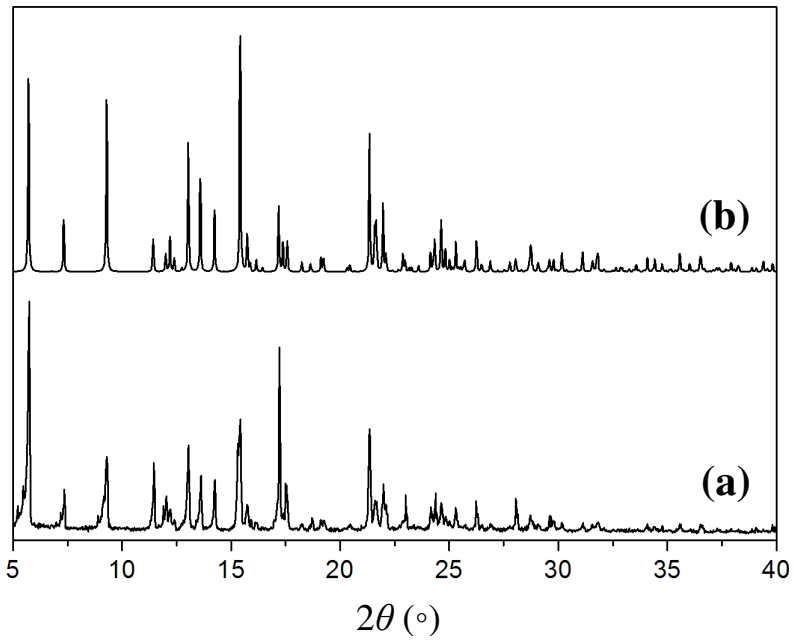


Fig. S13 X-Ray powder diffraction (XRPD) patterns of **1**: (a) a freshly grounded sample at room temperature; (b) simulated from the single-crystal data.

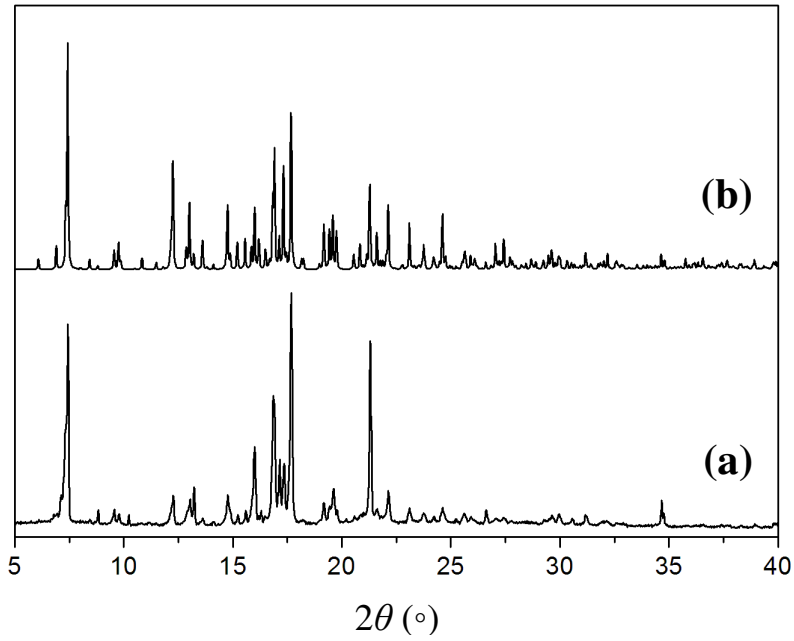


Fig. S14 X-Ray powder diffraction (XRPD) patterns of **2**: (a) a freshly grounded sample at room temperature; (b) simulated from the single-crystal data. The sample of compound **2** was contained a small amount of compound **3**, making the experimental and simulated XRPD patterns do not fit quite well.

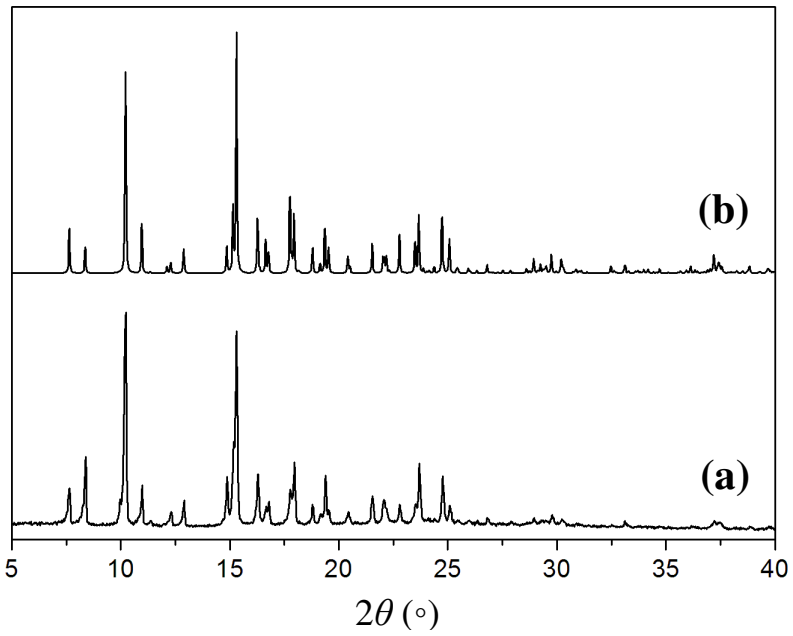


Fig. S15 X-Ray powder diffraction (XRPD) patterns of **3**: (a) a freshly grounded sample at room temperature; (b) simulated from the single-crystal data.

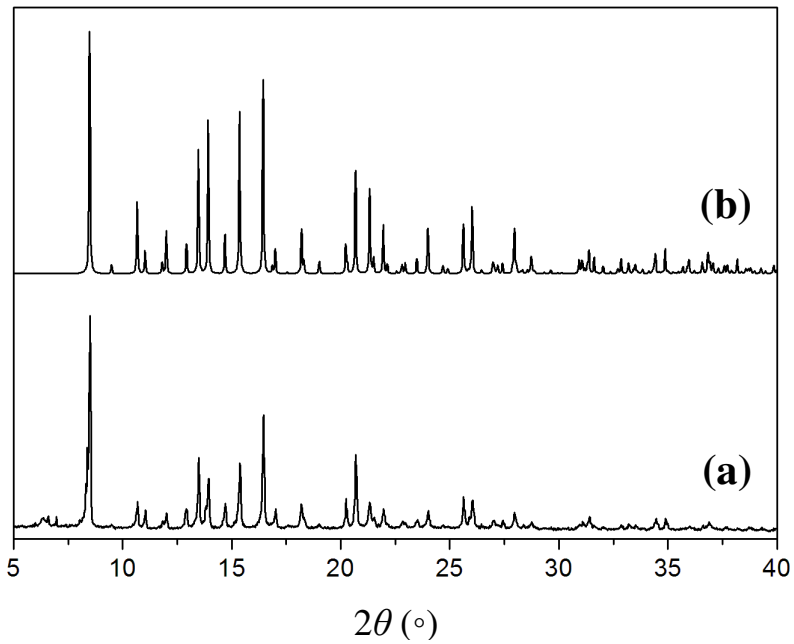


Fig. S16 X-Ray powder diffraction (XRPD) patterns of **4**: (a) a freshly grounded sample at room temperature; (b) simulated from the single-crystal data.

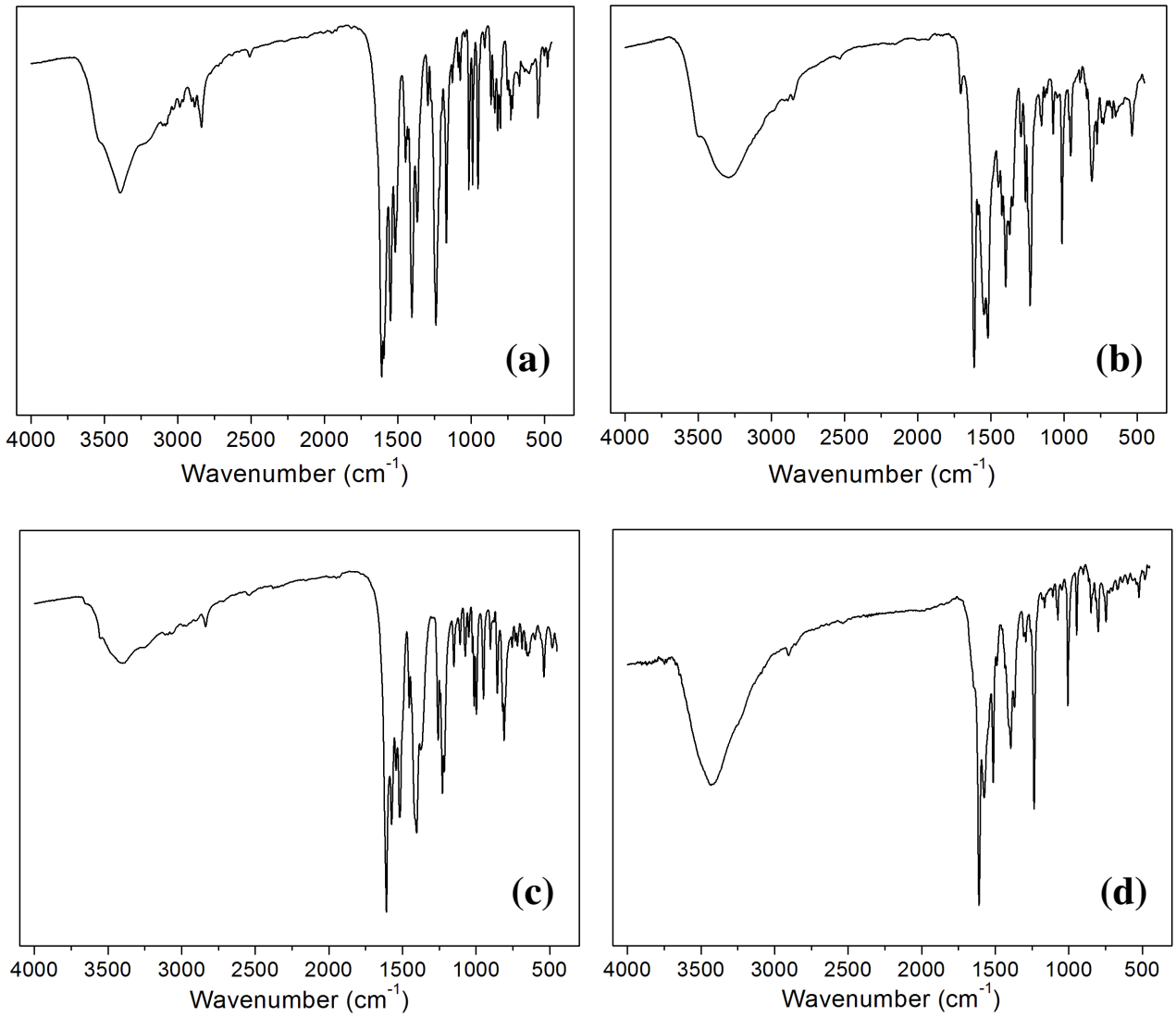


Fig. S17 Infrared (IR) spectra of (a–d) **1**–**4**.

Table S1 Hydrogen bonding parameters for compounds **1**–**4**

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
1				
O5–H101···O6#1	0.84	1.98	2.751(7)	153
O5–H102···O4#1	0.83	2.00	2.817(6)	166
O5–H102···O3#2	0.83	2.58	3.108(6)	123
O6–H103···O7	0.86	2.24	3.096(7)	174
O6–H104···O2	0.85	2.23	2.822(9)	127
O7–H105···O1#3	0.85	2.34	2.849(7)	119
C6–H6···F3#4	0.93	2.36	3.010(9)	126
C15–H15···O5	0.93	2.56	3.079(9)	115
C16–H16···N6#5	0.93	2.53	3.381(11)	153
C19–H19···O3	0.93	2.45	2.997(8)	118
C26–H26A···O7#6	0.97	2.55	3.123(16)	118
C30–H30···O2#7	0.93	2.42	3.264(9)	151
2				
O8–H101···O7A	0.99	1.40	2.352(17)	160
O17A–H10A···O16A	0.85	1.72	2.472	145
O17B–H10B···O16B	0.87	1.79	2.611	156
O17A–H10A···O16B	0.85	1.66	2.475	160
O17B–H10B···O16A	0.87	1.52	2.382	169
O19–H103···O25#1	0.79	2.20	2.799(6)	134
O19–H104···O5	0.85	1.93	2.607(7)	136
O20–H105···O2#2	0.85	1.92	2.720(8)	157
O20–H106···O3	0.86	1.96	2.812(7)	173
O21–H107···O3#2	0.88	1.93	2.752(6)	156
O21–H108···O2	0.87	2.27	3.141(7)	174
O22–H109···O14	0.85	1.85	2.673(8)	163
O22–H110···O2#3	0.85	1.99	2.830(7)	168
O23–H111···O12	0.85	1.96	2.809(7)	172
O23–H112···O11#4	0.84	2.00	2.816(8)	164
O24–H113···O12#4	0.85	1.95	2.795(7)	174
O25–H115···O9#5	0.86	1.92	2.706(9)	153
O25–H116···O19#1	0.79	2.40	2.799(6)	113
O26–H117···O8#5	0.88	2.18	3.051(11)	176
O26–H118···O7A#6	0.87	2.09	2.758(14)	133
O27–H119···O16A	0.86	2.16	2.852(12)	138
O27–H120···O6#6	0.85	1.94	2.783(9)	172
3				
O6–H101···O2	0.83	1.66	2.416(9)	151
O6–H102···O3B	0.86	2.87	3.700	162
4				
O6–H101···O4	0.85	2.01	2.762(8)	147
O6–H102···O3#1	0.85	1.87	2.677(9)	157
O7–H103···O2#2	0.82	2.39	3.144(18)	152

Symmetry code: For **1**: #1, *x*, *y* + 1, *z*; #2, –*x* + 1/2, *y* + 1/2, –*z*; #3, *x*, *y* – 1, *z*; #4, –*x* + 1, –*y* + 1, *z*; #5, –*x* + 1/2, *y* + 3/2, –*z* + 1; #6, *x* – 1/2, –*y* + 1/2, –*z* + 1; #7, –*x* + 1/2, *y* –1/2, –*z* + 1. For **2**: #1, –*x*, –*y* + 2, –*z*; #2, –*x* – 1, –*y* + 1, –*z* – 1; #3, –*x*, –*y* + 1, –*z*; #4, –*x* + 1, –*y* + 2, –*z* + 1; #5, –*x* – 1, –*y* + 1, –*z*; #6, *x* + 1, *y* + 1, *z*. For **4**: #1, –*x*, –*y*, –*z* + 1; #2, *x* + 1/2, *y* + 1/2, –*z* + 1/2.