Supporting Information for Crystal Growth & Design

Homochiral Metal–Organic Frameworks of Lead(II) and Cadmium(II) Constructed by Amino Acid-Functionalized Isophthalic Acid: Synthesis, Structure Diversity, and Optical Properties

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Table S1. Selected Bond Lengths (Å) and Angles (°) for 1−4

1			
Pb1−O2A	2.494(18)	Pb1−O3	2.515(9)
Pb1−O6B	2.563(17)	Pb1−O4	2.577(15)
Pb1−O1A	2.635(16)	Pb1−O5B	2.719(14)
Pb2−O7C	2.516(17)	Pb2−O10	2.519(15)
Pb2−O11D	2.523(15)	Pb2−O8C	2.676(16)
Pb2−O12D	2.703(14)	Pb2−O9	2.704(12)
O2A−Pb1−O3	127.7(5)	O2A−Pb1−O6B	80.6(7)
O3−Pb1−O6B	84.8(7)	O2A−Pb1−O4	76.8(5)
O3−Pb1−O4	51.9(4)	O6B−Pb1−O4	84.1(6)
O2A−Pb1−O1A	49.8(5)	O3−Pb1−O1A	161.5(4)
O6B−Pb1−O1A	76.7(7)	O4− Pb1−O1A	125.1(4)
O2A−Pb1−O5B	117.3(8)	O3−Pb1−O5B	87.1(9)
O6B−Pb1−O5B	48.9(5)	O4−Pb1−O5B	122.1(7)
O1A−Pb1−O5B	80.5(9)	O7C−Pb2−O10	74.1(5)
O7C−Pb2−O11D	80.4(6)	O10− Pb2−O11D	85.5(5)
O7C−Pb2−O8C	51.6(5)	O10−Pb2−O8C	125.5(4)
O11D−Pb2−O8C	83.1(6)	O7C−Pb2−O12D	118.9(7)

O10−Pb2−O12D	123.2(6)	O11D−Pb2−O12D	49.0(4)
O8C−Pb2−O12D	86.0(7)	O7C−Pb2−O9	118.4(5)
O10−Pb2−O9	49.0(4)	O11D−Pb2−O9	74.4(6)
O8C−Pb2−O9	157.0(4)	O12D−Pb2−O9	82.8(7)
		2	
Pb1−O4A	2.45(2)	Pb1−O1	2.47(2)
Pb1−O3A	2.51(2)	Pb1−O6B	2.54(2)
Pb1−O2	2.66(2)	Pb1−O5B	2.73(2)
Pb2−O12C	2.41(2)	Pb2−O10A	2.53(2)
Pb2−O7	2.53(2)	Pb2−O8	2.655(19)
Pb2−O11C	2.69(2)	O4A−Pb1−O1	76.8(7)
O4A−Pb1−O3A	50.1(7)	O1−Pb1−O3A	126.5(7)
O4A−Pb1−O6B	81.8(8)	O1−Pb1−O6B	83.6(7)
O3A−Pb1−O6B	82.7(8)	O4A−Pb1−O2	123.2(7)
O1−Pb1−O2	49.1(7)	O3A−Pb1−O2	159.6(7)
O6B−Pb1−O2	77.1(7)	O4A−Pb1−O5B	119.0(8)
O1−Pb1−O5B	121.2(8)	O3A− Pb1−O5B	85.3(8)
O6B−Pb1−O5B	49.1(6)	O2− Pb1−O5B	83.4(8)
O12C−Pb2−O10A	81.4(7)	O12C−Pb2−O7	79.9(8)
O10A−Pb2−O7	74.2(6)	O12C−Pb2−O8	79.6(8)
O10A−Pb2−O8	125.2(6)	O7−Pb2−O8	52.0(6)
O12C−Pb2−O11C	50.2(7)	O10A−Pb2−O11C	121.8(6)
O7−Pb2−O11C	117.6(7)	O8−Pb2−O11C	80.8(7)
		3	
Cd1−O11A	2.268(10)	Cd1−O7	2.328(11)
Cd1−N2B	2.339(11)	Cd1−O1	2.351(10)
Cd1−O12B	2.368(10)	Cd1−O2	2.461(10)
Cd2−O4	2.288(12)	Cd2−O14	2.289(14)
Cd2−O9	2.297(10)	Cd2−N1C	2.302(12)

Cd2−O6C	2.403(11)	Cd2−O3	2.444(11)
Cd2−O8	2.645(12)	Cd3−O5D	2.164(12)
Cd3−O15	2.230(13)	Cd3−O13	2.264(14)
Cd3−O16	2.324(14)	Cd3−O17	2.381(13)
Cd3−O12	2.647(9)	Cd4−O20C	2.268(11)
Cd4−O24	2.339(11)	Cd4−N3	2.342(11)
Cd4−O28E	2.362(12)	Cd4−O18	2.365(14)
Cd4−O27E	2.457(13)	Cd4−O22	2.306(10)
Cd5−N4C	2.338(13)	Cd5−O25	2.359(13)
Cd5−O31	2.375(11)	Cd5−O29C	2.380(12)
Cd5−O26	2.429(12)	Cd5−O23	2.549(11)
Cd6−O19F	2.131(16)	Cd6−O34	2.189(14)
Cd6−O32	2.29(3)	Cd6−O29	2.334(10)
Cd6−O33	2.41(2)	Cd6−O35	2.46(2)
O11A−Cd1−O7	89.1(5)	O11A− Cd1−N2B	141.9(3)
O7−Cd1−N2B	90.4(4)	O11A−Cd1−O1	85.7(3)
O7−Cd1−O1	90.4(4)	N2B−Cd1−O1	132.5(4)
O11A−Cd1−O12B	91.4(4)	O7−Cd1−O12B	151.4(4)
N2B−Cd1−O12B	72.0(4)	O1−Cd1−O12B	118.2(4)
O11A−Cd1−O2	138.9(3)	O7−Cd1−O2	86.2(4)
N2B−Cd1−O2	79.0(4)	O1−Cd1−O2	53.6(3)
O12B−Cd1−O2	111.3(4)	O4−Cd2−O14	92.4(5)
O4−Cd2−O9	83.9(4)	O14−Cd2−O9	90.8(6)
O4−Cd2−N1C	143.2(4)	O14−Cd2−N1C	95.6(5)
O9−Cd2−N1C	131.7(4)	O4−Cd2−O6C	110.1(5)
O14−Cd2−O6C	155.2(5)	O9−Cd2−O6C	81.7(4)
N1C−Cd2−O6C	72.9(4)	O4−Cd2−O3	55.0(4)
O14−Cd2−O3	93.6(6)	O9−Cd2−O3	138.8(4)

N1C−Cd2−O3	88.6(4)	O6C−Cd2−O3	107.7(5)
O4−Cd2−O8	134.9(4)	O14−Cd2−O8	79.6(5)
O9−Cd2−O8	52.3(4)	N1C−Cd2−O8	81.9(4)
O6C−Cd2−O8	77.0(4)	O3−Cd2−O8	167.7(4)
O5D−Cd3−O15	123.5(6)	O5D−Cd3−O13	117.8(5)
O15−Cd3−O13	88.3(7)	O5D−Cd3−O16	137.2(5)
O15−Cd3−O16	91.7(6)	O13−Cd3−O16	83.2(5)
O5D−Cd3−O17	81.9(5)	O15−Cd3−O17	83.6(7)
O13−Cd3−O17	159.7(5)	O16−Cd3−O17	78.5(6)
O5D−Cd3−O12	82.7(4)	O15−Cd3−O12	75.7(4)
O13−Cd3−O12	52.5(3)	O16−Cd3−O12	133.6(4)
O17−Cd3−O12	141.3(5)	O20C−Cd4−O24	84.2(4)
O20C−Cd4−N3	141.6(4)	O24−Cd4−N3	94.2(4)
O20C−Cd4−O28E	136.8(4)	O24−Cd4−O28E	89.8(5)
N3−Cd4−O28E	81.4(4)	O20C−Cd4−O18	94.2(5)
O24−Cd4−O18	155.2(4)	N3−Cd4−O18	71.8(4)
O28E−Cd4−O18	107.6(5)	O20C−Cd4−O27E	84.3(4)
O24−Cd4−O27E	98.0(5)	N3−Cd4−O27E	133.6(4)
O28E−Cd4−O27E	54.2(4)	O18−Cd4−O27E	106.4(5)
O22−Cd5−N4C	135.8(4)	O22−Cd5−O25	87.1(4)
N4C−Cd5−O25	134.1(5)	O22−Cd5−O31	84.7(4)
O4C−Cd5−O31	97.0(5)	O25−Cd5−O31	103.8(5)
O22−Cd5−O29C	88.8(4)	N4C−Cd5−O29C	73.4(4)
O25−Cd5−O29C	96.8(5)	O31−Cd5−O29C	158.0(5)
O22−Cd5−O26	132.1(4)	N4C−Cd5−O26	91.2(4)
O25−Cd5−O26	53.9(4)	O31−Cd5−O26	80.1(4)
O29C−Cd5−O26	119.1(4)	O22−Cd5−O23	53.7(4)
N4C−Cd5−O23	82.9(4)	O25−Cd5−O23	140.3(4)
O31−Cd5−O23	80.5(4)	O29C−Cd5−O23	78.7(5)

O26−Cd5−O23	158.8(4)	O19F−Cd6−O34	94.3(13)
O19F−Cd6−O32	160.8(10)	O34−Cd6−O32	94.6(14)
O19F−Cd6−O29	94.6(5)	O34−Cd6−O29	110.8(11)
O32−Cd6−O29	98.1(8)	O19F−Cd6−O33	79.7(8)
O34−Cd6−O33	88.0(12)	O32−Cd6−O33	83.6(10)
O29−Cd6−O33	160.9(6)	O19F−Cd6−O35	84.6(8)
O34−Cd6−O35	163.9(12)	O32−Cd6−O35	82.2(10)
O29−Cd6−O35	85.3(6)	O33−Cd6−O35	76.0(7)
		4	
Pb1−O5	2.462(7)	Pb1−O3A	2.509(6)
Pb1−O4A	2.558(7)	Pb1−O1B	2.575(7)
Pb1−O2C	2.692(6)	O5−Pb1−O3A	103.3(2)
O5−Pb1−O4A	80.4(3)	O3A−Pb1−O4A	50.9(2)
O5−Pb1−O1B	124.1(3)	O3A−Pb1−O1B	95.3(3)
O4A−Pb1−O1B	71.9(3)	O5−Pb1−O2C	68.5(2)
O3A−Pb1−O2C	73.7(2)	O4A−Pb1−O2C	106.4(2)
O1B−Pb1−O2C	165.6(2)		

Symmetry codes: (A) *x*, *y* + 1, *z*; (B) *x* − 1/2, *y* + 1/2, *z*; (C) *x*, *y* −1, *z*; (D) *x* + 1/2, *y* −1/2, *z* for **1**. (A) *x* + 1, *y*, *z*; (B) *x*, *y* −1, *z*; (C) *x* + 1, *y* + 1, *z*; (D) *x* − 1, *y*, *z*; (E) *x*, *y* + 1, *z*; (F) *x* – 1, *y* −1, *z* for **2**. (A) *x* + 1, *y*, *z*; (B) *x* + 1, *y* − 1, *z*; (C) *x*, *y* + 1, *z*; (D) – *x* + 1, *y* + 3/2, −*z* + 1; (E) *x* + 1, *y* + 1, *z*; (F) – *x* + 2, *y* −3/2, −*z* + 2 (G) – *x* + 1, *y* – 3/2, –*z* + 1; (H) *x*, *y*–1, *z;* (I) *x* – 1, *y*, *z*; (J) *x* – 1, *y* + 1, *z*; (K) – *x* + 2, *y* + 3/2, – *z* + 2; (L) *x* – 1, *y* – 1, *z* for **3**. (A) − *x*, *y* + 1/2, − z + 1/2; (B) *x* + 1/2, − *y* + 3/2, − *z* + 1; (C) *x* + 1, *y*, *z*; (D) *x* − 1/2, − *y* + 3/2, − *z* + 1; (E) *x* − 1, *y*, *z*; (F) − *x*, *y* − 1/2, − *z* + 1/2 for **4**.

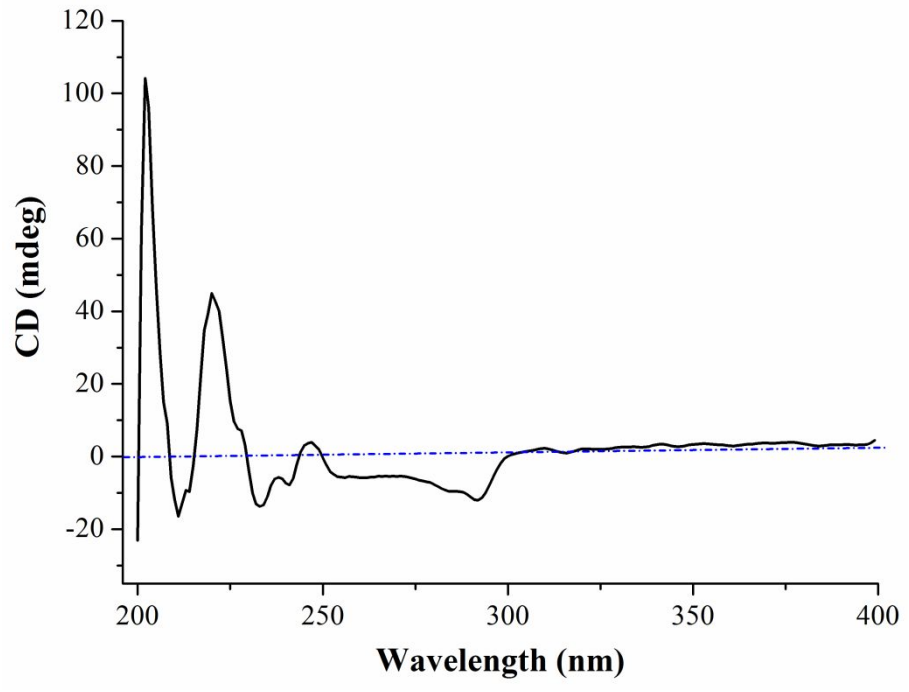

Figure S1. Solid-state CD spectra of H_3L^2 ligand in KBr.

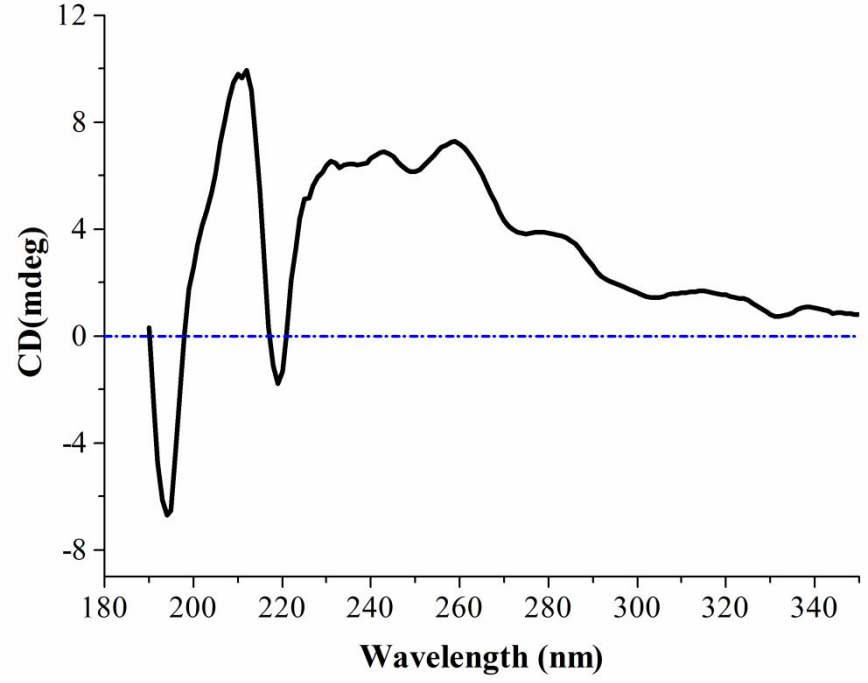

Figure S2. Solid-state CD spectra of H_3L^3 ligand in KBr.

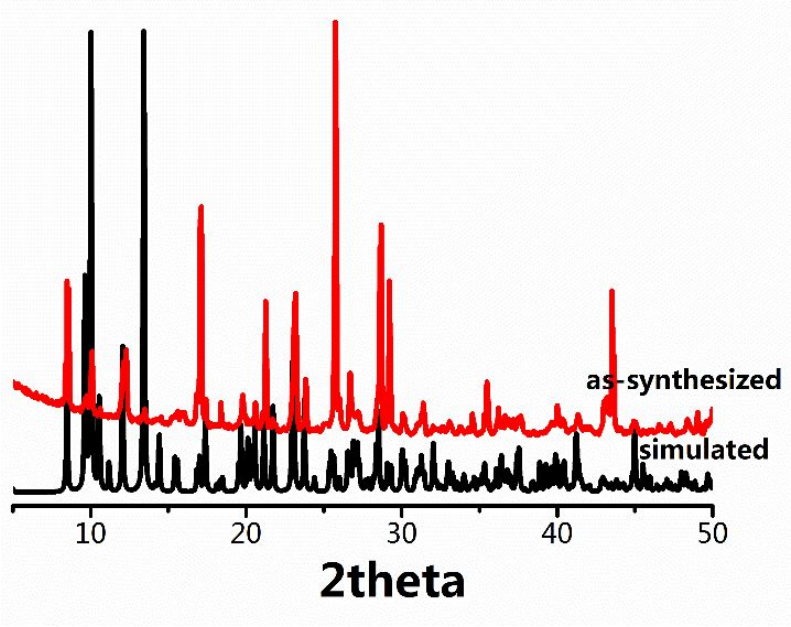

Figure S3. As-synthesized and simulated PXRD patterns of compound **1**.

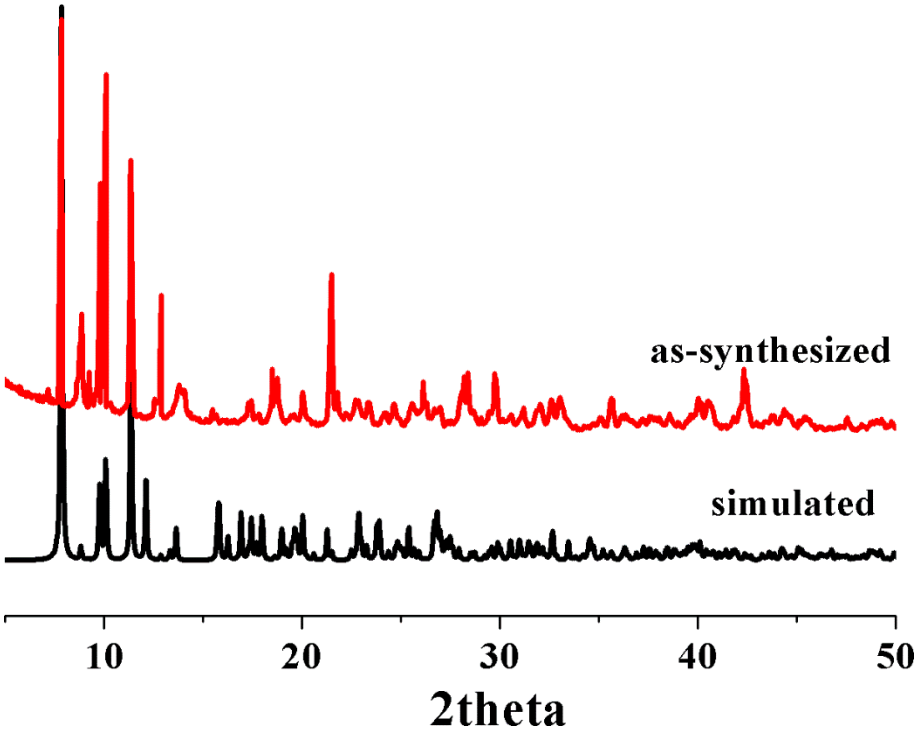

Figure S4. As-synthesized and simulated PXRD patterns of compound **2**.

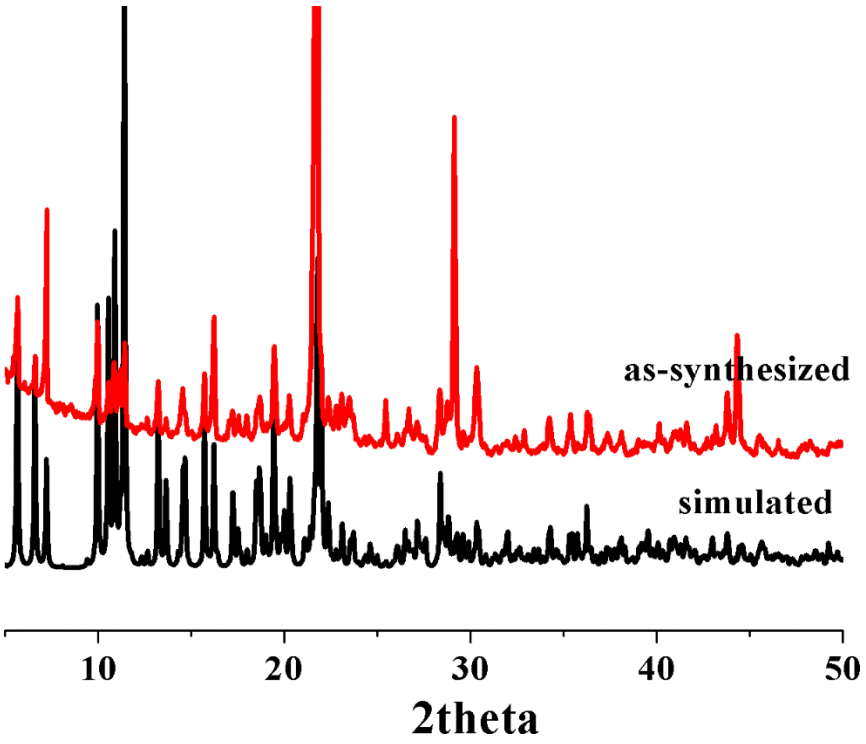

Figure S5. As-synthesized and simulated PXRD patterns of compound **3**.

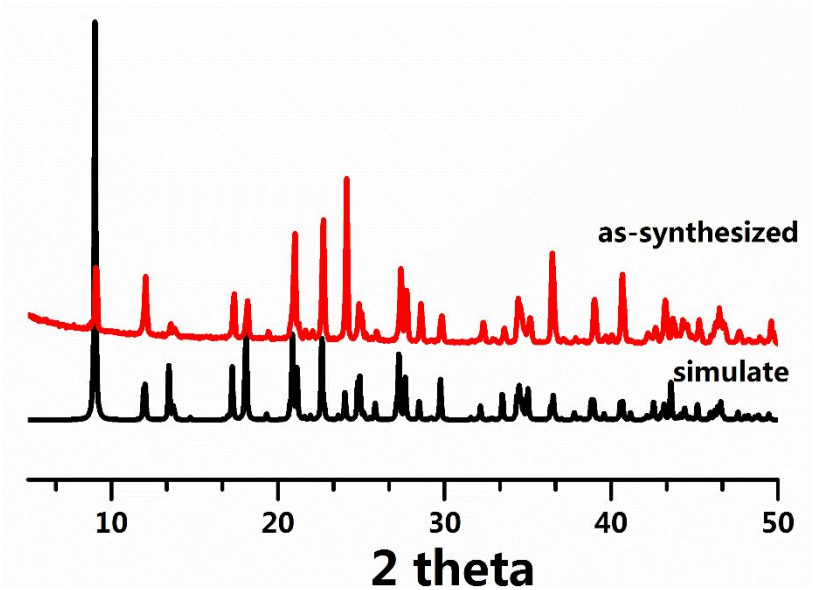

Figure S6. As-synthesized and simulated PXRD patterns of compound **4**.

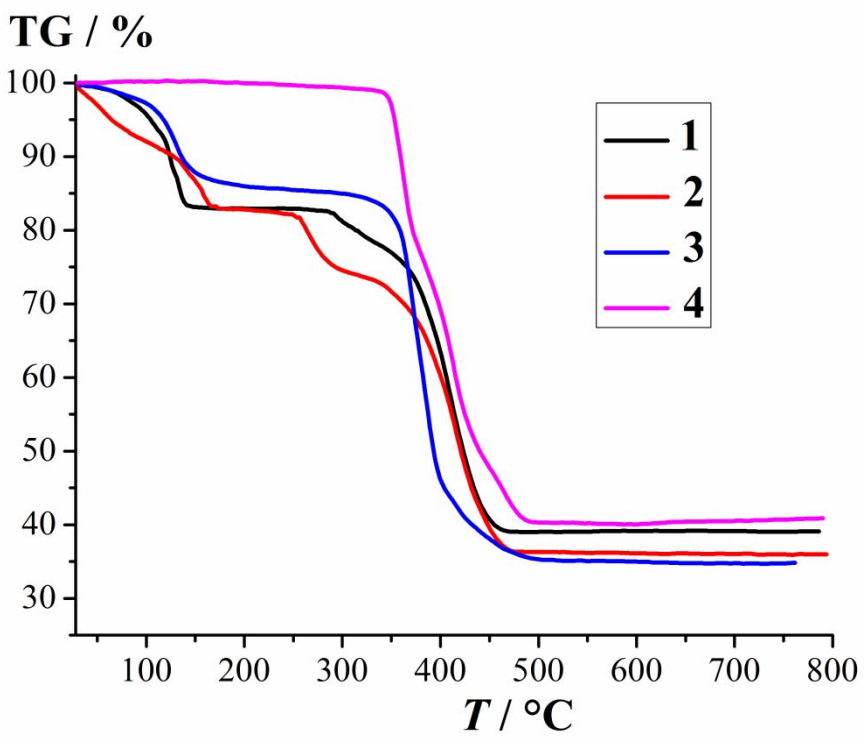

Figure S7. TGA curves of compounds **1**–**4**.

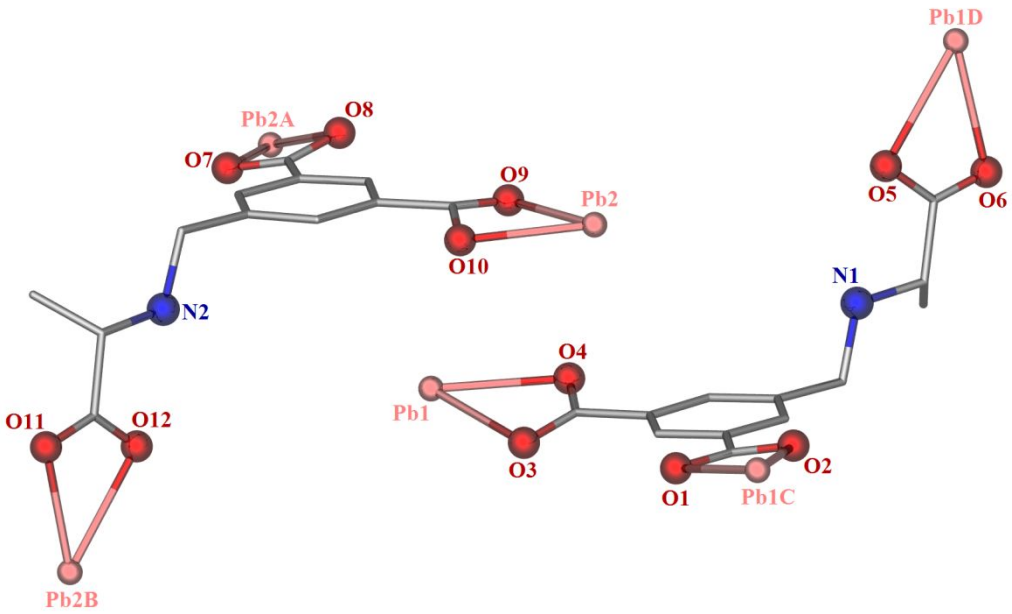

Figure S8. View of two independent zwitterionic $(HL^2)^{2-}$ ligands acting as κ_6- and κ_5-linkers to connect three symmetry-related Pb1 and Pb2 in **1**, respectively. Symmetry code: (A) x, $1 + y$, z; (B) $-1/2 + x$, $1/2 + y$, z; (C) x, $-1 + y$, z; (D) $1/2 + x$,

−1/2 + *y*, *z*.

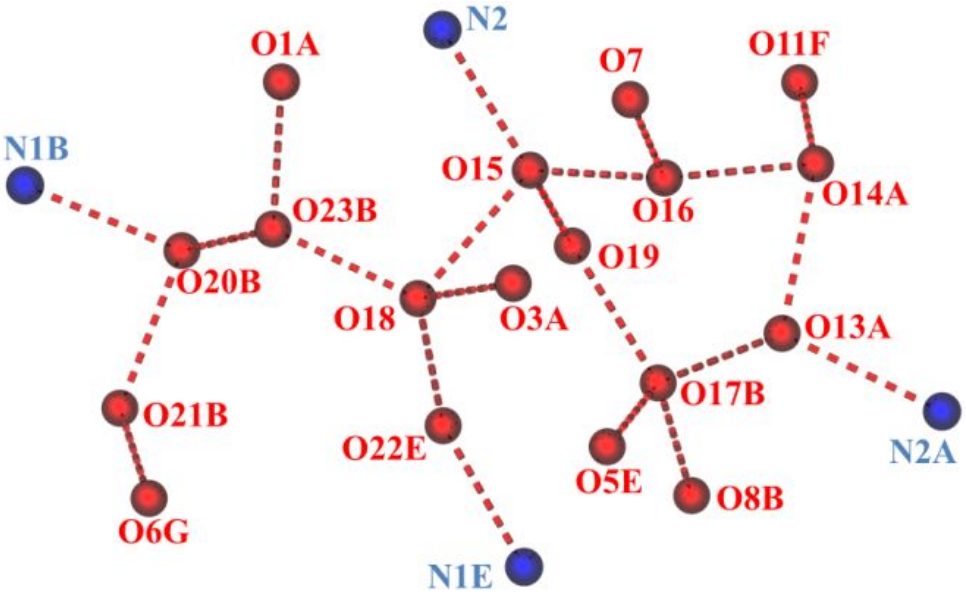

Figure S9. Water cluster $(H_2O)_{11}$ formed through hydrogen-bonding interactions between lattice water molecules O13A, O14A, O15, O16, O17B, O18, O19, O20B, O21B, O22E, and O23B (O18···O22E = 2.651 Å, O15···O18 = 2.816 Å, O15···O19 = 2.688 Å, O23B···O18 = 2.567 Å, O16···O15 = 2.622 Å, O14A···O16 = 2.817 Å, O13A···O14A = 2.642 Å, O13A···O17B = 2.783 Å, O20B···O23B = 2.669 Å, O20B···O21B = 2.858 Å) in **1**. Hydrogen-bonding connections between water cluster $(H_2O)_{11}$ and N_{amino} and $O_{carboxylate}$ of ligands $(HL^1)^{2-}$ (N1E···O22E = 2.798 Å, O18···O3A = 2.879 Å, N2···O15 = 2.775 Å, O16···O7 = 2.740 Å, O14A···O11F = 2.935 Å, N2A···O13A = 2.871 Å, O21B···O6G = 2.731 Å, O17B···O5E = 2.658 Å, N1B···O20B = 2.756 Å, O17B···O8B = 2.704 Å, O23B···O1A = 2.599 Å). Hydrogen bond lengths calculated by Mercury program. Symmetry code: (A) *x*, 1 + *y*, *z*; (B) −1/2 + *x*, 1/2 + *y*, *z*; (E) −1/2 + *x*, 3/2 + *y*, *z*; (F) −1/2 + *x*, 1/2 + *y*, −2 + *z*; (G) 1 − *x*, 1 + *y*, 1 − *z*.

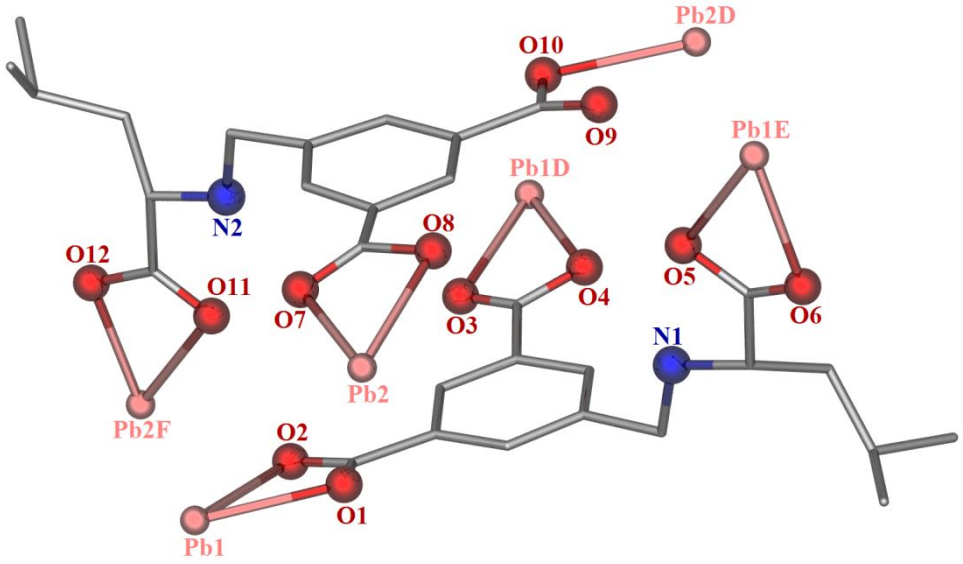

Figure S10. View of two independent zwitterionic $(HL^1)^{2-}$ ligands chelating three symmetry-related Pb1 and three symmetry-related Pb2 in **2** , respectively. Symmetry code: (D) −1 + *x*, *y*, *z*; (E) *x*, 1 + *y*, *z*; (F) −1 + *x*, −1 + *y*, *z*.

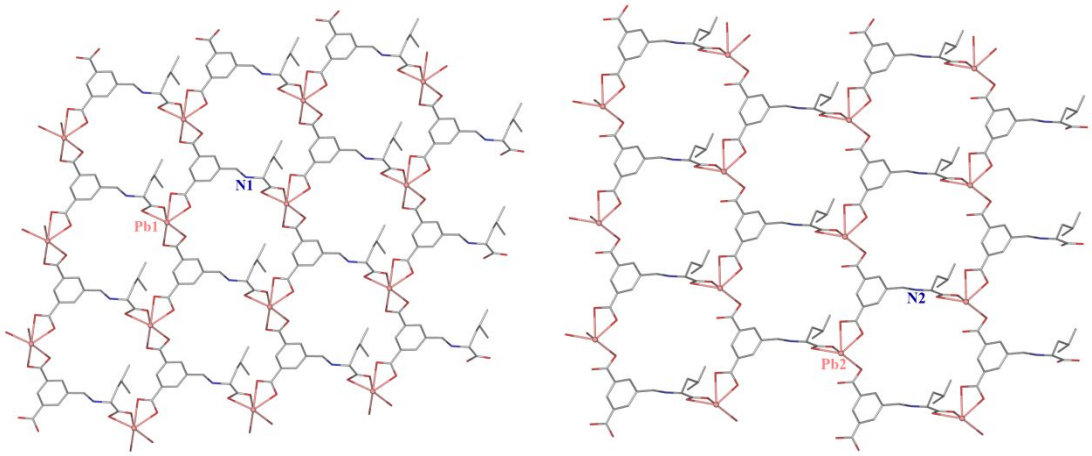

Figure S11. View of two types of unsupported wave-like homochiral polymeric layers with 6^3 topologies in **2**, namely, Pb1-layer being fabricated by the coordination of the symmetry-related $[(HL^2)_{\text{including N1}}]^{2-}$ ligands and symmetry-related Pb1 nodes, and Pb2-layer being created by the coordination of the symmetry-related $[(HL^2)_{\text{including N2}}]^{2-}$ ligands and symmetry-related Pb2 nodes.

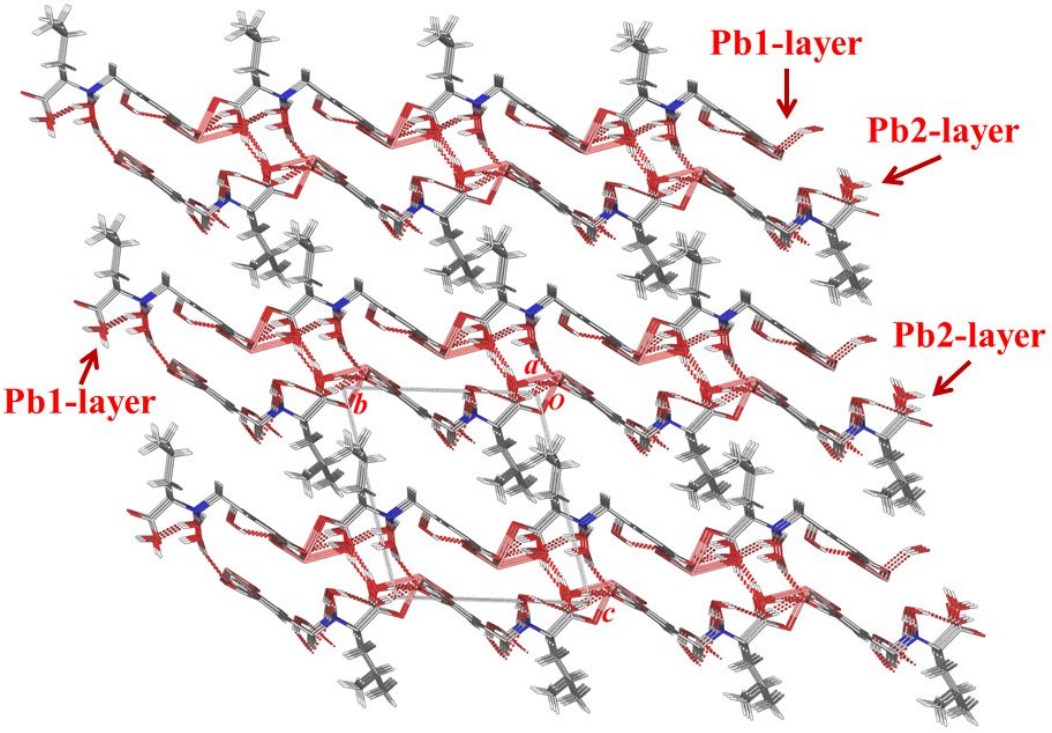

Figure S12. Interdigitation of isobutyl groups between two bilayers in **2**, showing the stacking of Pb1-layer and Pb2-layer following the ABAB pattern.

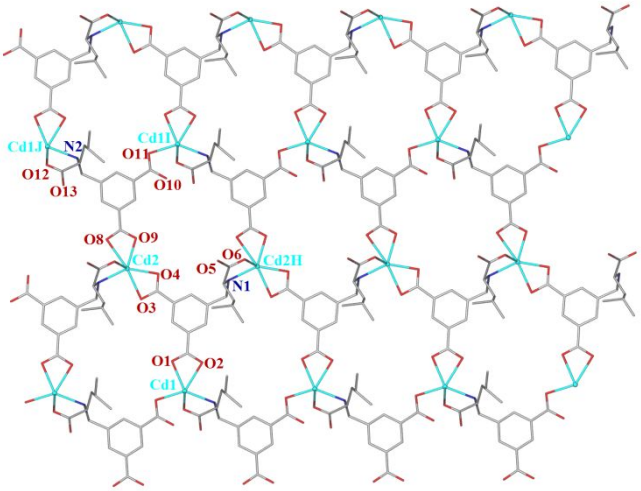

Figure S13. View of 6^3-network formed by the two independent $(L^2)^{3-}$ ligands linking with Cd1 and Cd2 centers in **3**, with coordination water molecules being omitted for clarity. Symmetry code: (H) x, $-1 + y$, z; (I) $-1 + x$, y, z; (J) $-1 + x$, $1 + y$, z.

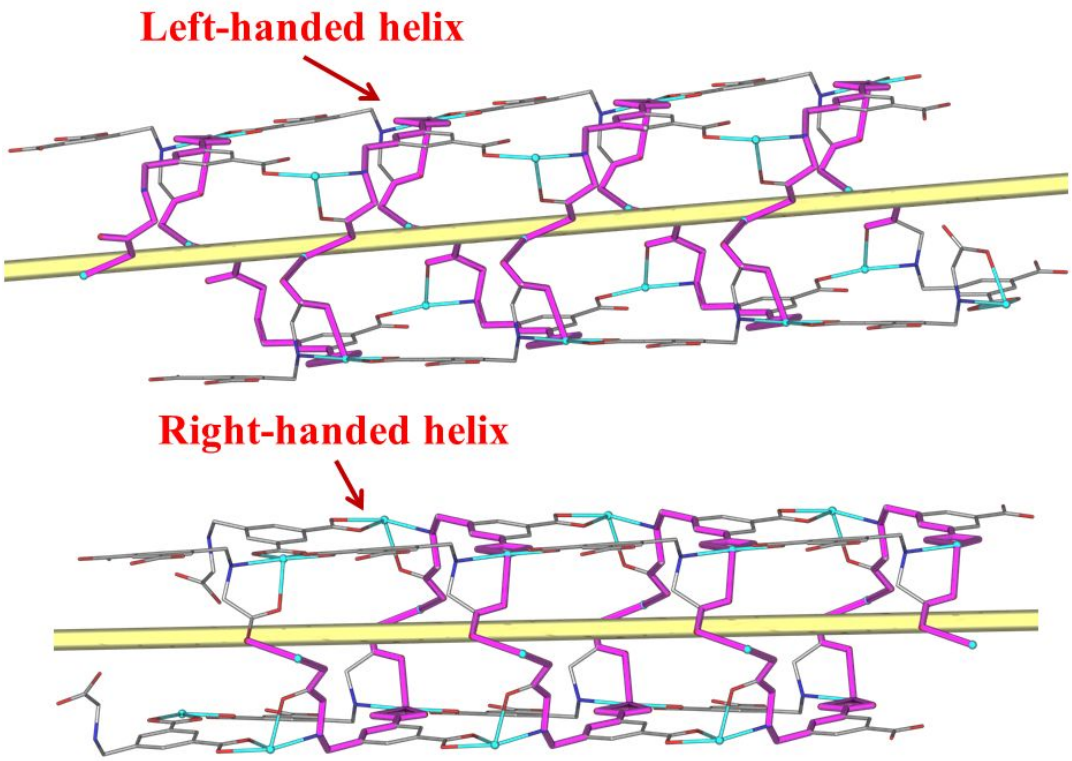

Figure S14. View of *b*-axially extending left- and right-handed 2_1 helixes in the double-layer framework containing symmetry-related Cd1, Cd2, and Cd3 in **3**, with coordination water molecules and the isobutyls of amino acid groups in ligands $(L^2)^{3-}$ being omitted for clarity.

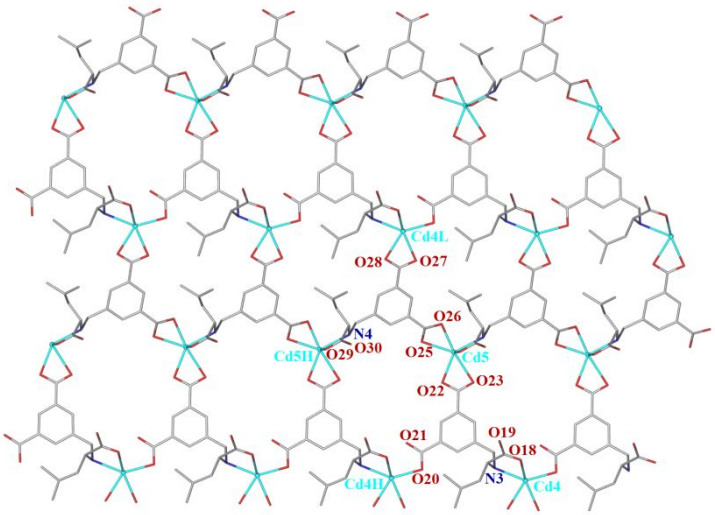

Figure S15. View of 6^3-network formed by the two independent $(L^2)^{3-}$ ligands linking with Cd4 and Cd5 centers in **3**, with coordination water molecules being omitted for clarity. Symmetry code: (H) $x, -1 + y, z$; (L) $-1 + x, -1 + y, z$.

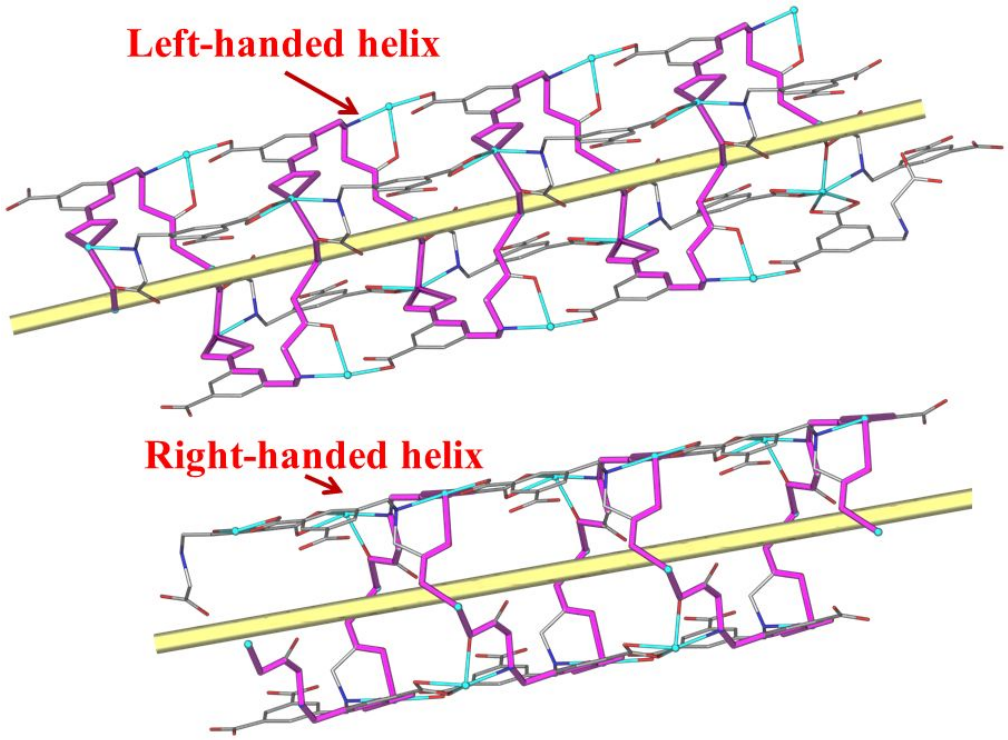

Figure S16. View of *b*-axially extending left- and right-handed 2_1 helixes in the double-layer framework containing symmetry-related Cd4, Cd5, and Cd6 in **3**, with coordination water molecules and the isobutyls of amino acid groups in ligands $(L^2)^{3-}$ being omitted for clarity.

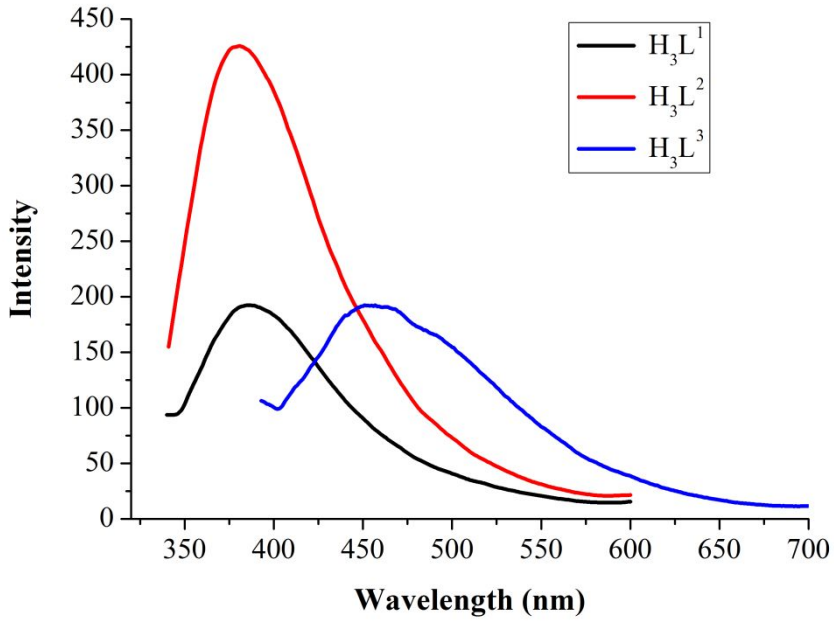

Figure S17. Solid-state fluorescent behaviors of free ligands H_3L^1–H_3L^3 at room temperature excited at 310, 309 and 373 nm, respectively.

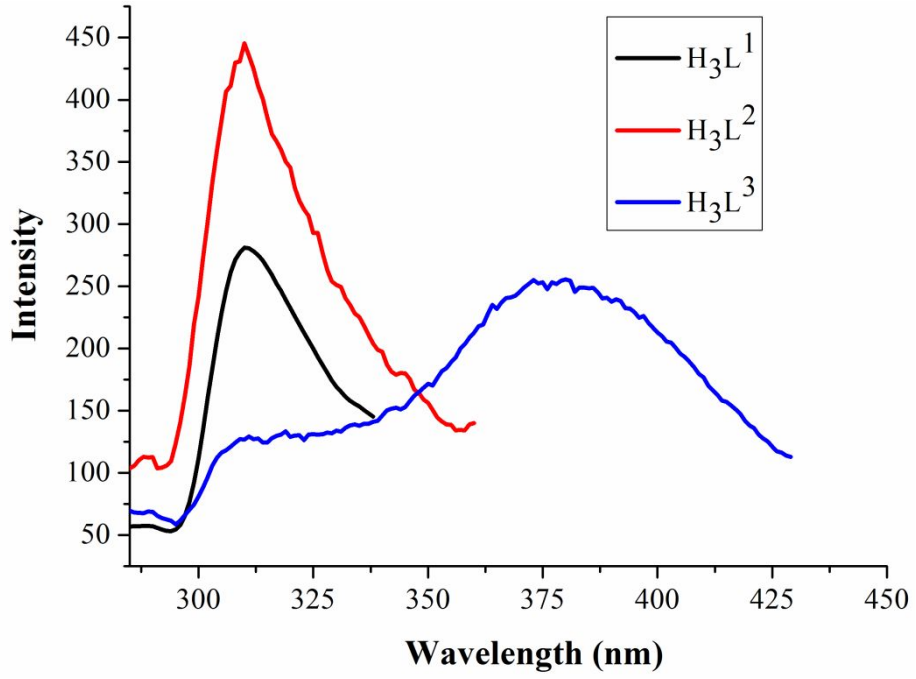

Figure S18. Solid-state excitation spectra of free ligands H_3L^1–H_3L^3 at room temperature.

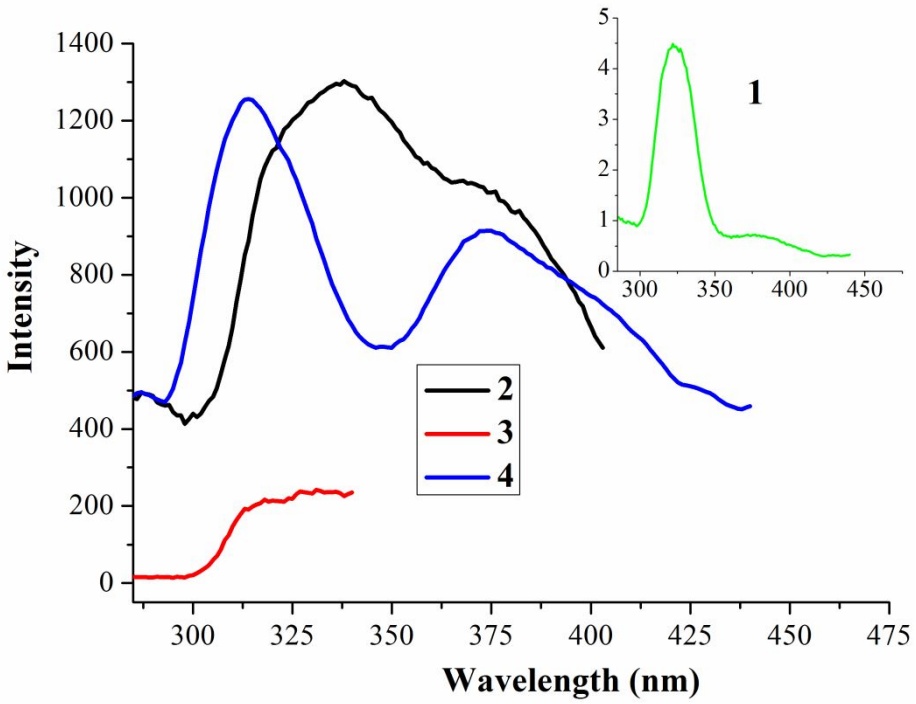

Figure S19. Solid-state excitation spectra of free ligands **1**–**4** at room temperature.

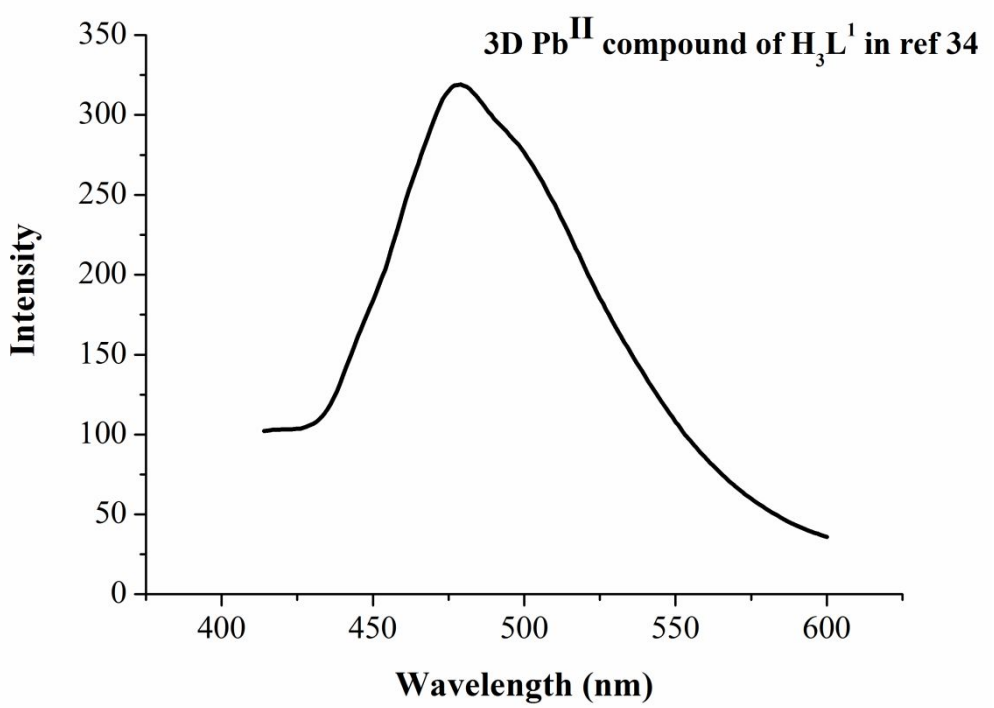

Figure S20. Solid-state fluorescent behavior of 3D Pb^{II} compound of H_3L^1 in ref 37 at room temperature.

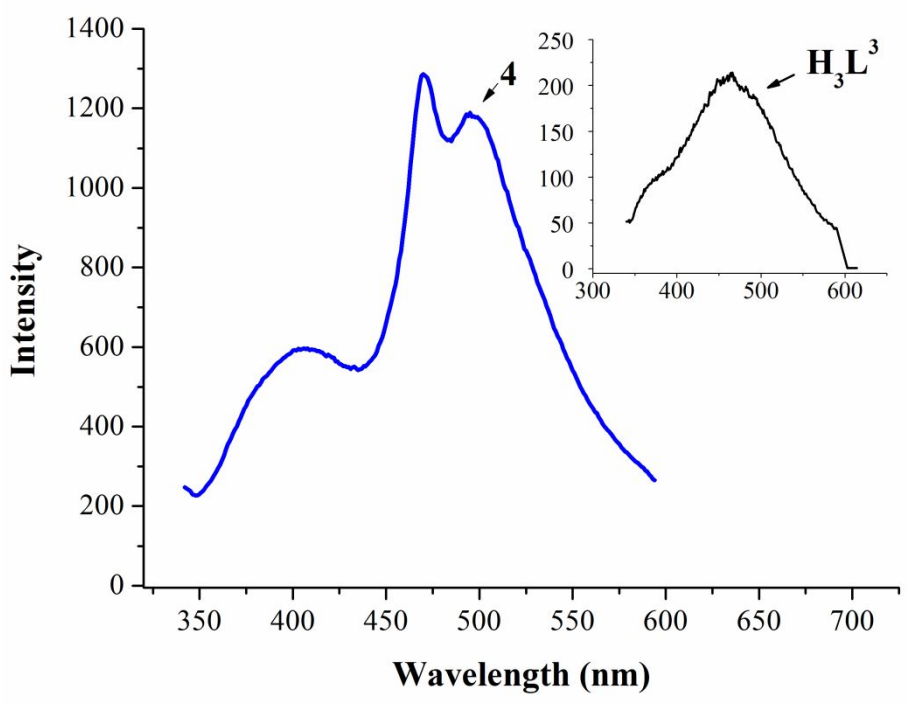

Figure S21. Solid-state fluorescent behaviors of free ligands H_3L^3 and its complex **4** at room temperature excited at 310 and 314 nm, respectively.

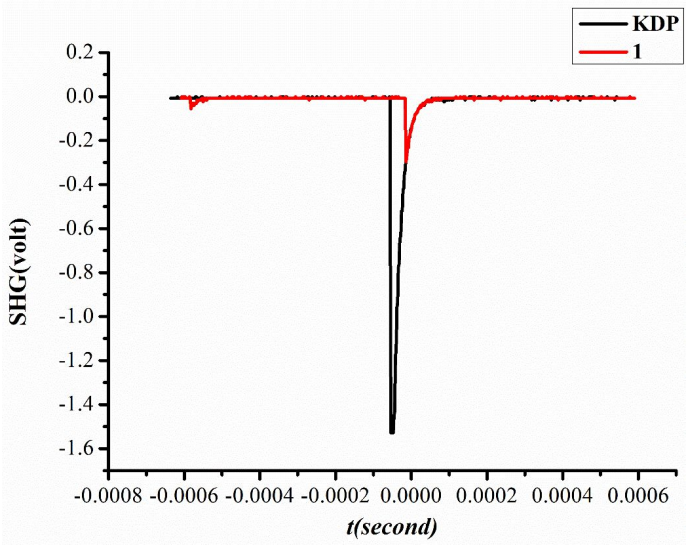

Figure S22. Second-harmonic generation efficiency of **1**.

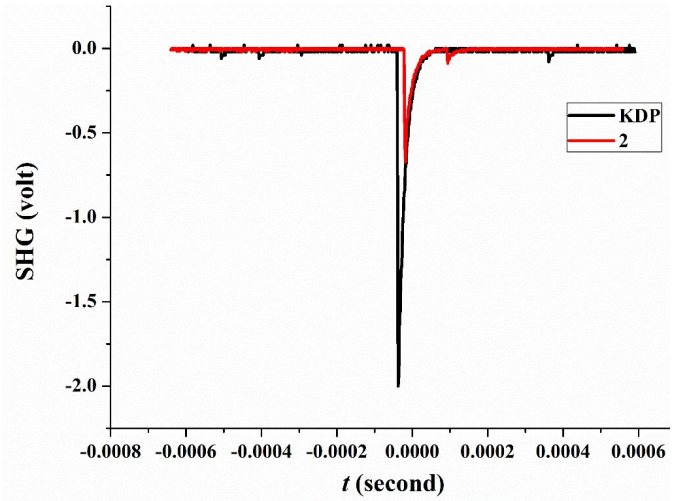

Figure S23. Second-harmonic generation efficiency of **2**.

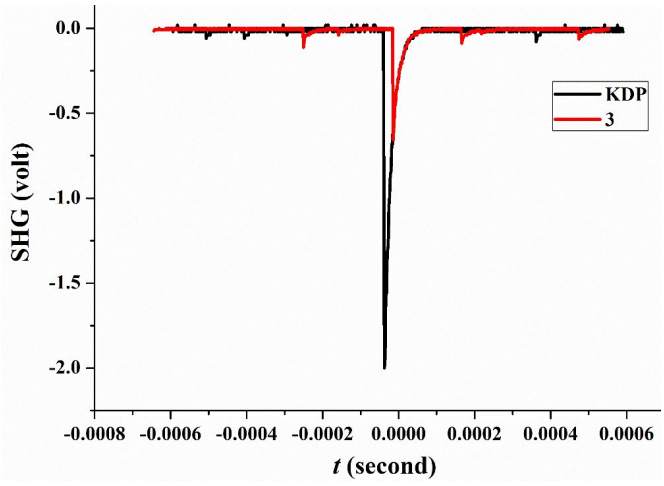

Figure S24. Second-harmonic generation efficiency of **3**.