Table S1. Selected bond lengths (Å) and angles (°) for complexes **1**–**3**.

		1	
Pb1–N1	2.668(4)	Pb1–N2	2.639(4)
Pb1–O1	2.403(3)	Pb1–O2	2.680(3)
Pb1–O3A	2.396(3)	Pb1–O1W	2.976(5)
C39–C40	1.215(8)		
O1–Pb1–O1W	94.58(12)	O1–Pb1–N1	76.51(11)
O1–Pb1–O3A	84.74(12)	O2–Pb1–N1	115.30(10)
O1W–Pb1–N1	79.77(12)	O1W–Pb1–O2	71.16(11)
O2–Pb1–O3A	77.48(10)	O2–Pb1–N2	125.09(11)
N1–Pb1–N2	61.38(10)	O1–Pb1–O2	50.95(10)
N1–Pb1–O3A	138.19(12)	O1W–Pb1–N2	141.14(11)
O1–Pb1–N2	78.31(11)	O1W–Pb1–O3A	139.47(12)
Symmetry code for **1**: A) –*x* – 2, –*y* + 1, –*z* + 1.			
		2	
Pb(1)–O(1)	2.440(5)	Pb(1)–N(1)	2.721(6)
Pb(1)–O(2)	2.492(6)	Pb(1)–N(2)	2.666(6)
Pb(1)–O(3)	2.688(7)	Pb(1)–N(4)	2.811(7)
Pb(1)–O(5)	3.003(10)	Pb(1)–N(5)	2.826(6)
O(1)–Pb(1)–O(2)	52.53(19)	O(1)–Pb(1)–N(4)	93.09(19)
O(1)–Pb(1)–N(2)	74.18(18)	O(2)–Pb(1)–N(4)	73.10(19)
O(2)–Pb(1)–N(2)	74.04(19)	N(2)–Pb(1)–N(4)	145.76(18)
O(1)–Pb(1)–O(3)	76.6(2)	O(3)–Pb(1)–N(4)	133.4(2)
O(2)–Pb(1)–O(3)	125.8(2)	N(1)–Pb(1)–N(4)	98.59(19)
N(2)–Pb(1)–O(3)	75.39(19)	O(1)–Pb(1)–N(5)	77.58(16)
O(1)–Pb(1)–N(1)	113.95(17)	O(2)–Pb(1)–N(5)	106.02(19)
O(2)–Pb(1)–N(1)	69.6(2)	N(2)–Pb(1)–N(5)	143.45(18)
N(2)–Pb(1)–N(1)	60.64(19)	O(3)–Pb(1)–N(5)	75.9(2)
O(3)–Pb(1)–N(1)	127.4(2)	N(1)–Pb(1)–N(5)	154.99(19)
N(4)–Pb(1)–N(5)	57.51(17)	O(3)–Pb(1)–O(5)	42.8(3)
O(1)–Pb(1)–O(5)	114.4(3)	N(1)–Pb(1)–O(5)	92.5(3)
O(2)–Pb(1)–O(5)	143.3(3)	N(4)–Pb(1)–O(5)	143.0(3)
N(2)–Pb(1)–O(5)	69.3(2)	N(5)–Pb(1)–O(5)	102.9(2)
		3	
Pb(1)–N(1)	2.611(6)	Pb(1)–N(2)	2.692(7)
Pb(1)–O(1)	2.625(7)	Pb(1)–O(2)	2.551(8)
Pb(1)–O(3)	2.553(7)	Pb(1)–O(4)	2.349(7)
Pb(1)–O(8)C	3.030(94)		
Pb(2)–N(3)	2.654(6)	Pb(2)–N(4)	2.577(6)
Pb(2)–O(5)A	2.376(8)	Pb(2)–O(8)	2.506(8)

Pb(2)–O(3)D	2.8477(70)	Pb(2)–O(6)A	2.623(11)
Pb(2)–O(7)	2.952(78)	Pb(2)–O(7)E	3.061(76)
Pb(3)–N(7)	2.752(6)	Pb(3)–N(8)	2.849(6)
Pb(3)–O(10)	2.462(6)	Pb(3)–O(9)	2.568(6)
Pb(3)–O(12)B	2.602(6)	Pb(3)–O(11)B	2.412(7)
O(4)–Pb(1)–O(2)	82.4(3)	O(4)–Pb(1)–O(3)	53.5(2)
O(2)–Pb(1)–O(3)	77.2(2)	O(4)–Pb(1)–N(1)	76.7(2)
O(2)–Pb(1)–N(1)	127.1(2)	O(3)–Pb(1)–N(1)	122.40(19)
O(4)–Pb(1)–O(1)	87.0(3)	O(2)–Pb(1)–O(1)	50.1(2)
O(3)–Pb(1)–O(1)	118.8(3)	N(1)–Pb(1)–O(1)	80.4(2)
O(4)–Pb(1)–N(2)	74.4(2)	O(2)–Pb(1)–N(2)	153.2(3)
O(3)–Pb(1)–N(2)	78.3(2)	N(1)–Pb(1)–N(2)	60.42(19)
O(1)–Pb(1)–N(2)	139.3(2)	O(5)A–Pb(2)–O(8)	95.4(4)
O(5)A–Pb(2)–N(4)	72.3(3)	O(8)–Pb(2)–N(4)	75.5(2)
O(5)A–Pb(2)–O(6)A	50.5(4)	O(8)–Pb(2)–O(6)A	77.9(4)
N(4)–Pb(2)–O(6)A	112.9(4)	O(5)A–Pb(2)–N(3)	85.8(3)
O(8)–Pb(2)–N(3)	134.6(2)	N(4)–Pb(2)–N(3)	61.7(2)
O(6)A–Pb(2)–N(3)	131.1(4)	O(11)B–Pb(3)–O(10)	83.0(2)
O(11)B–Pb(3)–O(9)	78.3(2)	O(10)–Pb(3)–O(9)	51.9(2)
O(11)B–Pb(3)–O(12)B	51.2(2)	O(10)–Pb(3)–O(12)B	123.2(2)
O(9)–Pb(3)–O(12)B	83.6(2)	O(11)B–Pb(3)–N(7)	84.5(2)
O(10)–Pb(3)–N(7)	74.03(19)	O(9)–Pb(3)–N(7)	124.55(19)
O(12)B–Pb(3)–N(7)	123.43(18)		

Symmetry code for **3**: A) $-x-1, -y+1, -z+2$; B) $-x, -y, -z+2$; C) $-x-1, -y, -z+2$; D) $x, y, z-1$; E) $-x-1, -y, -z+1$.

Table S2. Hydrogen–bonding geometry (Å, °) for complex **1**.

D–H···A	D–H···A	D–D···A	D–H···A
O1W–H1WB···O3w	2.07	2.856(6)	154
O2W–H2WA···O4W(A)	1.92	2.764(5)	171
O2W–H2WB···O4(B)	1.91	2.761(5)	176
O3W–H3WA···O2W	1.87	2.708(5)	167
O3W–H3WB···O1(C)	2.13	2.947(5)	160
O4W–H4WB···O1(C)	2.16	2.922(5)	150

Symmetry operations: A) $-x+1, y-1/2, -z+1/2$; B) $x+2, -y+1/2, z-1/2$; C) $x+1, y, z$; D) $x+2, y, z$.

Analysis of Short Ring-Interactions with Cg-Cg Distances

Cg(I) = Plane number I (= ring number in () above)

Alpha = Dihedral Angle between Planes I and J (°)

Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (°)

Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (°)

Cg-Cg = Distance between ring Centroids (Å)

CgI_Perp = Perpendicular distance of Cg(I) on ring J (Å)

CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Å)

Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Å).

P,Q,R,S = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)

1

Cg1 = N1-C1-C2-C3-C4-C12

Cg2 = N2-C10-C9-C8-C7-C11

Cg3 = N3-C17-C16-C15-C14-C18

Cg4 = N4-C19-C23-C22-C21-C20

Cg5 = N5-C6-C5-N6-C13-C24

Cg6 = C4-C5-C6-C7-C11-C12

Cg7 = C13-C14-C18-C19-C23-C24.

Cg(I)-Cg(J)	Cg-Cg	Transformed	J-Plane	P,Q,R,S	Alpha	Beta	Gamma	CgI_Perp	CgJ_Perp	Slippage
Cg1-Cg7A	3.784(3)	-0.8498	-0.2835	0.4444	2.6878	1.9(2)	28.39	27.95	3.3423(19)	3.3287(19)
Cg4-Cg6B	3.706(3)	-0.8347	-0.2938	0.4657	9.0948	1.8(2)	26.78	28.44	-3.259(2)	-3.3091(19)
Cg5-Cg6A	3.647(3)	-0.8347	-0.2938	0.4657	2.5081	0.6(2)	22.7	22.17	3.3774(18)	3.3648(19)
Cg5-Cg7B	3.595(3)	-0.8498	-0.2835	0.4444	9.3934	1.0(2)	24.41	23.75	-3.2902(18)	-3.2733(19)
Cg5-Cg5A	3.538(3)	-0.8403	-0.291	0.4574	2.5923	0	17.92	17.92	3.3664(18)	3.3666(18)
Cg4-Cg1A	3.539(3)	-0.8371	-0.2747	0.473	2.6893	2.8(2)	18.06	18.86	3.349(2)	3.3644(19)
Cg3-Cg2A	3.537(3)	-0.8241	-0.324	0.4646	2.2048	5.9(2)	13.64	18.9	3.346(2)	3.436(2)
Cg6-Cg7A	3.527(3)	-0.8498	-0.2835	0.4444	2.6878	1.6(2)	18.53	16.92	3.3744(19)	3.3443(19)
Cg4-Cg5B	3.428(3)	-0.8403	-0.291	0.4574	9.2231	1.5(2)	17.19	17.36	-3.273(2)	-3.2756(18)

A: $-x-2, -y+1, -z$; B: $-x-3, 1-y, -z$.

2

Cg1 = N1-C6-C14-C15-C16-C17

Cg3 = N3-C12-C13-N3a-C12a-C13a

Cg4 = N4-C18-C28-C29-C30-C31

Cg5 = N5-C19-C23-C22-C21-C20

Cg6 = N6-C24-C27-N7-C26-C25

Cg7 = N8-C33-C32-C36-C35-C34

Cg9 = C6-C7-C11-C12-C13-C14

Cg10 = C18-C19-C23-C24-C27-C28

Cg11 = C25-C26-C32-C33-C37-C41

Cg(I)-Cg(J)	Cg-Cg	Transformed	J-Plane	P,Q,R,S	Alpha	Beta	Gamma	CgI_Perp	CgJ_Perp	Slippage
Cg1-Cg5A	3.606(4)	-0.9664	0.2567	0.0144	-1.2544	2.27	23.62	21.37	3.359	3.304
Cg1-Cg10A	3.633(4)	0.9626	-0.2585	0.081	-1.2275	4.53	23.95	21.14	3.388	3.319
Cg3-Cg6B	3.715(4)	-0.963	0.264	-0.0542	-5.4782	3.37	22.84	24.18	3.389	3.424
Cg3-Cg6A	3.716(4)	0.963	-0.264	0.0542	-1.3011	3.37	22.84	24.18	3.39	3.424
Cg4-Cg11D	3.723(4)	-0.967	-0.2494	-0.052	-2.8429	6.17	20.92	14.76	3.601	3.478
Cg5-Cg7D	3.772(5)	-0.9649	-0.2538	-0.0673	-2.9467	3.03	26.57	23.63	3.455	3.374
Cg6-Cg6D	3.722(4)	-0.963	-0.264	-0.0542	-2.8603	0	23.34	23.34	3.418	3.418
Cg6-Cg9C	3.576(4)	0.9611	0.276	0.0054	9.2987	2.88	14.49	16.73	3.424	3.462
Cg6-Cg10D	3.884(4)	-0.9626	-0.2585	-0.081	-3.0426	1.56	27.48	27.41	3.448	3.446
Cg10-Cg11D	3.746(4)	-0.967	-0.2494	-0.052	-2.8429	1.76	22.1	23.53	3.434	3.471

A: $x - 1/2, -y + 1/2, z - 1/2$; B: $-x + 3/2, y + 1/2, -z + 1/2$; C: $x + 1/2, -y + 1/2, z + 1/2$; D: $-x + 1, -y, -z + 1$.

3

Cg2 = N(2)-C(10)-C(9)-C(8)-C(7)-C(11)

Cg4 = N(4)-C(22)-C(21)-C(20)-C(19)-C(23)

Cg5 = N(5)-C(5)-C(6)-N(6)-C(18)-C(17)

Cg7 = C(16)-C(17)-C(18)-C(19)-C(23)-C(24)

Cg8 = N(7)-C(25)-C(26)-C(27)-C(28)-C(36)

Cg9 = N(8)-C(34)-C(33)-C(32)-C(31)-C(35)

Cg10 = N(9)-C(37)-C(38)-C(39)-C(40)-C(48)

Cg13 = C(28)-C(29)-C(30)-C(31)-C(35)-C(36)

Cg14 = C(40)-C(41)-C(42)-C(43)-C(47)-C(48)

Cg12 = N(11)-C(29)-C(30)-N(12)-C(42)-C(41)

Cg(I)-Cg(J)	Cg-Cg	Transformed	J-Plane	P,Q,R,S	Alpha	Beta	Gamma	CgI_Perp	CgJ_Perp	Slippage
Cg(4)-Cg(2)A	3.596(5)	0.2042	-0.9767	-0.0666	-1.226	1.9(4)	19.54	21.39	-3.348(3)	-3.389(3)
Cg(5)-Cg(13)B	3.500(4)	-0.157	0.9823	0.1019	8.2612	3.1(3)	11.25	13.7	-3.400(3)	3.433(3)
Cg(8)-Cg(7)C	3.545(5)	-0.2555	0.9576	0.133	2.0757	6.6(4)	19.91	14.45	3.433(3)	-3.333(3)
Cg(13)-Cg(5)C	3.501(4)	-0.2014	0.9706	0.1315	2.5861	3.1(3)	13.7	11.25	3.433(3)	-3.401(3)
Cg(4)-Cg(8)B	3.757(5)	-0.1739	0.9832	0.0562	7.7206	3.0(4)	24.54	21.63	-3.493(3)	3.418(3)
Cg(5)-Cg(12)B	3.751(4)	-0.1648	0.9803	0.1092	8.3984	2.5(3)	27.24	25	-3.399(3)	3.335(3)
Cg(2)-Cg(7)A	3.782(5)	0.2555	-0.9576	-0.133	-2.5784	4.9(4)	24.61	28.95	-3.310(3)	-3.439(3)
Cg(14)-Cg(9)D	3.503(5)	0.1408	-0.9817	-0.1285	-10.0299	1.3(4)	16.18	16.05	3.366(3)	3.364(3)
Cg(13)-Cg(14)D	3.729(4)	0.1637	-0.9785	-0.1258	-9.7067	1.4(3)	25.32	23.99	3.407(3)	3.370(3)
Cg(10)-Cg(9)D	3.627(5)	0.1408	-0.9817	-0.1285	-10.0299	3.5(4)	22.03	25.04	3.285(4)	3.362(3)
Cg(12)-Cg(12)D	3.745(4)	0.1648	-0.9803	-0.1092	-9.435	0	24.92	24.92	3.397(3)	3.397(3)

A: $-x - 1, -y, -z + 2$; B: $x - 1, y, z$; C: $x + 1, y, z$; D: $-x + 1, -y + 1, -z + 2$.

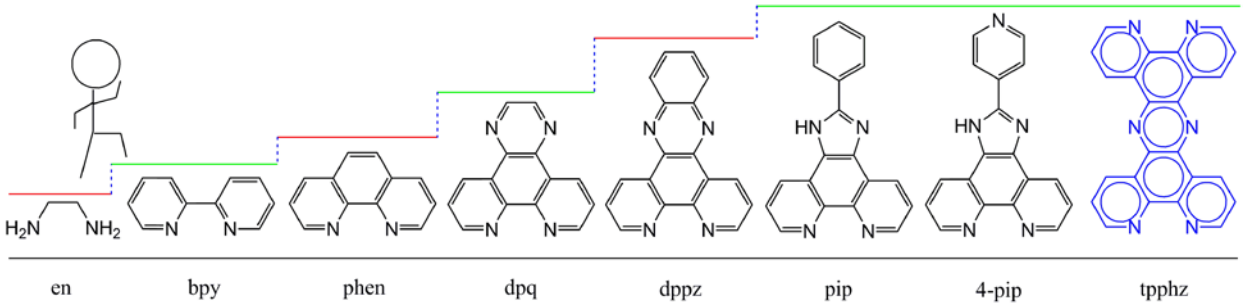


Chart S1. The development of chelating ligands.

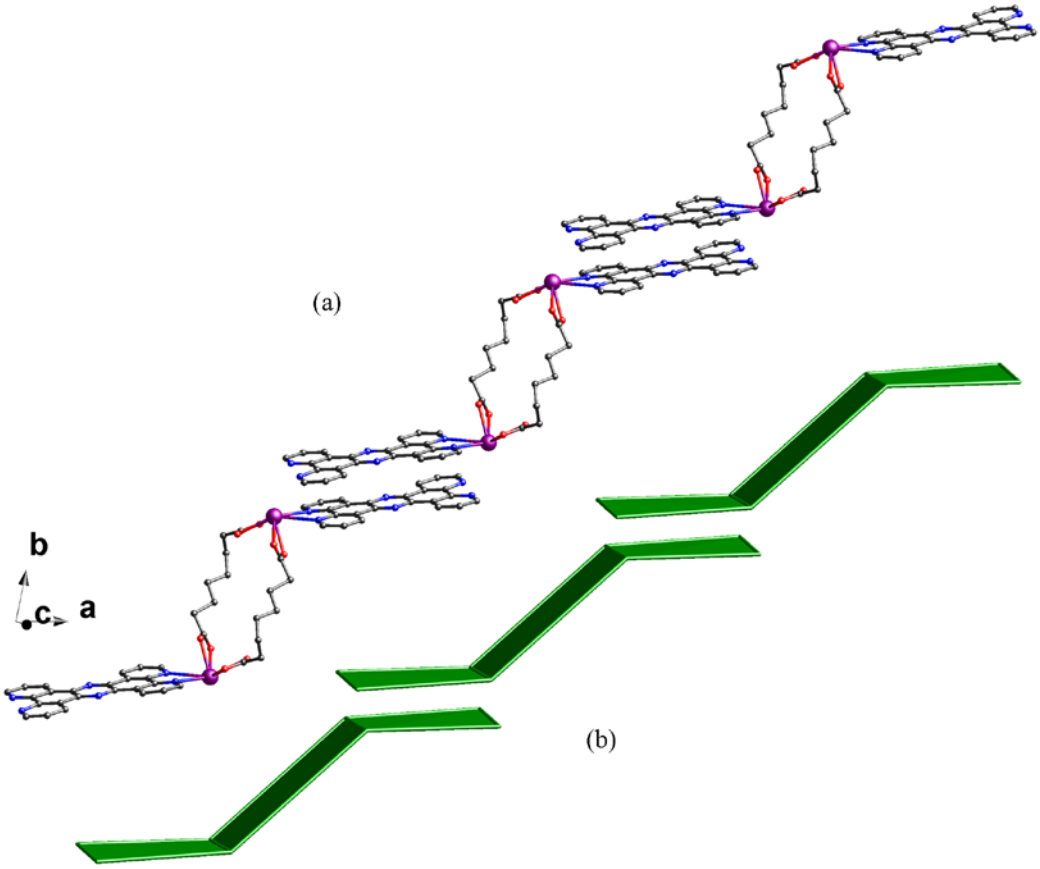


Figure S1. 1D staircase-like supramolecular chain derived from nano-scale metal-ring in complex **3**.

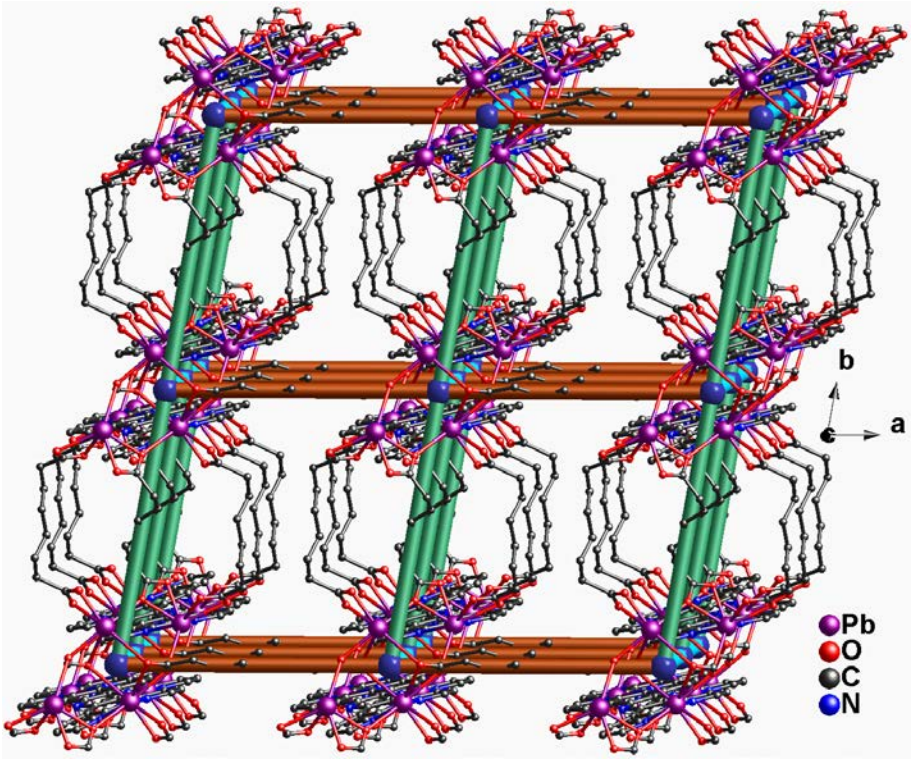
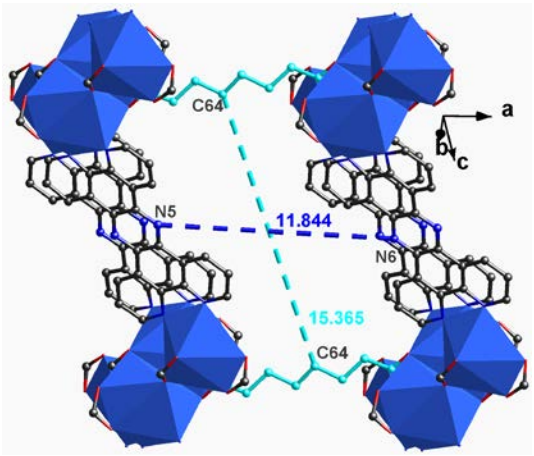
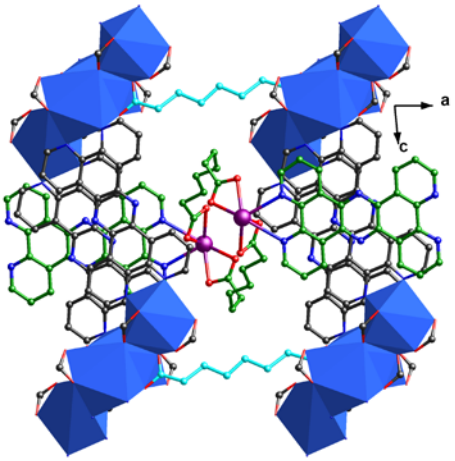


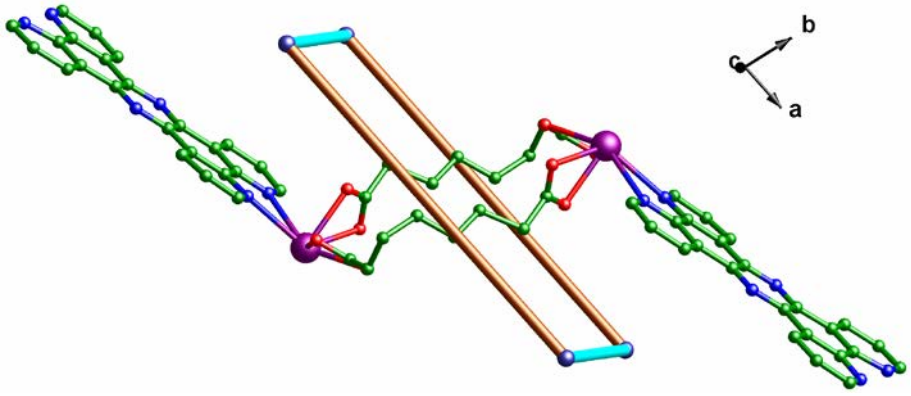
Figure S2. 3D open framework with α-Po type topology network in complex **3**.



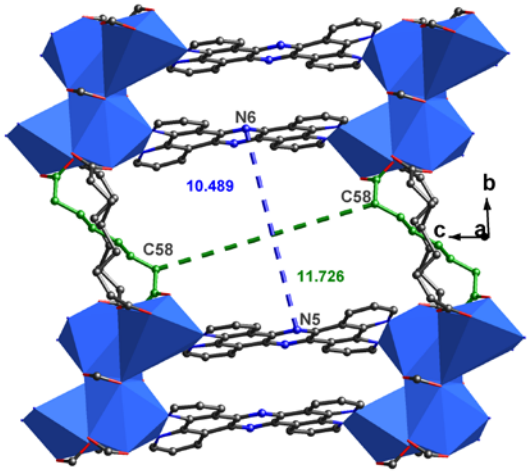
(a)



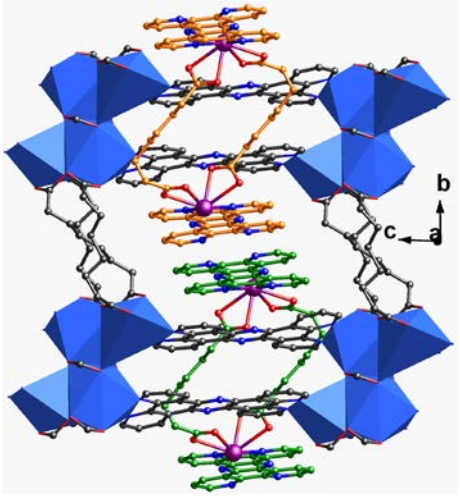
(b)



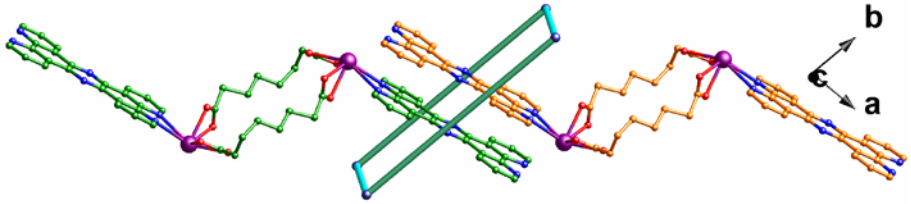
(c)



(d)



(e)



(f)

Figure S3. Two kinds of 4-members nano-scale rings derived from tpphz and L^3 anions, showing two types of penetrating modes in complex **3**.

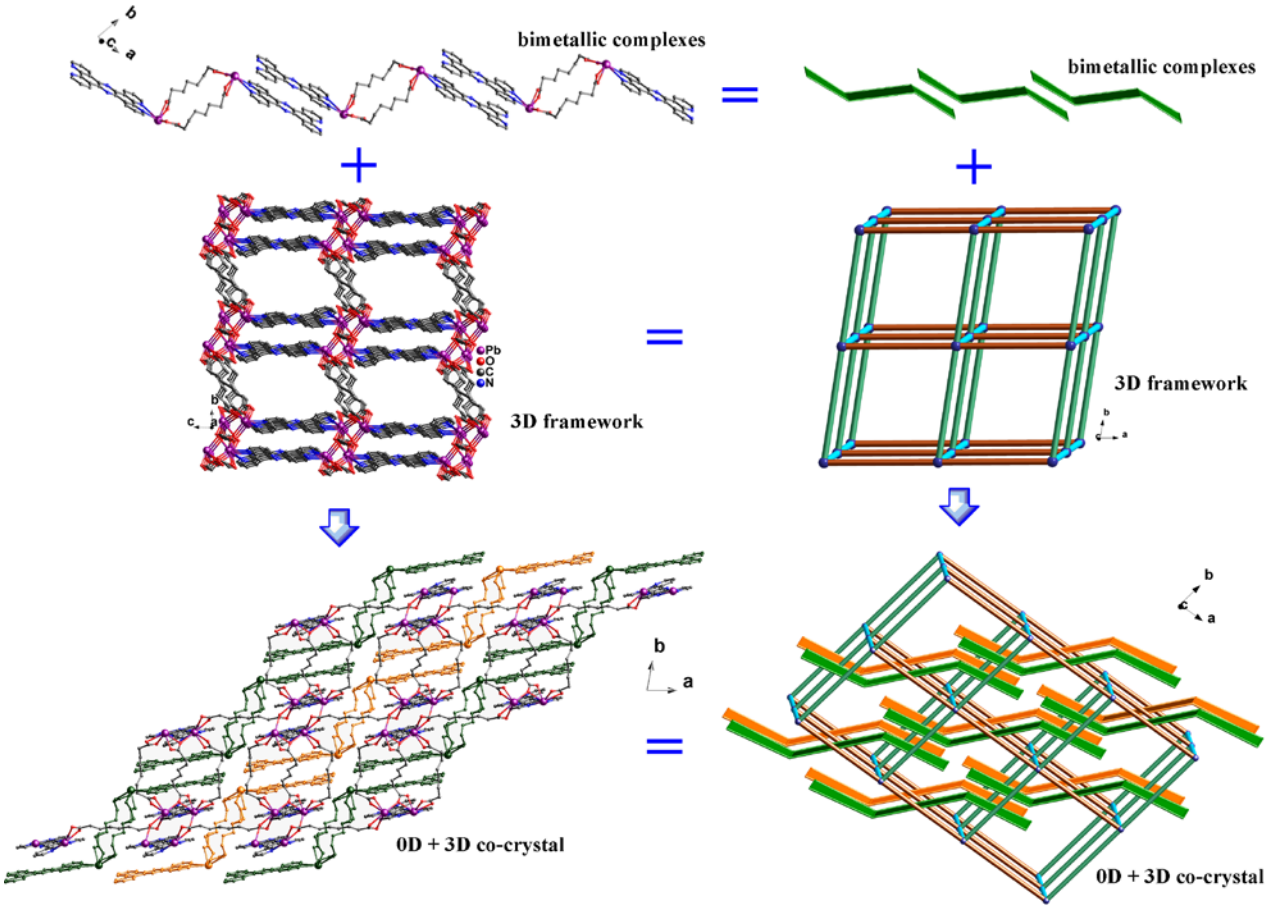


Figure S4. Schematic view of 0D+3D co-crystal of complex **3**.

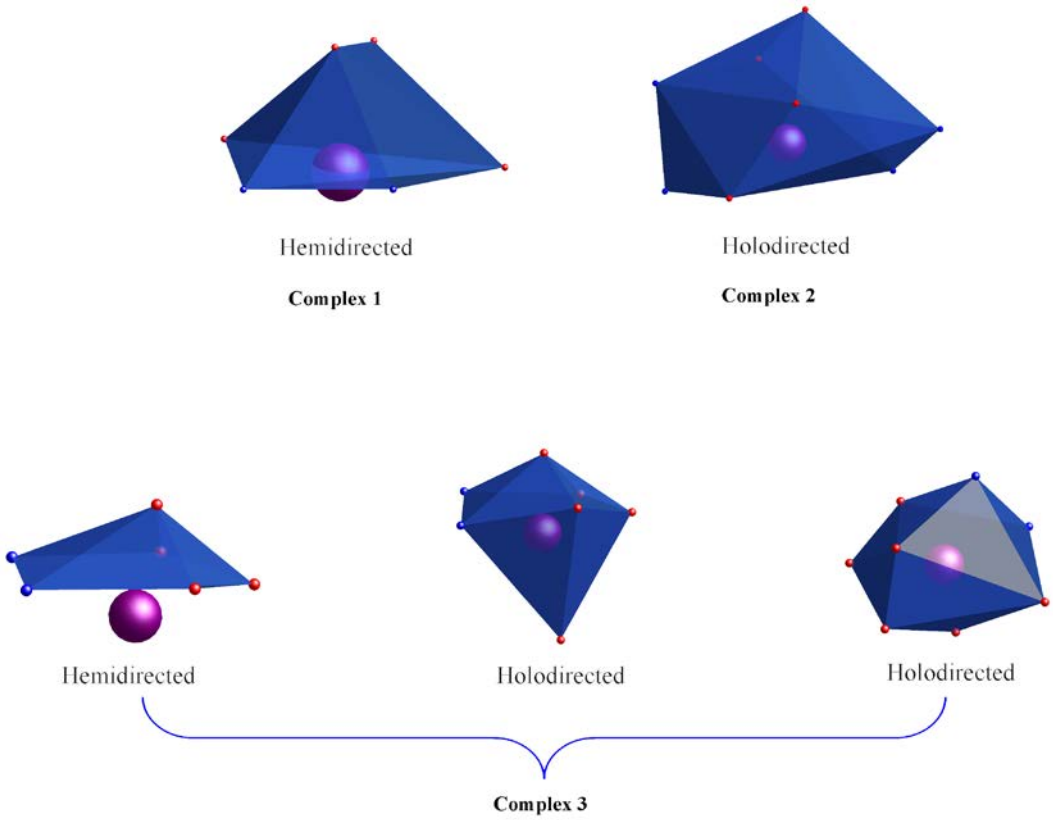


Figure S5. The versatile coordination environments of Pb(II) atoms in complexes **1-3**.

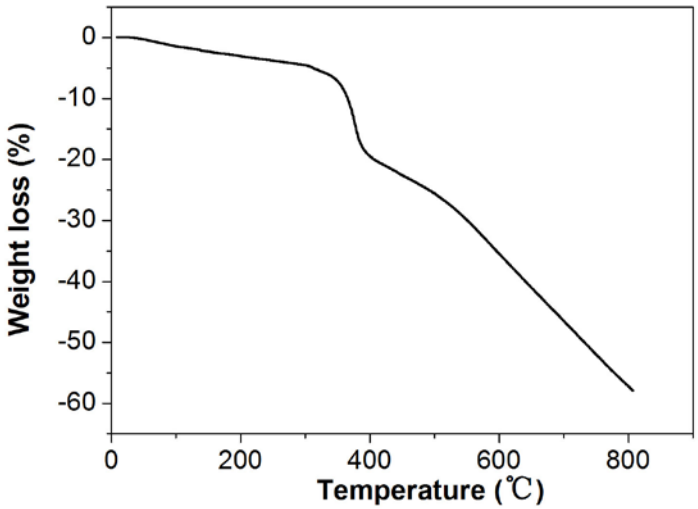


Figure S6. The TG curve of complex **3**.