Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic supplementary information

for

Cation-directed assembly of polyrotaxane and polycatenane

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Table S1 Crystallographic data and structure refinement for **1** and **2**

	1	**2**
Formula	$C_{21}H_{16}N_2O_6Pb_1S_1$	$C_{62}H_{62}N_{10}O_{14}S_2Zn_2$
Formula weight	631.61	1366.08
Temperature (K)	173(2)	173(2)
Crystal system	Triclinic	Monoclinic
Space group	*P-1*	*C2/c*
Z	2	8
a (Å)	7.9089(4)	47.233(6)
b (Å)	11.4057(6)	11.4571(17)
c (Å)	12.6968(6)	25.455(4)
α (°)	65.743(2)	90
β (°)	77.931(2)	119.856(7)
γ (°)	85.251(2)	90
V (Å^3)	1021.13(9)	11947(3)
D_{calc} (g/cm^3)	2.054	1.519
μ (mm^{-1})	8.406	0.950
$2\theta_{max}$ (°)	52.00	50.00
reflections collected	16687	53855
independent reflections	4005 [R(int) = 0.0356]	9977 [R(int) = 0.1224]
goodness-of-fit on F2	1.067	1.089
R1, wR2 [I > 2σ(I)]	R1 = 0.0167, wR2 = 0.0407	R1 = 0.1110, wR2 = 0.2781
R1, wR2 (all data)	R1 = 0.0175, wR2 = 0.0410	R1 = 0.1626, wR2 = 0.3087

Table S2 Selected bond lengths (Å) and bond angles (°) for **1**[a]

Pb1-O2	2.309(2)	Pb1-O5A	2.348(2)
Pb1-N1	2.469(2)	Pb1-O6A	2.681(2)
Pb1-O1	2.765(2)		
O2-Pb1-O5A	87.02(7)	O2-Pb1-N1	77.58(7)
O5A-Pb1-N1	78.64(8)	O2-Pb1-O6A	80.37(7)
O5A-Pb1-O6A	51.67(7)	N1-Pb1-O6A	126.23(7)
O2-Pb1-O1	50.88(6)	O5A-Pb1-O1	114.35(7)
N1-Pb1-O1	123.78(7)	O6A-Pb1-O1	71.14(6)

[a]Symmetry operations: (A) -x-1, -y, -z-1.

Table S3 Selected bond lengths (Å) and bond angles (°) for **2**[a]

Zn1-O1	1.937(7)	Zn1-N4	2.023(9)
Zn2-N5	2.044(8)	Zn2-N1B	2.044(9)
Zn2-O8	2.047(7)	Zn2-O6	2.074(8)
Zn3-O11	1.970(7)	Zn3-N8	2.047(8)
O1-Zn1-O1A	112.5(4)	O1-Zn1-N4	119.0(3)
O1A-Zn1-N4	99.2(3)	N4-Zn1-N4A	108.9(5)
N5-Zn2-N1A	102.8(3)	N5-Zn2-O8	106.3(3)
N1B-Zn2-O8	99.0(3)	N5-Zn2-O6	98.8(3)
N1B-Zn2-O6	105.0(3)	O8-Zn2-O6	140.2(3)
O11A-Zn3-O11	110.4(5)	O11A-Zn3-N8	99.4(3)
O11-Zn3-N8	120.0(3)	N8A-Zn3-N8	108.9(5)

[a]Symmetry operations: (A) –x, y, -z+1/2; (B) –x+1/2, -y+3/2, -z+1.

Experimental

General. All chemicals and solvents employed in the syntheses were of reagent grade and were used without further purification. The FT-IR spectra were measured with a Thermo Scientific Nicolet iS10 spectrometer. The elemental analysis was carried out on a Thermo Scientific Flash 2000 Series elemental analyzer. The solid-state excitation and emission spectra were performed on a RF-5301 spectrophotometer. The powder X-ray diffraction (PXRD) experiments were performed in a transmission mode with a Bruker GADDS diffractometer equipped with graphite-monochromated Cu Kα radiation (λ = 1.54073 Å).

Preparation of $[Pb_2(sdb)_2(bpp)]_n$ (1). A mixture of bpp (10 mg, 0.042 mmol), H_2sdb (13 mg, 0.042 mmol), and $Pb(NO_3)_2$ (14 mg, 0.042 mmol) dissolved in DMF (2 mL) and H_2O (1 mL) were placed in a 10 mL glass tube. The tube was sealed and kept at 120 °C for 48 h, followed by cooling to room temperature over 5 h. Colorless block-shaped crystalline product **1** suitable for X-ray analysis were obtained. IR (KBr): 3108, 2850, 1561, 1522, 1404, 1380, 1297, 1232, 1165, 1101, 1072, 1011, 951, 813, 782, 747, 725 and 622. Elemental analysis (%) calcd for $[C_{42}H_{32}N_4O_{12}S_2Pb_2]$: C, 39.93; H, 2.55; N, 4.44; S, 5.08; Found: C, 40.33; H, 2.65; N, 4.81; S, 4.81.

Preparation of $\{[Zn_2(sdb)_2(bpp)_2]\cdot 2DMA\}_n$ (2). A mixture of bpp (10 mg, 0.042 mmol), H_2sdb (13 mg, 0.042 mmol), and $Zn(NO_3)_2\cdot 4H_2O$ (11 mg, 0.042 mmol) dissolved in DMA (2 mL) and 0.1 M HCl (1 mL) were placed in a 10 mL glass tube. The tube was sealed and kept at 120 °C for 48 h, followed by cooling to room temperature over 5 h. Pink block-shaped crystalline product **2** suitable for X-ray analysis were obtained. IR (KBr, cm^{-1}): 3482, 3109, 2839, 1564, 1521, 1375, 1231, 1165, 1101, 1071, 1012, 952, 813, 783, 748, 725, 699 and 622. Elemental analysis (%) calcd for $[C_{64}H_{68}N_{10}O_{15}S_2Zn_2]$: C, 54.43; H, 4.85; N, 9.92; S, 4.54; Found: C, 54.29; H,4.40; N,9.78; S, 4.63.

X-ray crystallographic analysis. All data were collected on a Bruker SMART APEX2 ULTRA diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) generated by a rotating anode. Data collection, data reduction, and semiempirical absorption correction were carried out using the software package APEX2.[S1] All of the calculations for the structure determination were carried out using the SHELXTL package.[S2] Relevant crystal data collection and refinement data for the crystal structures are summarized in Table S1. Since the compound **2** is slowly decomposed when exposed to air, it shows the larger *R*-values.

CCDC 1450365 (**1**) and 1450366 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References:

S1. Bruker, APEX2 Version 2009.1-0 Data Collection and Processing Software; Bruker AXS Inc., Madison, Wisconsin, U.S.A., 2008.

S2. Bruker, SHELXTL-PC Version 6.22 Program for Solution and Refinement of Crystal Structures; Bruker AXS Inc., Madison, Wisconsin, U.S.A. 2001.

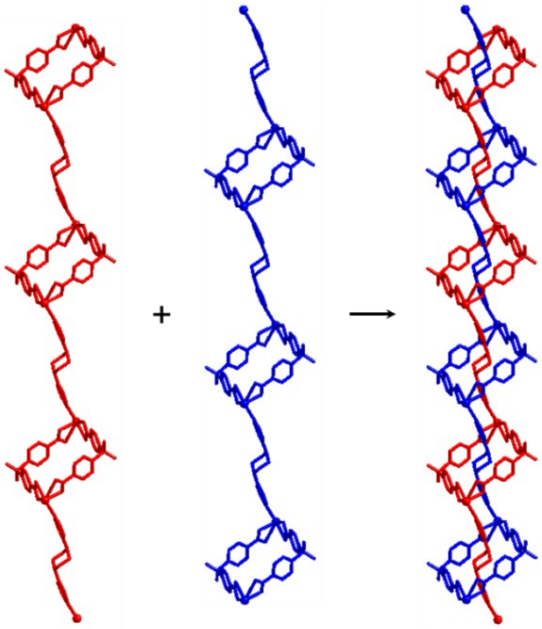
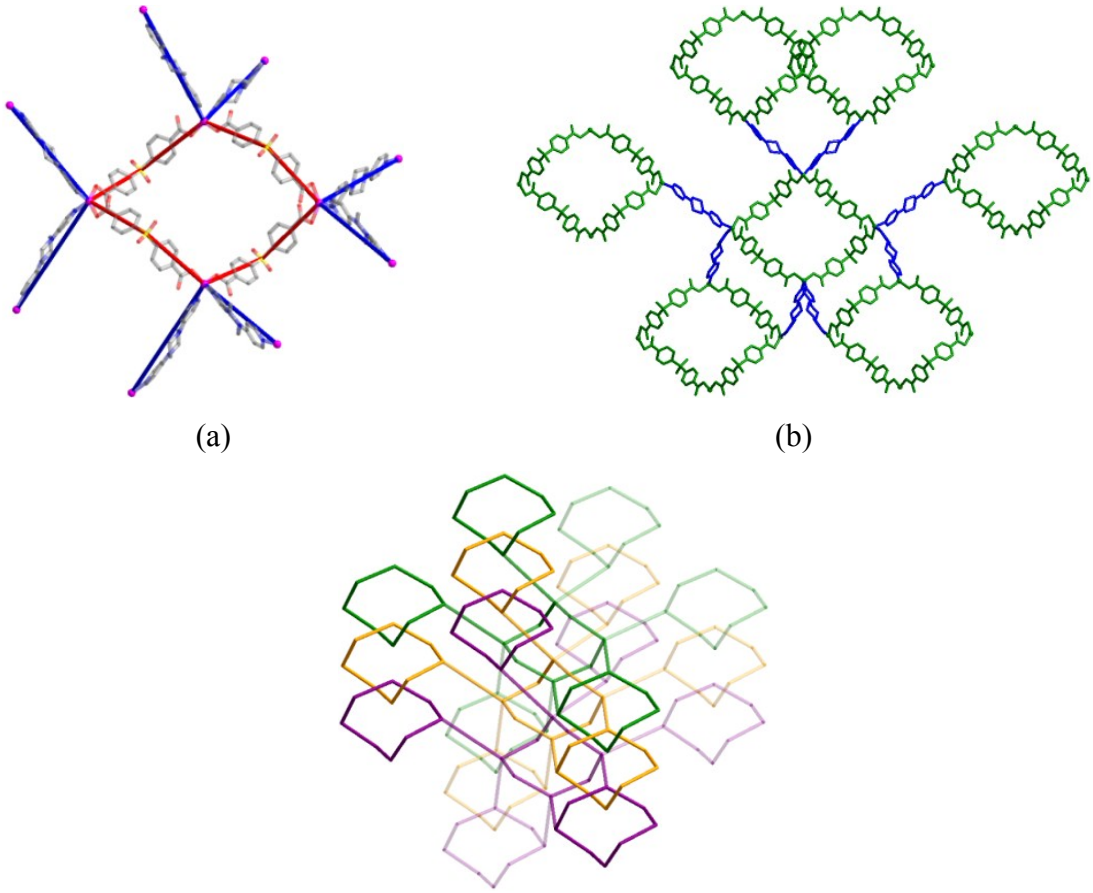


Fig. S1 The polymeric chains entangled in pairs to form a polyrotaxane (**1**).



(a) (b)

(c)

Fig. S2 Polycatenane structure of **2**, $[Zn_2(sdb)_2(bpp)_2]\cdot 2DMA\}_n$: (a) one tetrameric metallacycle unit (green part) with the coordinated bpp linkers (blue part), (b) basic linking of the metallacycles (green part) with bpp ligands (blue part) and (c) schematic perspective view.

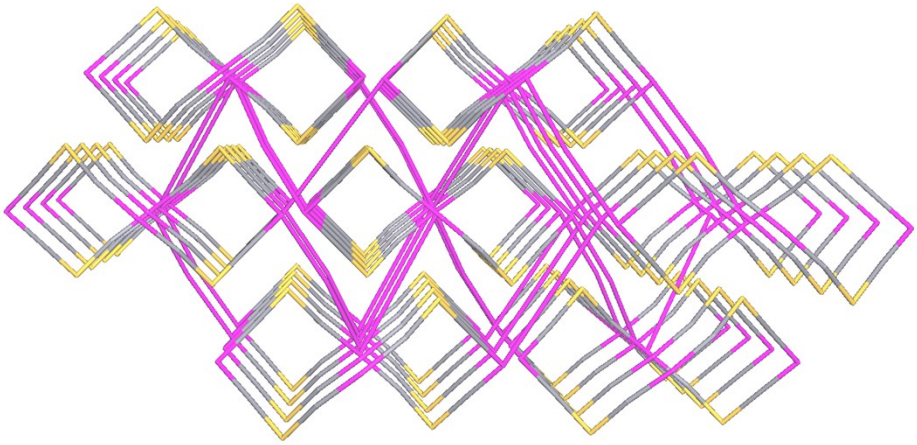


Fig. S3 Simplified 3D framework of the 4,4,4-connected 3-nodal net showing the *ssl*2 topology in **2**.

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Structural group analysis
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Structural group No 1
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Structure consists of 3D framework with Zn

Coordination sequences
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Zn1:  1  2  3  4   5   6   7    8    9   10
Num   4  9 22 54 123 233 388  587  862 1219
Cum   5 14 36 90 213 446 834 1421 2283 3502
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Zn2:  1  2  3  4   5   6   7    8    9   10
Num   4 10 23 57 130 238 387  602  874 1199
Cum   5 15 38 95 225 463 850 1452 2326 3525
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Zn3:  1  2  3   4   5   6   7    8    9   10
Num   4 11 28  66 135 241 400  613  872 1207
Cum   5 16 44 110 245 486 886 1499 2371 3578
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TD10=3532

Vertex symbols for selected sublattice
--------------------------------------
Zn1 Point symbol:{4^3.6^2.8}
Extended point symbol:[4.4.4.8.6.6]
--------------------------------------
Zn2 Point symbol:{4^2.6.10^3}
Extended point symbol:[4.10(6).4.10(10).6.10(6)]
--------------------------------------
Zn3 Point symbol:{4.10^5}
Extended point symbol:[4.10(5).10(2).10(2).10(3).10(3)]
--------------------------------------
Point symbol for net: {4.10^5}{4^2.6.10^3}2{4^3.6^2.8}
4,4,4-c net with stoichiometry (4-c)(4-c)2(4-c); 3-nodal net

New topology, please, contact the authors (102511 types in 11 databases)
Elapsed time: 4.27 sec.
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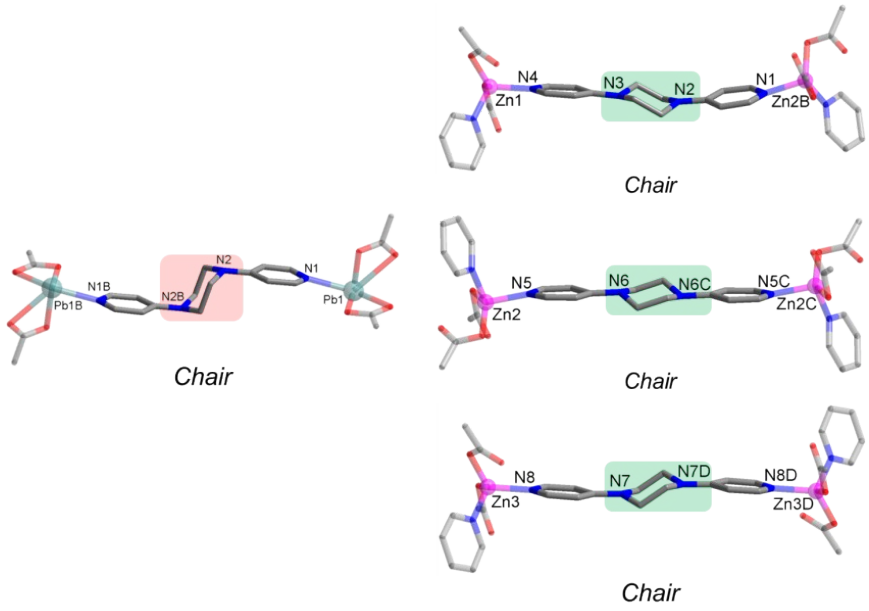
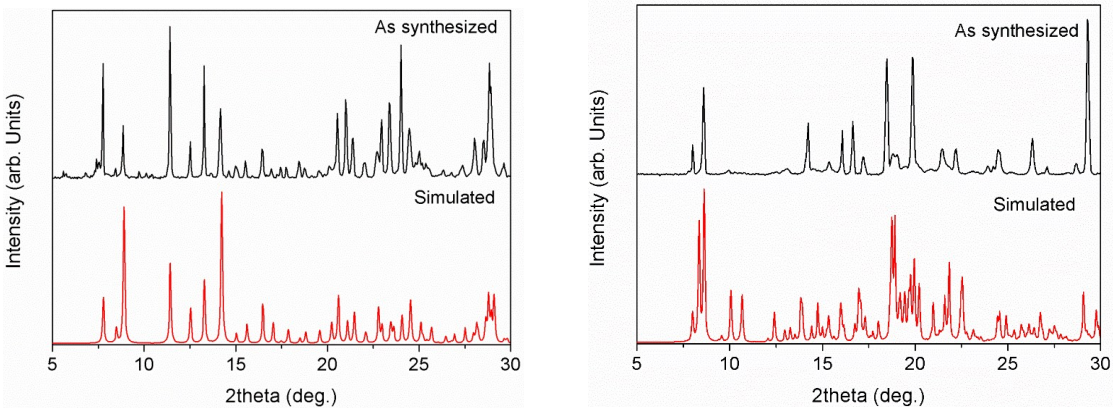
Fig. S4 An output of the topological analysis of **2** by *ToposPro* program.



(a) (b)

Fig. S5 Comparison of the bpp conformations in (a) **1** and (b) **2**.



(a) (b)

Fig. S6 PXRD patterns for (a) **1** and (b) **2**.