Supporting Information

General methods

All starting materials used in these synthetic reactions are purchased commercially and were used as obtained from the supplier. The power X-ray diffraction (PXRD) patterns were collected by a RIGAKU DMAX2500 X-ray diffractometer with Cu K α radiation (λ =0.154 nm). The FT-IR spectra were obtained on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000-400 cm⁻¹. Elemental analysis for C, H, N was performed on a German Elementary Vario EL III instrument. Thermogravimetric analysis was recorded on a NETZSCH STA 449C unit with a heating rate of 10°C · min⁻¹ in nitrogen atmosphere. Magnetic susceptibility data were measured using a Quantum Design MPMS-XL5 SQUID magnetometer.

Preparation of $[Cd_2(sal)_4(bpe)_3]$ (1)

Cadmium(II) nitrate tetrahydrate (62 mg, 0.2 mmol), Hsal (14 mg, 0.1 mmol) and bpe (37 mg, 0.2 mmol) were placed into 8 mL of distilled H₂O in a Teflon-lined 23 mL steel autoclave. The autoclave was sealed and heated at 120 °C for 72 h, and then cooled to 25 °C for 24 h. Colorless blocks of **1** (32% yield based on Cd) were isolated after washing with distilled water and drying in air. Anal. Calc. for $C_{64}H_{56}Cd_2N_6O_{12}$ **1**: C, 57.97; H, 4.26; N, 6.34. Found: C, 58.18; H, 4.19; N, 6.42. Selected IR data (KBr pellet, 4000 - 400 cm⁻¹): 3428 (m), 3066 (w), 1611 (vs), 1576 (s), 1485 (s), 1426 (s), 1388 (s), 760 (m).

Preparation of [Co(tdsal)(bpe)] (2)

Cobalt(II) nitrate hexahydrate (58 mg, 0.2 mmol), H₂tdsal (31 mg, 0.1 mmol) and bpe (37 mg, 0.2 mmol) were placed into 8 mL of distilled H₂O in a Teflon-lined 23 mL steel autoclave. The autoclave was sealed and heated at 120 °C for 72 h, and then cooled to 25 °C for 24 h. Pink plates of **2** (35% yield based on Co) were isolated after washing with distilled water and drying in air. Anal. Calc. for C₂₆H₂₀CoN₂O₆S **2**: C, 57.04; H, 3.68; N, 5.12. Found: C, 56.81; H, 3.76; N, 5.05%. Selected IR data (KBr pellet, 4000 - 400 cm⁻¹): 3427 (m), 1618 (vs), 1586 (m), 1468 (s), 1429 (s), 1248 (m), 827 (m), 722 (m).

X-Ray crystallography

Diffraction data for **1** and **2** were collected on a Rigaku SCXmini CCD and Rigaku Mercury CCD diffractometers respectively, with graphite monochromated Mo-K α radiation. The structures were solved using direct methods and refined on F² using SHELXTL¹. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were placed in calculated positions and refined isotropically with a riding model. Selected bond distances and angles of the complexes **1-2** are listed in Table S1.



Fig. S1 Coordination environments of 1 (a) and 2 (b).



Fig. S2 (a) The $\pi \cdots \pi$ interactions (the red dotted lines) between the sal⁻ and bpe rings from a parallel layer set in **1**. (b) The $\pi \cdots \pi$ interactions (the red dotted lines) between parallel tdsal²⁻ rings in the stacking of the 2D polyrotaxane layers in **2**.



Fig. S3 (a) Schematic view of $2D + 2D \rightarrow 3D$ parallel/parallel inclined polycatenation motif in **1**; (b) 2D polyrotaxane-like interpenetration layers in **2**.



Fig. S4 PXRD patterns of **1**(a) and **2**(b).



Fig. S5 Thermal gravimetric curves for 1 and 2.

The mass of **1** remained relatively constant before 240 °C, at which temperature the complex decomposed rapidly on further heating. Similarly, **2** underwent no obvious weight loss before 280 °C, and the compound decomposes rapidly on further heating.



Fig. S6 Solid-state emission spectra of 1, Hsal and bpe at room temperature.

Irradiation of a crystalline sample of **1** with ultraviolet light ($\lambda_{max} = 350$ nm) in the solid state resulted in a strong emission band centered at 410 nm. Compared to the Hsal and bpe ligands ($\lambda_{max} = 430$, 440 nm), a moderate blue shift is observed. This

emission band may be caused by LMCT of Hsal and bpe ligands or metal-perturbed intraligand charge transfers of Hsal and bpe ligands.



Fig. S7 The temperature dependence of $\chi_M T$ at 1 kOe for 2.

Solid-state, variable-temperature magnetic susceptibility was measured on crystalline samples of **2** in the range 2 – 300 K at 1 kOe. The χ_M T value at 300 K is 2.51 cm³ K mol⁻¹ per Co(II) ion, higher than the spin-only value 1.875 cm³ K mol⁻¹. This is probably induced by the presence of orbital contribution of octahedral Co(II) ion. The value decreases very slowly from 300 to 50 K, whereupon it drops more rapidly, reaching 1.66 cm³ K mol⁻¹ at 2 K. The χ_M^{-1} versus T plot follows the Curie-Weiss law with C = 2.55 cm⁻³ K mol⁻¹, θ = -6 K. The above features all indicate antiferromagnetic interactions between Co(II) ions.

Complex 1			
Cd1—O2	2.324 (3)	Cd2—O8	2.334 (3)
Cd1—N1	2.333 (3)	Cd2—N4	2.341 (3)
Cd1—N2	2.366 (3)	Cd2—N3	2.353 (3)
Cd1—N6 ⁱ	2.378 (3)	Cd2—N5	2.368 (3)
Cd1—O4	2.421 (3)	Cd2—O10	2.408 (3)
Cd1—O5	2.426 (3)	Cd2—O11	2.440 (3)
Cd1—O1	2.600 (4)	Cd2—O7	2.580 (3)
O2—Cd1—N1	94.85 (11)	N3—Cd2—N5	85.74 (10)
O2—Cd1—N2	132.87 (11)	O8—Cd2—O10	87.51 (10)

Table S1. Selected bond lengths (Å) and angles (°) for complexes 1-2

N1—Cd1—N2	90.29 (11)	N4—Cd2—O10	88.35 (11)
O2—Cd1—N6 ⁱ	88.23 (10)	N3—Cd2—O10	94.67 (11)
N1—Cd1—N6 ⁱ	173.32 (11)	N5-Cd2-O10	139.44 (10)
N2—Cd1—N6 ⁱ	83.29 (11)	O8—Cd2—O11	141.34 (10)
O2—Cd1—O4	143.26 (10)	N4—Cd2—O11	87.90 (12)
N1—Cd1—O4	90.45 (11)	N3—Cd2—O11	94.01 (12)
N2—Cd1—O4	83.30 (10)	N5-Cd2-O11	85.64 (11)
N6 ⁱ —Cd1—O4	90.61 (11)	O10-Cd2-O11	53.83 (10)
O2—Cd1—O5	89.69 (10)	O8—Cd2—O7	52.90 (10)
N1—Cd1—O5	90.00 (11)	N4—Cd2—O7	84.04 (11)
N2—Cd1—O5	137.21 (10)	N3—Cd2—O7	93.55 (11)
N6 ⁱ —Cd1—O5	95.95 (11)	N5-Cd2-O7	81.00 (10)
O4—Cd1—O5	53.92 (9)	O10-Cd2-O7	139.20 (10)
O2—Cd1—O1	52.68 (10)	O11—Cd2—O7	164.11 (10)
N1—Cd1—O1	87.75 (10)	O8—Cd2—N3	88.14 (11)
N2—Cd1—O1	80.87 (10)	N4—Cd2—N3	176.97 (11)
N6 ⁱ —Cd1—O1	89.42 (11)	O8—Cd2—N5	132.97 (11)
O4—Cd1—O1	164.05 (10)	N4—Cd2—N5	92.07 (11)
O5-Cd1-O1	141.88 (10)	O8—Cd2—N4	91.84 (12)
Complex 2			
Col—Ol	2.018 (4)	Co1—N1	2.068 (5)
Co1—O3 ⁱ	2.051 (4)	Co1—O4 ⁱ	2.319 (4)
Co1—N2	2.063 (4)		
O1—Co1—O3 ⁱ	135.28 (19)	N2—Co1—N1	99.22 (19)
O1—Co1—N2	103.72 (19)	O1—Co1—O4 ⁱ	94.14 (18)
O3 ⁱ —Co1—N2	100.02 (18)	O3 ⁱ —Co1—O4 ⁱ	59.77 (16)
O1—Co1—N1	97.6 (2)	N2—Co1—O4 ⁱ	159.55 (18)
O3 ⁱ —Co1—N1	115.29 (19)	N1—Co1—O4 ⁱ	88.03 (18)

Symmetry code for 1: (i) x, y, 1+z; symmetry code for 2: (i) 2-x, -y, 1-z

Reference

1 G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution and Refinement, 1997, University of Göttingen.