ELECTRONIC SUPPLEMENTARY INFORMATION

for

A Robust Microporous 3D Cobalt(II) Coordination Polymer with New Magnetically Frustrated 2D Lattices: Single-Crystal Transformation and Modulation of Cooperative Magnetic Properties via Variety of Guest

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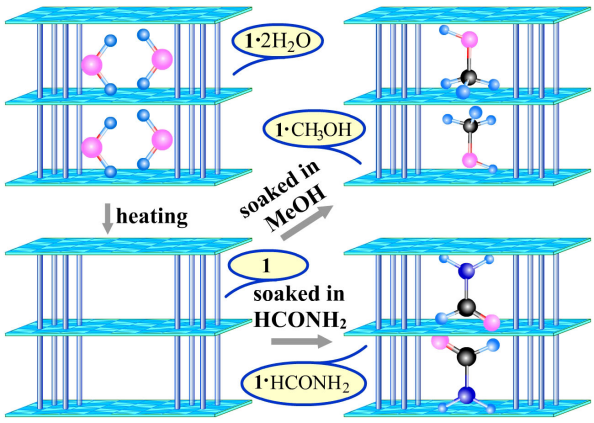

Scheme S1. Schematic representation of the guest removal/exchange.

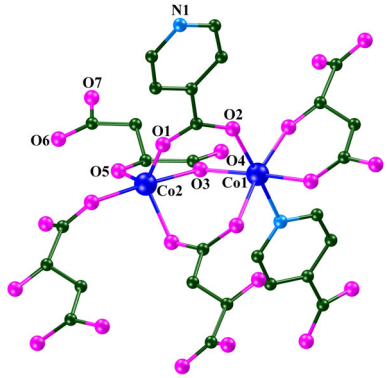

Fig. S1 Perspective view of the coordination environments of Co^{II} ions in **1**·$2H_2O$.

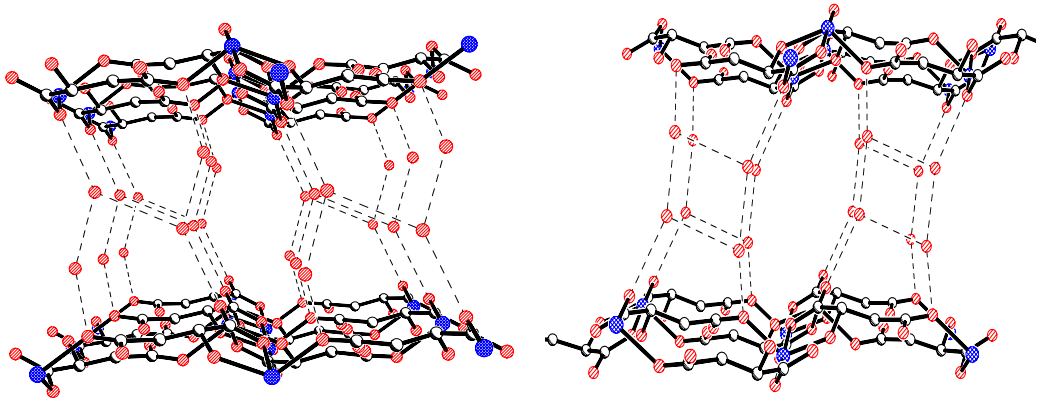

Figure S2. The H-bonding interactions in **1**·$2H_2O$ (a: 293 K, b: 93 K) viewed along the *b*-axis. The part of atoms omitted for clarity. The ma carboxylate oxygen atoms involving with hydrogen bonds are coordinated to the trigonal-bipyramid CoO_5 spin centers.

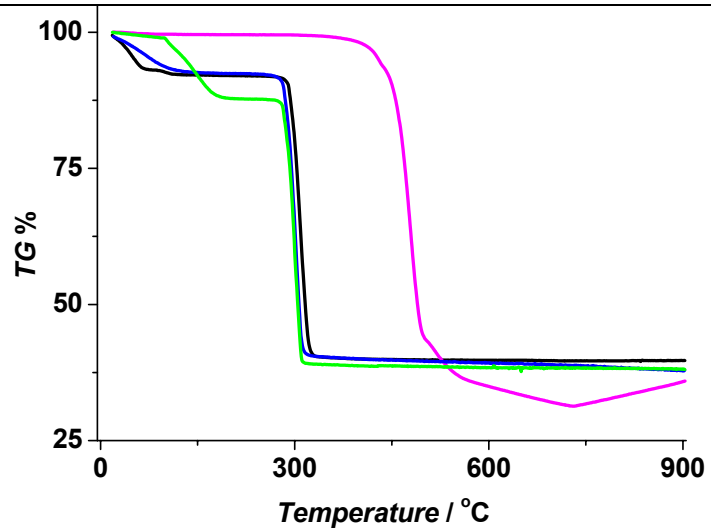

Figure S3. The TGA curves of **1**·2H_2O (black), **1**·MeOH (blue), **1**·$HCONH_2$ (green) under flowing air, and **1** (magenta) under flowing dinitrogen. **1**·2H_2O shows the first weight loss of 8.2% at ca. 260°C corresponding to the loss of the lattice water molecules (*ca*. 8.8% weight); **1**·MeOH shows the first weight loss of 7.7% at ca. 260 °C corresponding to the loss of the lattice MeOH molecules (*ca*. 8.0 % weight); **1**·$HCONH_2$ shows the first weight loss of 11.7% at ca. 260 °C corresponding to the loss of the lattice $HCONH_2$ molecules (*ca*. 10.8% weight); the TGA curve in flowing N_2 for **1** shows no weight loss up to ~340 ºC.

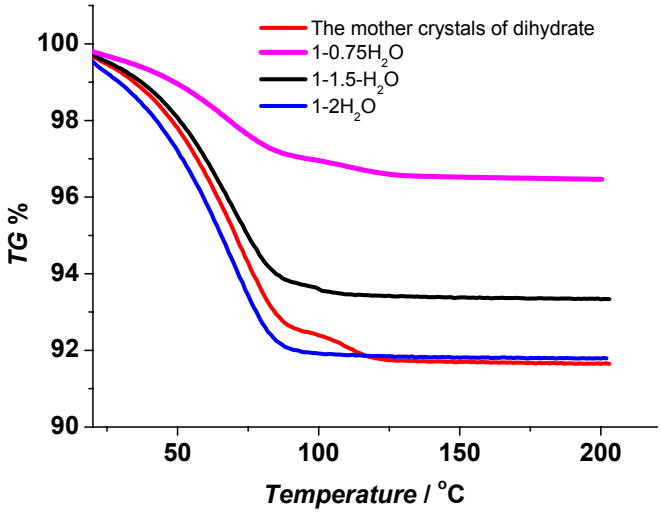

Figure S4. The TGA curves (20~200°C) of the rehydration of **1** in air (at T = 22(2) °C, relative humidity = 35(5)%) for one day (magenta), three days (black), and six days (blue).

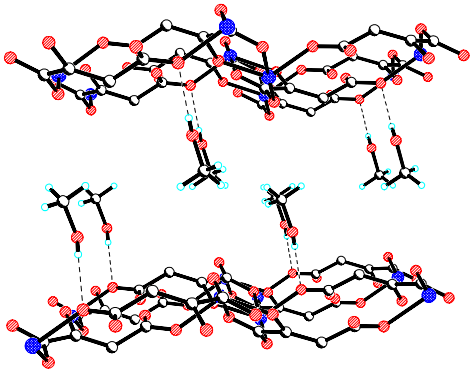

Figure S5. The H-bonding interactions in **1**·MeOH viewed along the *b*-axis. Part of atoms are omitted for clarity.

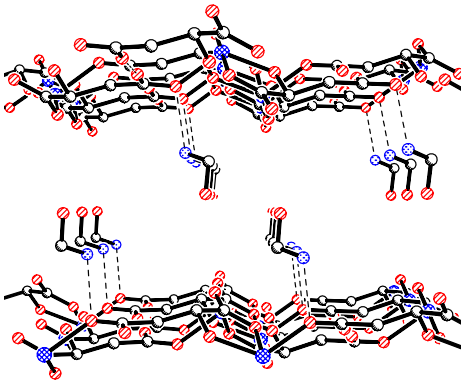

Figure S6. The H-bonding interactions in **1**·$HCONH_2$ viewed along the *b*-axis.

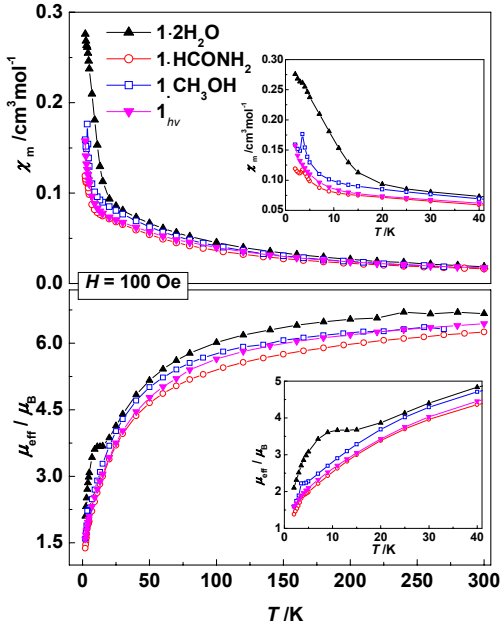

Fig. S7 Magnetic curves for **1**·2H_2O, **1**·$HCONH_2$, **1**·MeOH, and **1** (χ_M: upper, μ_{eff}: lower, per Co^{II}_2 under H = 100 Oe). Inset: the amplificationcurves below 40 K.

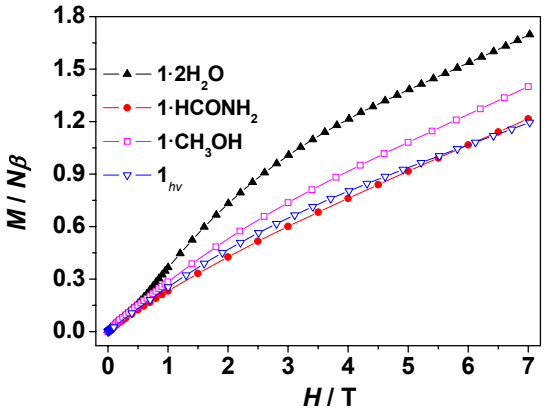

Figure S8. First magnetization at 2 K for **1**·2H_2O, **1**·$HCONH_2$, **1**·MeOH, and **1**.

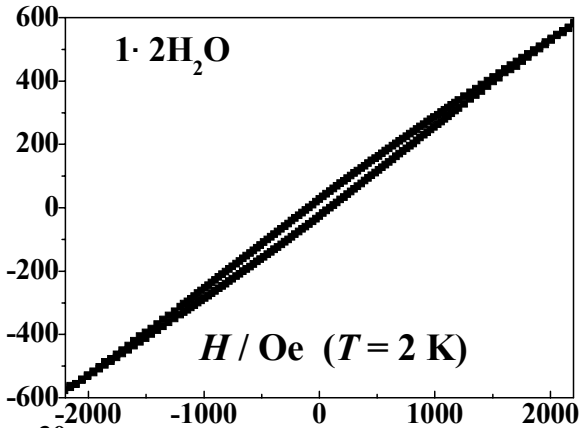

Figure S9. Hysteresis loops at 2 K for **1**·2H_2O.

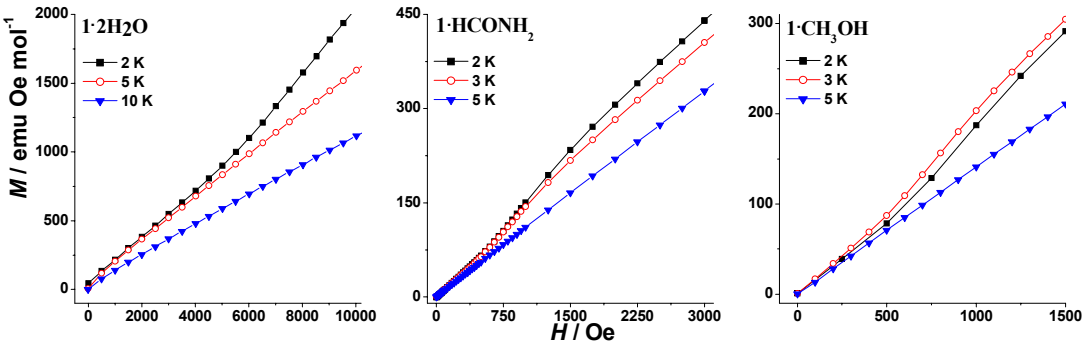

Figure S10. Magnification of the first magnetization at 2~10 K for **1**·2H_2O, **1**·MeOH and **1**·$HCONH_2$ at low field.

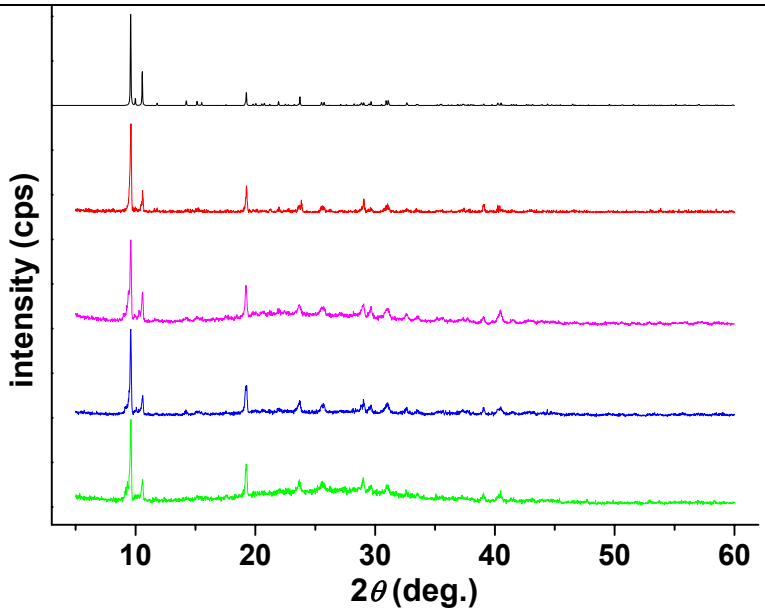

Figure S11. The simulated (black) and experimental powder X-ray diffraction patterns of **1**·2H_2O (red), **1** (magenta), **1**·MeOH (blue) and **1**·$HCONH_2$ (green).

Table S1. Crystallographic data and structure refinements of **1**·2H_2O'.

Compound	**1**·2H_2O'
T /K	293
Formula	$C_{10}H_{11}Co_2NO_9$
FW	407.07
a / Å	23.62(2)
b / Å	10.096(6)
c / Å	14.99(1)
β / deg	128.71(2)
V / Å^3	2790(3)
D_c / g·cm^{-3}	1.938
μ / mm^{-1}	2.424
R_{int}	0.055
R_1 ($I > 2\theta$)	0.0634
wR_2 (all data)	0.1909
GOF	1.23
$\Delta\rho_{min/max}$ (e/ Å^3)	-1.04~2.32
Free volume	26.2%

Table S2. Summary of the cell-parameter deviations of the crystal structures

	1·2H_2O (293 K) → **1** (293 K)	**1**·2H_2O (293 K) →**1**·2H_2O (93 K)	**1**·2H_2O (293 K) →**1**·MeOH (293 K)	**1**·2H_2O (93 K) → **1**·MeOH (93 K)	**1**·2H_2O (293 K) →**1**·$HCONH_2$ (293 K)	**1**·2H_2O (93 K) →**1**·$HCONH_2$ (93 K)	Max deviation (293 K)	Max deviation (93 K)
a / Å	-0.29%	-0.095%	-0.39%	+1.3%	+0.14%	+2.0%	0.57%	2.0%
b / Å	-0.23%	+0.25%	+0.11%	-0.78%	+0.21%	-0.45%	0.44%	0.45%
c / Å	-0.19%	-0.59%	+0.44%	0.64%	+0.55%	+0.87%	0.74%	0.87%
β / deg	-0.10%	-0.51%	-0.17%	0.63%	+0.054%	+0.99%	0.36%	1.0%
V / $Å^3$	-0.52%	-0.46%	+0.46%	0.0036%	+0.80%	0.70%	1.3%	0.70%

Table S3. Selected bond lengths (Å) for the compounds

	1·2H_2O (293 K)	**1**·2H_2O (93 K)	**1**·2H_2O' (293 K)	**1**·MeOH (293 K)	**1**·MeOH (93 K)	**1**·$HCONH_2$ (293 K)	**1**·$HCONH_2$ (93 K)	**1** (293 K)	Max deviation for 93 K	Max deviation for all
Co1-O1	2.089(4)	2.082(4)	2.100(6)	2.089(5)	2.079(4)	2.097(5)	2.083(4)	2.100(6)	0.19%	0.91%
Co1-O3	2.082(3)	2.082(4)	2.082(5)	2.084(4)	2.080(4)	2.085(5)	2.081(4)	2.082(5)	0.19%	0.58%
Co1-O5[a]	2.013(3)	2.010(3)	2.008(4)	2.017(4)	2.012(3)	2.022(4)	2.020(3)	2.008(4)	0.50%	0.70%
Co1-O6[a]	2.124(3)	2.113(3)	2.121(5)	2.128(5)	2.117(4)	2.120(5)	2.123(4)	2.121(5)	0.47%	0.76%
Co1-O6[c]	2.149(3)	2.146(3)	2.160(5)	2.156(4)	2.148(4)	2.163(4)	2.152(4)	2.160(5)	0.23%	0.89%
Co1-N1[b]	2.161(5)	2.150(5)	2.163(7)	2.149(6)	2.146(5)	2.165(6)	2.147(5)	2.163(7)	0.19%	0.84%
Co2-O2	1.968(5)	1.972(4)	1.959(6)	1.970(6)	1.977(5)	1.972(6)	1.974(5)	1.959(6)	0.25%	0.87%
Co2-O3	2.114(3)	2.107(3)	2.118(5)	2.111(4)	2.114(3)	2.116(4)	2.109(3)	2.118(5)	0.33%	0.47%
Co2-O4[d]	2.077(3)	2.078(3)	2.081(5)	2.079(4)	2.079(4)	2.078(5)	2.071(3)	2.081(5)	0.43%	0.53%
Co2-O5	1.939(4)	1.936(3)	1.945(5)	1.939(5)	1.942(5)	1.944(5)	1.941(5)	1.945(5)	0.26%	0.47%
Co2-O7[c]	2.007(4)	2.006(5)	2.009(5)	2.000(4)	1.996(4)	2.000(5)	2.004(4)	2.009(5)	0.45%	0.65%

Symmetry codes: a) 0.5-x, y-0.5, 0.5-z; b) x, 2-y, z-0.5; c) x-0.5, 1.5-y, z-0.5; d) 0.5-x, 0.5+y, 0.5-z; e) x, 2-y, z+0.5.

Table S4. Selected bond angles (°) for the compounds

	1·2H$_2$O (293 K)	**1**·2H$_2$O (93 K)	**1**·2H$_2$O' (293 K)	**1**·MeOH (293 K)	**1**·MeOH (93 K)	**1**·HCONH$_2$ (293K)	**1**·HCONH$_2$ (93 K)	**1** (293 K)	Max deviation at 93 K	Max deviation of all
O1-Co1-O5^a	90.4(2)	90.7(2)	90.6(2)	90.7(2)	90.5(2)	90.6(2)	90.7(2)	90.6(2)	0.11%	0.33%
O3-Co1-O5^a	96.7(1)	97.0(1)	96.8(2)	97.0(2)	96.5(2)	96.7(2)	95.8(2)	96.8(2)	1.25%	1.25%
O1-Co1-O3	88.0(1)	87.5(2)	87.5(2)	88.0(2)	88.8(2)	88.3(2)	88.2(2)	87.5(2)	1.49%	1.49%
O5^a-Co1-O6^a	89.8(2)	89.7(1)	89.8(2)	90.0(2)	89.6(2)	89.9(2)	90.3(2)	89.8(2)	0.78%	0.78%
O1-Co1-O6^a	87.8(1)	87.1(1)	88.1(2)	88.1(2)	87.9(2)	87.7(2)	87.3(2)	88.1(2)	0.80%	1.15%
O3-Co1-O6^a	172.3(1)	171.5(1)	172.1(2)	172.1(2)	173.1(2)	172.3(2)	172.5(2)	172.1(2)	0.93%	0.93%
O5^a-Co1-N1^b	90.5(2)	89.5(2)	90.5(2)	90.3(2)	90.3(2)	90.3(2)	90.4(2)	90.5(2)	1.01%	1.01%
O1-Co1-N1^b	177.6(2)	177.2(2)	177.3(2)	178.0(2)	178.5(2)	178.1(2)	178.3(2)	177.3(2)	0.73%	0.73%
O3-Co1-N1^b	89.7(2)	89.7(2)	89.9(2)	90.1(2)	89.8(2)	89.9(2)	90.4(2)	89.9(2)	0.78%	0.78%
O6^a-Co1-N1^b	94.5(1)	95.7(2)	94.4(2)	93.7(2)	93.5(2)	94.0(2)	93.9(2)	94.4(2)	2.35%	2.35%
O5^a-Co1-O6^c	168.2(2)	168.1(1)	167.9(2)	168.4(2)	168.9(2)	168.1(2)	169.2(2)	167.9(2)	0.65%	0.65%
O1-Co1-O6^c	89.9(1)	88.9(1)	89.3(2)	89.9(2)	90.1(2)	89.6(2)	89.5(2)	89.3(2)	1.24%	1.24%
O3-Co1-O6^c	95.2(1)	94.9(1)	95.3(2)	94.6(1)	94.6(1)	95.2(2)	95.0(1)	95.3(2)	0.42%	0.74%
O6^a-Co1-O6^c	78.4(1)	78.5(1)	78.1(2)	78.5(1)	79.4(1)	78.2(2)	78.9(1)	78.1(2)	1.40%	1.79%
O6^c-Co1-N1^b	89.8(1)	91.6(2)	90.1(2)	89.5(2)	89.5(2)	89.9(2)	89.6(2)	90.1(2)	2.35%	2.35%
O2-Co2-O5	128.9(2)	130.0(2)	129.4(2)	126.5(2)	127.5(2)	127.4(2)	130.1(2)	129.4(2)	2.04%	2.85%
O5-Co2-O7^c	122.1(2)	121.4(2)	122.2(3)	124.6(2)	123.3(2)	124.6(3)	122.0(2)	122.2(3)	1.73%	2.64%
O2-Co2-O7^c	107.9(2)	107.7(2)	107.3(3)	107.9(2)	108.2(2)	107.0(3)	107.0(2)	107.3(3)	0.93%	1.31%
O4^d-Co2-O5	99.2(2)	98.8(2)	99.0(2)	98.6(2)	99.1(2)	98.6(2)	99.0(2)	99.0(2)	0.30%	0.71%
O2-Co2-O4^d	90.9(2)	90.4(1)	90.8(2)	91.0(2)	90.0(2)	91.3(2)	90.2(2)	90.8(2)	0.44%	1.44%
O4^d-Co2-O7^c	89.1(1)	88.8(2)	88.9(2)	89.7(2)	89.6(2)	89.0(2)	89.7(2)	88.9(2)	0.90%	1.13%
O3-Co2-O5	79.6(1)	80.1(1)	79.8(2)	80.1(2)	79.7(2)	79.8(2)	79.5(2)	79.8(2)	0.75%	0.75%
O2-Co2-O3	92.8(2)	93.0(1)	93.0(2)	92.0(2)	92.4(2)	92.5(2)	92.6(2)	93.0(2)	0.65%	0.87%
O3-Co2-O7^c	88.4(1)	88.9(2)	88.5(2)	88.7(2)	89.2(2)	88.9(2)	89.1(2)	88.5(2)	0.79%	1.7%
O3-Co2-O4^d	176.1(2)	176.4(2)	175.8(2)	176.9(2)	177.5(2)	176.0(2)	177.2(2)	175.8(2)	0.68%	0.97%

Symmetry codes: a) 0.5-x, y-0.5, 0.5-z; b) x, 2-y, z-0.5; c) x-0.5, 1.5-y, z-0.5; d) 0.5-x, 0.5+y, 0.5-z; e) x, 2-y, z+0.5.