Supporting Information

Magnetic Variation Induced by Structural Transformation from Coordination Chains to Layers upon Dehydration

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The structure determination of compound 2 by X-ray powder diffraction data

a) Data collection: The X-ray powder diffraction data for structure determine and refinement was collected on Bruker D8 Advance with Cu K_{α} X-ray (40 kV, 40 mA). The powder sample of **2** was recorded in the 2 θ range of 5 – 60° with 0.02° 2 θ step and 10 seconds/step scan speed.

b) Indexing: Indexing and Pawley refinement¹ of the PXRD pattern of **2** were carried out by using Reflex module of Material Studio.² The pattern was indexed by the DICVOL91 method.³ Pawley refinements were carried out with the cell parameters obtained from indexing in space group *P*-1 with the 2θ range of $5 - 60^{\circ}$. Peak profiles, zero-shift, background, and unit-cell parameters were refined simultaneously. The peak profiles were refined by the Pseudo-Voigt function with asymmetry correction parameters. The background was refined with a 20th-order polynomial. The final Pawley refinement results are as follows: a = 5.635(4) Å, b = 6.908(5) Å, c = 8.225(6) Å, $a = 102.247(3)^{\circ}$, $\beta = 118.25(4)^{\circ}$, $\gamma = 104.470(5)$, V = 296.4(4) Å³, $R_p = 0.62\%$ and $R_{wp} = 0.89\%$.

c) **Rietveld refinement:** As detailedly discussed in the text, the structure of compound **3** was adopted as initial structure model of compound **2**. Positions of all the atoms for the initial model of **2** were referred to fractional coordinates of the corresponding atoms in **3**. Before Rietveld refinement, the structure model was geometrically optimized by Forcite module of Material Studio. Then, the ligand bta and SCN⁻ anion were set to two individual motion groups, and the torsion angle C1-N3-N4-N4#1 in ligand bta was set to be refined for following Rietveld refinements. The coordinates of Cd²⁺ ion would not be refined because it was locating on special position (inversion center). In addition, there was an inversion center at center of the ligand bta. Thus, there were 4 degrees of freedom (3 transitions and 1 torsion angle) for ligand bta, 6 degrees of freedom (3 rotations and 3 transitions) for SCN⁻ anion for the Rietveld refinements. Retaining the cell parameters, the 10 structural parameters, Pseudo-Voigt profile parameters, background parameters, the zero point of the diffraction pattern, the global isotropic atom displacement parameters, the Berar-Baldinozzi asymmetry correction parameters and the March-Dollase preferred orientation correction parameters, were optimized step by step to improve the agreement between the calculated and the experimental powder diffraction patterns for **2**, respectively, which were performed with Reflex Powder Refinement module of Material Studio. As shown in Fiugre S1, the final Rietveld refinements gave the R factors: $R_p = 0.89\%$ and $R_{wp} = 1.28\%$.



Figure S1. An ORTEP view for asymmetry unit of **1**. Displacement ellipsoids are represented by 30% probability level.



Figure S2. Perspective view of the asymmetric unit of **2**.

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Figure S3. Perspective view of transformation of 1D chains in 1 to a 2D layer in 2 (The water molecules are highlighted in red; all the hydrogen atoms are omitted for clarity; pink dotted lines represent the interchain hydrogen-bonding interactions).

	1	2	3
[Co/Cd-O]	[2.094(1) Å]	N/A	N/A
[Co/Cd -N]	[2.100(2)-2.172(2) Å]	[2.053(7) -2.171(2)Å]	[2.264(2) -2.373(2)Å]
[Co/Cd -S]	uncoordinated	[2.595(6) Å]	[2.728(1) Å]
[O-H N]	2.835(2) Å	N/A	N/A
[O-HS]	3.233(2) Å	N/A	N/A
Co/Cd […] S distance	4.581(2) Å	N/A	N/A
Co/CdN (uncoordinated) distance	4.371(3) Å	4.870(1) Å	5.512(2) Å
Co/Cd -Co/Cd (SCN ⁻ -bridged)	N/A	5.635(4) Å	5.849(2) Å
Co/Cd -Co/Cd (bta-bridged)	11.928(4) Å	11.810(6) Å	12.238(2) Å
Nearest Co/Cd Co/Cd (adjacent two chains)	6.917(3) Å	N/A	N/A
Shortest distance of interlayer triazole rings	4.187(3) Å	3.468(5) Å	3.602(3) Å

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Figure S4. An ORTEP view for asymmetry unit of **3**. Displacement ellipsoids are represented by 30% probability level.



Figure S5. PXRD patterns for 1 and 2.



Figure S6. PXRD patterns for **3**.



Figure S7. TGA of 1.



Figure S8. Temperature dependence of the real and imaginary parts of the molar ac magnetic susceptibility of **1**, obtained at the indicated frequencies in a zero dc field.



Figure S9. M vs H for **2** measured at different temperatures.



Figure S10. Hysteresis loop at 2 K of 2.



Figure S11. Field dependence of the magnetization (M) for 2 at 1.8 K emphasizing the presence of significant magnetic anisotropy seen at high field.



Figure S12. ZFC-FC curves of 2 in a 10 Oe applied field.



Figure S13. $\ln(\chi T)$ vs. T^{-1} plot for **2**, the solid line is a linear analysis in the temperature region of 4.8–10.0 K.



Figure S14. LC-MS (ESI) spectrum for starting material 1,2-di(4H-1,2,4-triazol-4-yl)diazene (bta). m/z = 164.9 (M+H⁺).

References

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