Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

The impact of solution vs slurry vs mechanochemical syntheses upon the sorption performance of a 2D switching coordination network

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Experimental Section

All reagents and solvents were used as received from commercial sources.

Ball Milling (BM) Experiments

BM experiments were performed using a Retsch MM400 ball mill. $Co(NCS)_2$ (1 mmol, 175 mg) and 4,4′-bipyridine (2 mmol, 312 mg) were mixed in 10 mL jars containing one 8 mm stainless steel ball per jar. The mill was operated at 25 Hz frequency for 5, 10, 15, 30, 60 and 120 min, respectively. Water assisted BM experiments were conducted (25 Hz, 5 min) by adding different amounts of water (2, 3, 4, 5, 6, 8, 10, 12, 15 mmol, respectively) and the resulting samples were labelled BM1202 to BM1215 based on the molar ratio of $M:L:H_2O$.

Twin Screw Extrusion (TSE) Experiments

TSE experiments were conducted in a twin-screw extruder (ZE12, Three-Tec, Switzerland) with screw diameter 12 mm and length-to-diameter ratio 40:1. A gravimetric powder feeder was used for feeding the pre-mixed starting materials: $Co(NCS)_2$ and 4,4′-bipyridine (1:2 molar ratio). The feed rate was set to 50 g/h and the screw speed to 50 rpm. The water flow rate was set to 18, 20, 22, 24, and 26 mL/h, respectively. The corresponding molar ratios of $Co(NCS)_2$, 4,4′-bipyridine and water were converted in Table 1.

Table S1. Parameters for water-assisted TSE experiments.

Batch	**Feed rate (g/h)**	**Screw speed (rpm)**	**Water flow rate (mL/h)**	**Molar ratio of $M:L:H_2O$**
TSE1	50	50	18	~1:2:10
TSE2	50	50	20	~1:2:11
TSE3	50	50	22	~1:2:12
TSE4	50	50	24	~1:2:13
TSE5	50	50	26	~1:2:14

Water Slurry (WS) Experiments

$Co(NCS)_2$ (1 mmol, 175 mg) and 4,4′-bipyridine (2 mmol, 312 mg) were added to 10 mL water in a 15 mL vial. The slurry was stirred continuously for 3 h prior to filtering the suspended solid which was then washed with water and air dried. The reaction was also 10 times scaled-up.

Solvent Diffusion (SD) Experiments

0.5 mmol (87.5 mg) of $Co(NCS)_2$ was dissolved in 5 mL H_2O and used as the bottom layer. A mixture of 2.5 mL H_2O and 2.5 mL ethanol was carefully layered over the $Co(NCS)_2$ solution to serve as the middle layer. A solution of 4,4′-bipyridine (1 mmol, 156 mg) in 5 mL ethanol was carefully layered over the ethanol/H_2O layer and served as the top layer. The solution was left undisturbed for two weeks and yielded orange crystals in the middle layer.

Single Crystal X-ray Diffraction (SCXRD)

A suitable single crystal of **chn-1-Co-NCS-H_2O** was chosen for single crystal X-ray diffraction measurements. The data was collected on a Bruker D8 Quest diffractometer equipped with MoK_α source (λ = 0.71073 Å) and Photon 100 detector at 298 K. The data was indexed, integrated and scaled in APEX3. An absorption correction was performed by a multi-scan method using SADABS. The space group was determined using XPREP implemented in APEX3. Structures were solved using an intrinsic phasing method (SHELXT) and refined on F^2 using nonlinear least-squares techniques with SHELXL contained in OLEX2 v1.2.8 program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the molecular geometry at idealized positions and assigned isotropic thermal parameters depending on the equivalent displacement parameters of their carriers. Crystallographic data for **chn-1-Co-NCS-H_2O** are presented in Table S2. The crystal structure has been deposited in the Cambridge Crystallographic Data Centre (CCDC 2014135).

Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction experiments were conducted on a Panalytical Empyrean diffractometer (40 kV, 40 mA, Cu K$\alpha_{1,2}$, λ = 1.5418 Å) in Bragg-Brentano geometry. A scan speed of 0.111747°/s (6.7°/min), with a step size of 0.026° in 2θ was used at room temperature with a range of 5° < 2θ < 40°.

Thermogravimetric Analysis (TGA)

TGA for all the samples were carried out under N_2 atmosphere using a TA instruments Q50 thermal analyzer from room temperature to 300 °C and a heating rate of 10 °C/min.

Scanning electron microscopy (SEM)

SEM analysis was performed using SU 70 Hitachi instrument. The samples were sputter-coated with gold (20 mA, 90 s) prior to imaging.

CO_2 Adsorption Studies

195 K CO_2 adsorption experiments (up to 1 bar) upon **sql-1-Co-NCS** were conducted on a Micromeritics TriStar II PLUS 3030 instrument. Samples of **chn-1-Co-NCS-H_2O** prepared by SD, BM, TSE and WS methods were degassed under vacuum at 50 °C overnight (~ 10 h) to transform to **sql-1-Co-NCS** by using a Smart VacPrep instrument prior to the sorption analysis. The temperature was maintained by a 4 L Dewar flask filled with the mixture of acetone and dry ice.

Table S2. Crystallographic data of the 1D chain coordination polymer, **chn-1-Co-NCS-H_2O**.

	chn-1-Co-NCS-H_2O
Formula	$C_{22}H_{20}CoN_6O_2S_2$
Formula weight	523.49
Temperature/K	298
Crystal system	Triclinic
Space group	*P-1*
a/Å	7.427(2)
b/Å	9.009(3)
c/Å	10.099(3)
α/°	107.801(9)
β/°	103.971(9)
γ/°	97.079(9)
Volume/Å^3	610.0(3)
Z	1
ρ_{calc} g/cm^3	1.425
μ/mm^{-1}	0.905
F(000)	269.0
Radiation	MoKα
Reflections collected	8065
Independent reflections	2415 [R_{int} = 0.0433, R_{sigma} = 0.0519]
Data/restraints/parameters	2415/0/152
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0487, wR_2 = 0.1051
Final R indexes [all data]	R_1 = 0.0708, wR_2 = 0.1136

(a) $Co(NCS)_2 + 2bpy + 2TFT \leftrightarrow Co(bpy)_2(NCS)_2 \cdot 2TFT \leftrightarrow Co(bpy)_2(NCS)_2 + 2TFT$

sql-1-Co-NCS·2TFT **sql-1-Co-NCS** ✓

(b) $Co(NCS)_2 + 2bpy \leftrightarrow Co(bpy)_2(NCS)_2$ ✗

sql-1-Co-NCS

(c) $Co(NCS)_2 + 2bpy + 2H_2O \leftrightarrow Co(bpy)(NCS)_2(H_2O)_2 \cdot bpy \leftrightarrow Co(bpy)_2(NCS)_2 + 2H_2O$

chn-1-Co-NCS-H_2O **sql-1-Co-NCS** ✓

Figure S1. The chemical reaction equations of synthesis of **sql-1-Co-NCS** via different routes.

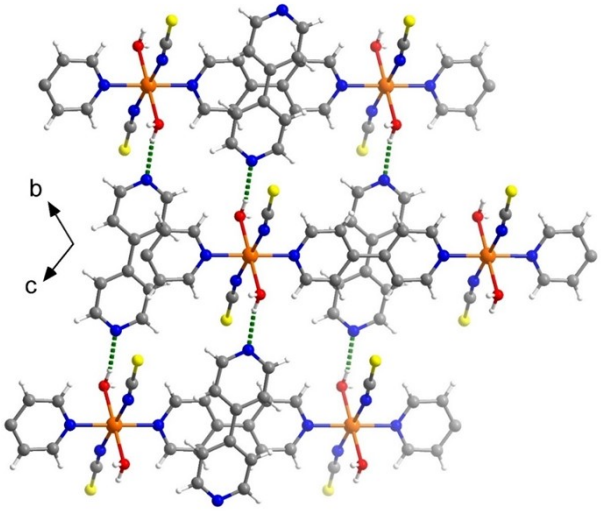

Figure S2. Packing mode of **chn-1-Co-NCS-H_2O** along *a* axis. Green dash lines stand for hydrogen bonds (OH···N distance: 1.887 Å, $\angle_{O\text{-}H\text{-}N}$: 161.3°).

Figure S3. Images of starting materials and neat BM products. a) $Co(NCS)_2$ (1 mmol), b) 4,4'-bipyridine (2 mmol), c) manual mixture of $Co(NCS)_2$ (1 mmol) and 4,4'-bipyridne (2 mmol); neat BM (25 Hz) of $Co(NCS)_2$ (1 mmol) and 4,4'-bipyridne (2 mmol) for d) 5 min, e) 10 min, f) 15 min, g) 30 min, h) 1 h, and i) 2 h.

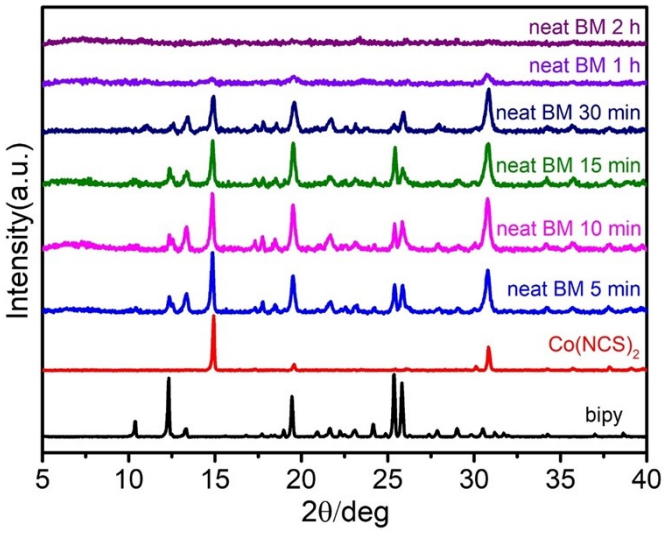

Figure S4. PXRD patterns of starting materials and neat BM products.

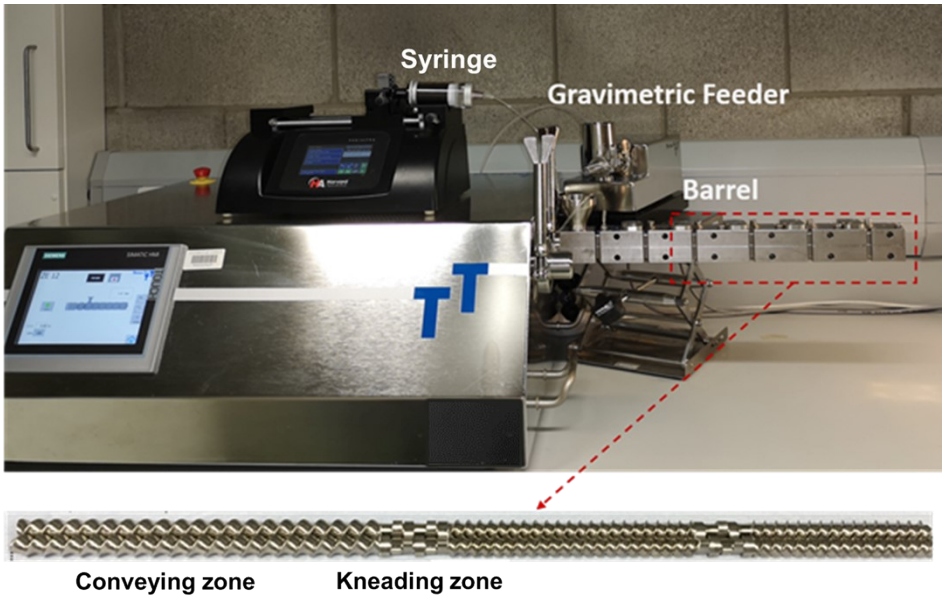

Figure S5. Image of twin-screw extruder setup.

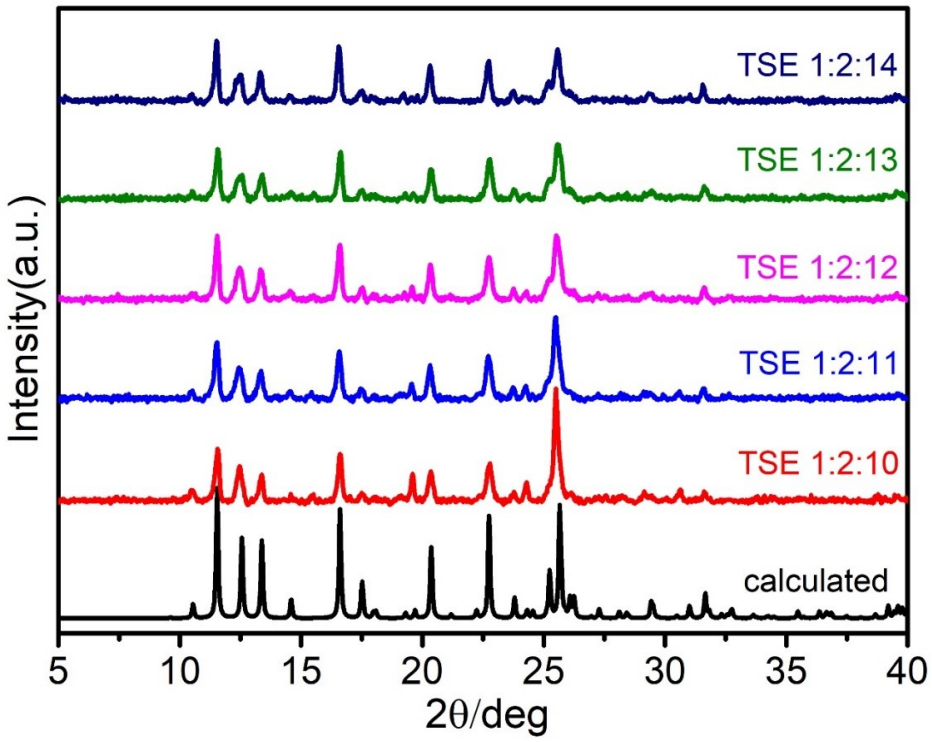

Figure S6. Comparison of calculated PXRD pattern of **chn-1-Co-NCS-H_2O** and those of water-assisted TSE with different molar ratios of M: L: H_2O.

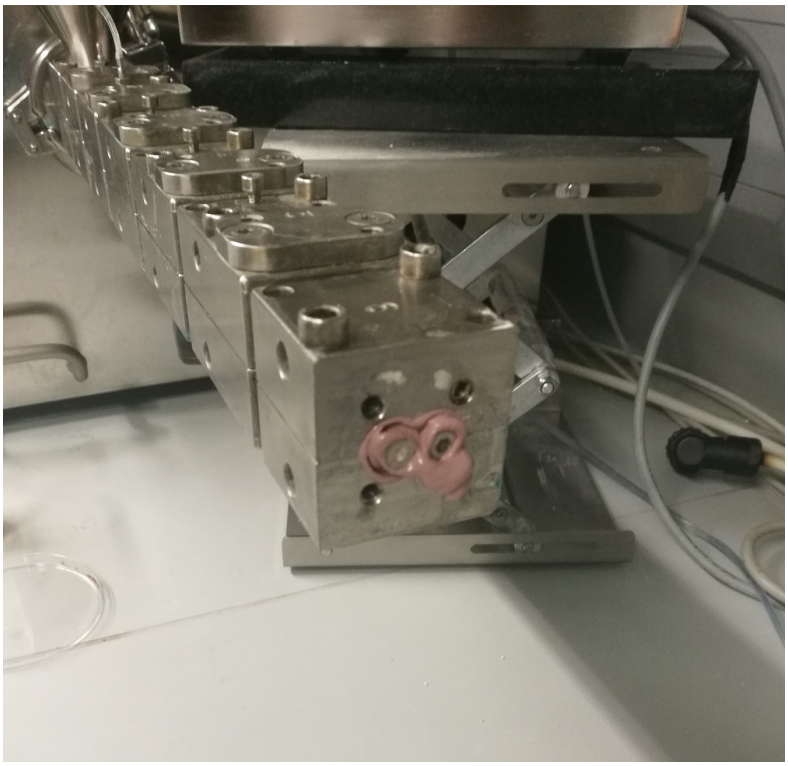

Figure S7. TSE product became overwet when water flow reaches 26 mL h^{-1}.

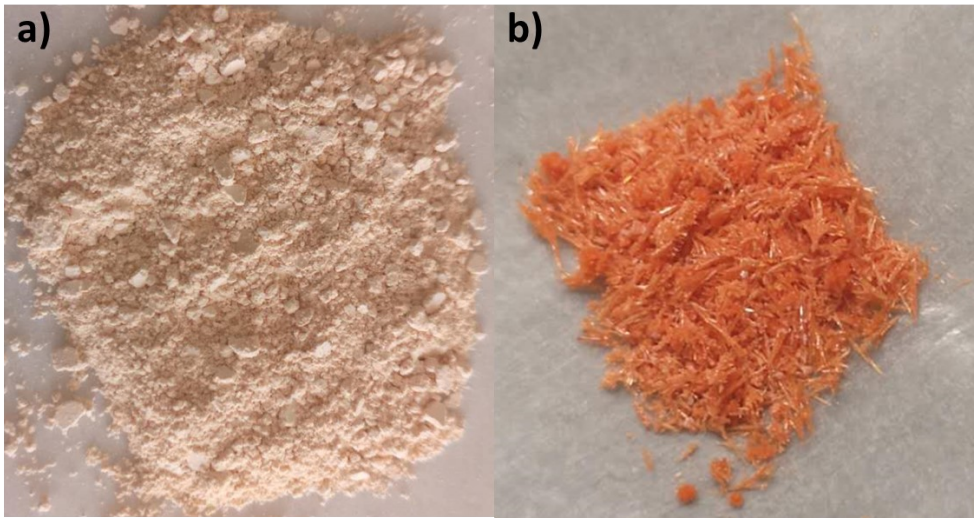

Figure S8. Optical images of **chn-1-Co-NCS-H_2O** prepared by a) WS and b) SD method.

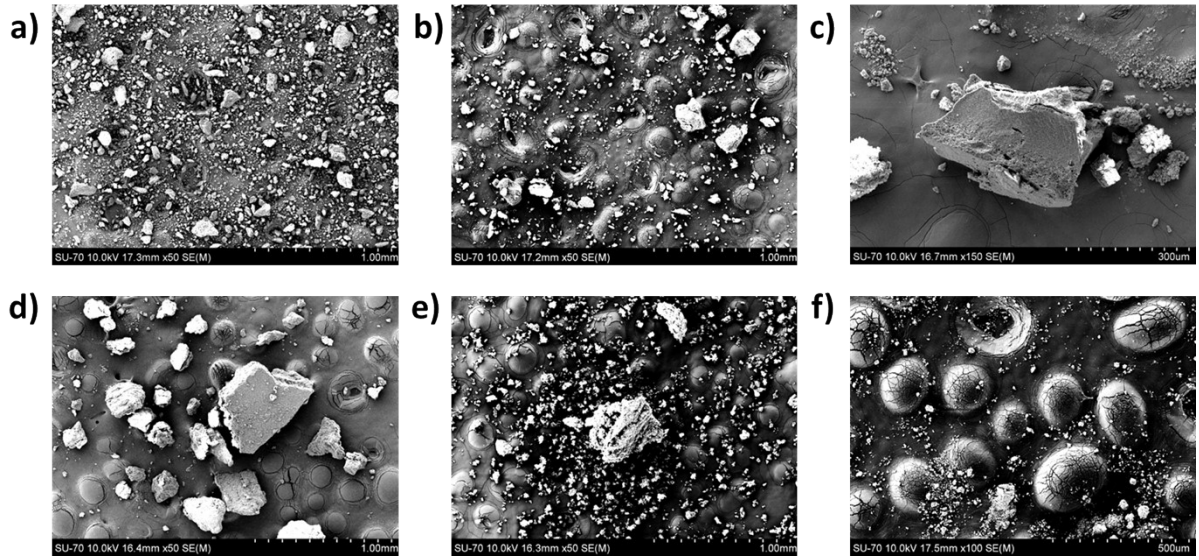

Figure S9. SEM images of aggregated **chn-1-Co-NCS-H_2O** for a) BM1206, b) BM1208, c) BM1210, d) BM1212, e) BM1215 and f) WS product.