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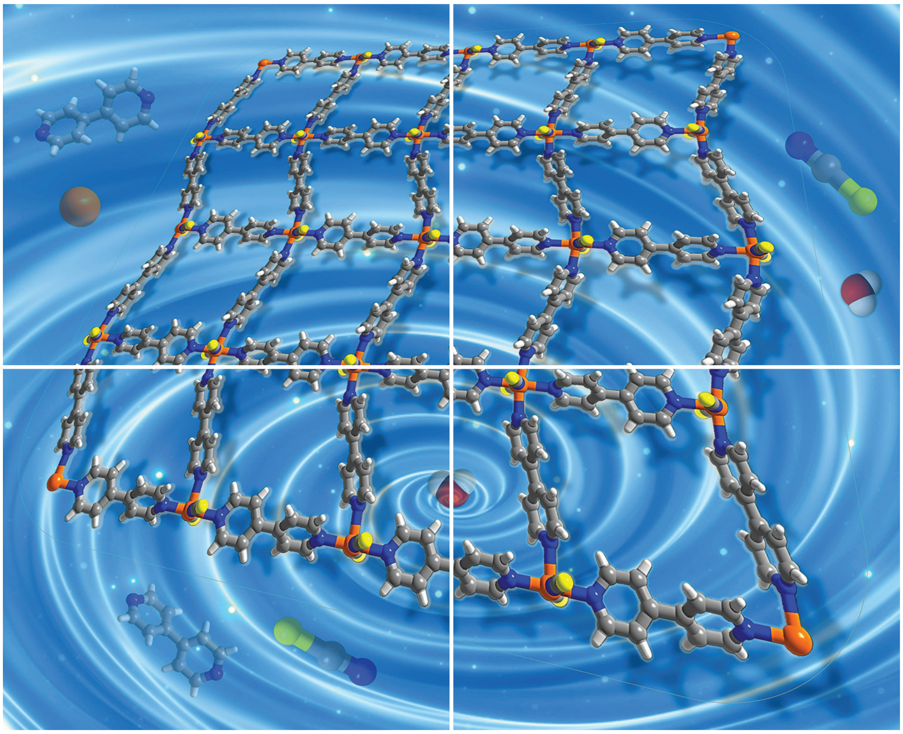

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The impact of solution *vs.* slurry *vs.* mechanochemical syntheses upon the sorption performance of a 2D switching coordination network†

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The selection and optimization of synthesis routes for porous metal–organic materials are critical for their large-scale manufacture but remain largely underexplored. In this study, we compare mechanochemistry *vs.* slurry *vs.* solution methods for the synthesis of a 1D chain coordination polymer $\{[Co(bpy)(NCS)_2(H_2O)_2]\cdot bpy\}_n$ (**chn-1-Co-NCS-H$_2$O**) that is an intermediate to the 2D switching coordination network $[Co(bpy)_2(NCS)_2]_n$, **sql-1-Co-NCS** (1 = bpy = 4,4′-bipyridine). Although neat mechanosynthesis using $Co(NCS)_2$ and bpy as the starting materials failed, both water slurry and water-assisted mechanochemical syntheses afforded the desired intermediate, **chn-1-Co-NCS-H$_2$O**, in high yield. Nevertheless, the resulting **sql-1-Co-NCS** products were observed to exhibit different CO_2 sorption profiles depending on the synthesis methods used to prepare **chn-1-Co-NCS-H$_2$O**. This study reveals that water can play an important role in mechanosynthesis, not only by inducing and accelerating the reaction process, but also by enhancing product quality in a manner that is not readily detectable by PXRD.

Introduction

Switching coordination networks (CNs) are a subclass of the third generation coordination polymers that undergo guest-induced structural transformation(s) between "closed" nonporous and "open" porous phases.[1–3] They represent a relatively small but potentially important and steadily growing type of flexible metal–organic frameworks (FMOFs) or soft porous crystals (SPCs).[4–9] The characteristic features of switching CNs are their responsiveness to specific guest species and the resulting stepped or type F-IV sorption isotherms, which could enhance the working capacity and selectivity for gas storage and separation applications.[10–13] It is widely recognized that CNs or MOFs have the potential to compete with conventional sorbents such as zeolites and activated carbons,[14–18] however, the promise of large-scale applications is largely unrealized despite >118 000 MOF entries having been archived in the Cambridge Structural Database.[19] A major issue that hinders the further development of CNs as industrial sorbents is their amenability to synthesis at large scale. This is perhaps the biggest hurdle between laboratory bench discovery, where solution synthesis has dominated, and commercial development, where the cost and efficiency of process methodology become paramount.[20–22]

With respect to the discovery of CNs, solvent mediated methods such as solvent diffusion (SD) and solvothermal (ST) methods are commonly used for mg and g scale synthesis. They offer an advantage of tending to result in single crystals, which enables determination of crystal structures *via* single crystal X-ray diffraction. Nevertheless, with respect to process development, more efficient approaches are desired for scale up of targeted CNs since SD and ST methods are generally low-yield, high-waste and time-consuming.[22] Recently, mechanochemical synthesis methods such as ball milling (BM), a batch method, or twin-screw extrusion (TSE), a continuous method, have emerged as candidates for large scale synthesis of CNs, as well as alloys, oxides, halides, cocrystals, polymers, and composites.[23,24] BM and TSE offer the potential of high space–time yield, low-waste processes and can thereby address the inefficiencies of solvent-based methods. Further, IUPAC recently highlighted mechanochemistry as one of "the top ten technologies to change the world".[25] However, the mantra that "the best solvent is no solvent" does not necessarily apply to water,[26–28] especially water slurry (WS), which could be suit-

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able for large-scale manufacture of water-stable, water-insoluble CNs.[29–32]

Recently, we reported that the previously known square lattice (**sql**) CN,[33,34] $[Co(bpy)_2(NCS)_2]_n$ (bpy = 4,4′-bipyridine), **sql-1-Co-NCS**, exhibits recyclable switching between its "closed" nonporous and "open" porous phases induced by CO_2 or C_8 aromatics.[35,36] We coined the term "switching adsorbent layered materials" (SALMAs) for such sorbents and they hold promise for gas storage and hydrocarbon separations,[36–42] prompting us to explore the feasibility of their large-scale manufacture. In our previous work,[35] we prepared **sql-1-Co-NCS** by applying heat under vacuum to its guest-loaded variant **sql-1-Co-NCS·2TFT** (TFT = α,α,α-trifluorotoluene), which was synthesized by self-assembly of $Co(NCS)_2$ and bpy using the SD method in the presence of organic solvents (Fig. 1a and c and S1a†). This procedure generally takes 1–2 weeks to grow crystals and results in significant solvent waste (ethanol and TFT). On the other hand, it was found that the 1D chain coordination polymer $\{[Co(bpy)(NCS)_2(H_2O)_2]\cdot bpy\}_n$ (**chn-1-Co-NCS-H_2O**) has the requisite stoichiometry to serve as an intermediate for preparing **sql-1-Co-NCS** simply by heating (Fig. 1b and S2†).[33,34] A similar phenomenon was also reported for $\{[Cu(bpy)(BF_4)_2(H_2O)_2]\cdot bpy\}_n$ (preELM-11) and $[Cu(bpy)_2(BF_4)_2(H_2O)_2]_n$ (ELM-11).[43] Whereas the structural transformation from **sql-1-Co-NCS·2TFT** to **sql-1-Co-NCS** involves noncovalent bonds only and chemical bonds are involved in activation of **chn-1-Co-NCS-H_2O**, the conditions required by the two routes are, perhaps surprisingly, comparable (*i.e.* 50 °C under vacuum for several hours).

With the above synthesis routes in hand, we wondered if mechanochemistry would be feasible for direct preparation of **sql-1-Co-NCS** or its intermediate **chn-1-Co-NCS-H_2O**, since we and others have been investigating the use of mechanochemical synthesis to prepare coordination polymers and related materials.[44–50] In particular, we have previously reported that reaction of a 1 : 1 molar ratio of bpy and hydrated metal nitrates *via* BM and TSE afforded four 1D chain coordination polymers.[44] Herein, we compare the effectiveness of mechanochemical synthesis for preparation of **chn-1-Co-NCS-H_2O** with solution and slurry methods. We also assess if the sorption properties of **sql-1-Co-NCS** are impacted by the synthesis methods used to prepare its intermediate, **chn-1-Co-NCS-H_2O**.

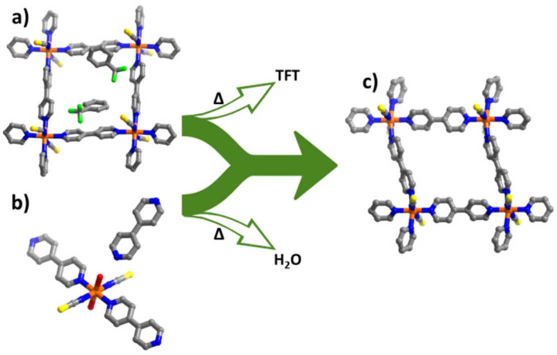

Fig. 1 Crystal structures of (a) **sql-1-Co-NCS·2TFT**; (b) **chn-1-Co-NCS-H_2O**; and (c) **sql-1-Co-NCS** prepared from **sql-1-Co-NCS·2TFT** or **chn-1-Co-NCS-H_2O** by heating. Brown: Co, blue: N, red: O, grey: C, green: F, yellow: S. Hydrogen atoms are omitted for clarification.

Results and discussion

With respect to the direct mechanosynthesis of **sql-1-Co-NCS**, we first investigated neat BM experiments with 1 : 2 molar ratio of $Co(NCS)_2$ and bpy, consistent with the chemical formula of **sql-1-Co-NCS** (Fig. S1b†). PXRD revealed that the reaction between $Co(NCS)_2$ and bpy did not occur during 5–30 min of BM, and the starting materials became amorphous with color change after 1–2 h of BM (Fig. S3 and S4†). We anticipated that the presence of water in the reaction medium might be important, as exemplified by success in previous reports.[51–55] We then conducted mechanochemical synthesis of **chn-1-Co-NCS-H_2O** by adding aliquots of water to the BM experiments. It was observed that such water-assisted BM reactions afforded **chn-1-Co-NCS-H_2O** and the amount of water used was found to be a key parameter (Fig. 2). When the $M : L : H_2O$ corresponded to its chemical formula (*i.e.* 1 : 2 : 2, Fig. S1c†), the formation of **chn-1-Co-NCS-H_2O** was not achieved after 5 min of BM. Increasing the $M : L : H_2O$ ratio to 1 : 2 : 3 was also unsuccessful. These results suggested to us that more water might be needed to accelerate the reaction. Indeed, pure samples of **chn-1-Co-NCS-H_2O** were ultimately obtained when $M : L : H_2O$ is 1 : 2 : 4 or higher, although ratios of 1 : 2 : 8 and above resulted in solids that were caked.

We next investigated the preparation of **chn-1-Co-NCS-H_2O** by TSE. Neat TSE resulted in a physical mixture of starting materials, consistent with the neat BM results. For water-assisted TSE (Fig. S5†), we added water to the starting materials by using an automatic syringe pump with variable water flow rates (Table S1†). The parameters of feed rate and screw speed were empirically optimized at 50 g h^{-1} and 50 rpm, respectively. PXRD studies revealed that **chn-1-Co-NCS-H_2O** was successfully formed with 18–26 mL h^{-1} of water flow rate (Fig. S6†) while overwetting occurred when water flow reached 26 mL h^{-1} or above (Fig. S7†).

That water plays a critical role in preparing **chn-1-Co-NCS-H_2O** using BM and TSE prompted us to consider the WS method and **chn-1-Co-NCS-H_2O** was indeed obtained by stirring a slurry of $Co(NCS)_2$ (1 mmol, 175 mg) and bpy (2 mmol, 312 mg) in water (10 mL) for 3 h (Fig. 3a and S8a†). This finding contradicts our previous report on **chn-1-M-NO_3** materials, in which WS resulted in different phases to those obtained through BM and TSE methods.[44] In addition, 10× scale-up of WS afforded almost 5 g of **chn-1-Co-NCS-H_2O** in *ca.* 95% yield, which is a more efficient outcome than slurry in ethanol conducted for 3 days.[34] We also prepared single-crystals of **chn-1-Co-NCS-H_2O** by SD method using water and ethanol as the solvents,[33] but it took 2 weeks to obtain reasonable yield of product (Fig. S8b†). **chn-1-Co-NCS-H_2O** is there-

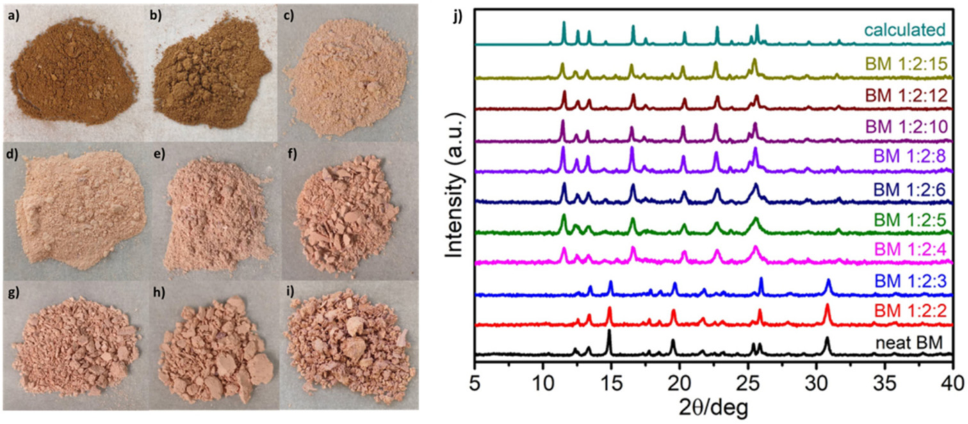

Fig. 2 (a–i) Images of the water-assisted BM products using $Co(NCS)_2$ (1 mmol) and 4,4′-bipyridne (2 mmol) with different amounts of water: (a) 2 mmol, (b) 3 mmol, (c) 4 mmol, (d) 5 mmol, (e) 6 mmol, (f) 8 mmol, (g) 10 mmol, (h) 12 mmol, and (i) 15 mmol; (j) comparison of the calculated PXRD pattern of **chn-1-Co-NCS-H_2O** with those of neat and water-assisted BM (25 Hz, 5 min) products using different molar ratios of M : L : H_2O.

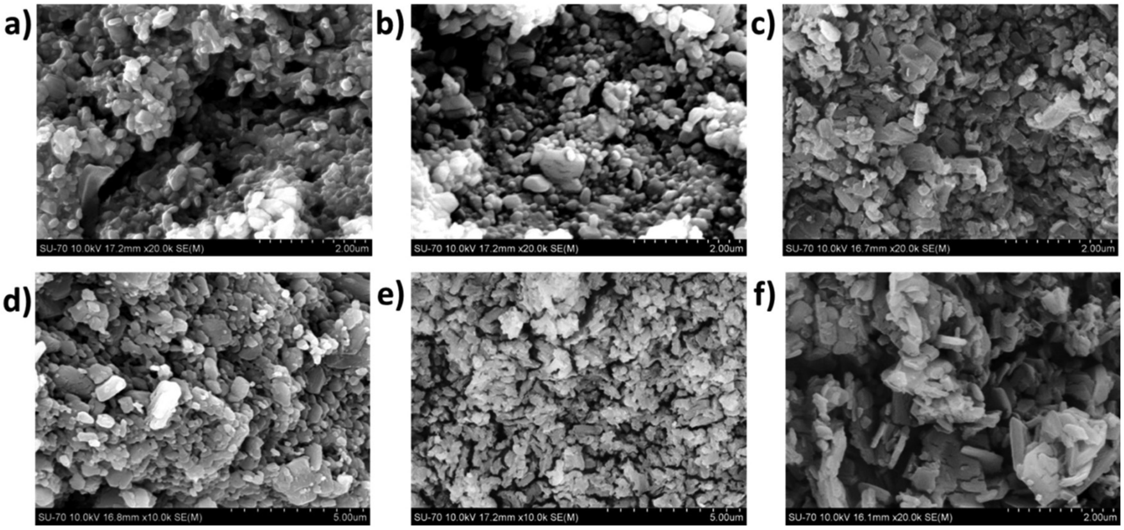

Fig. 3 SEM images of **chn-1-Co-NCS-H_2O** for (a) BM1206, (b) BM1208, (c) BM1210, (d) BM1212, (e) BM1215 and (f) WS product.

fore accessible by four methods: BM, TSE, WS and SD. SEM images of the BM and WS products are presented in Fig. 3. In general, sample morphologies may vary due to the different synthesis methods and conditions. The particle sizes of BM products were observed to be in the range of 200–500 nm and the primary particles further agglomerate to form aggregates with a wide diameter range from 10 to 200 μm (Fig. S9a–e†). The particle shapes of BM products appeared to have no regular facets (ellipsoid or sub-rounded), while the WS sample was observed to be flatter (plate-like) and formed agglomerates in a narrower diameter range of 5 to 50 μm (Fig. S9f†).

The SD, WS, BM and TSE products were found to exhibit matching PXRD patterns with the calculated PXRD of **chn-1-Co-NCS-H_2O** (Fig. 4a). The mechanochemically produced samples (*e.g.*, BM128 and TSE3, M : L : H_2O are 1 : 2 : 8 and 1 : 2 : 12, respectively) were observed to exhibit broader PXRD peaks than those produced by SD or WS. The TGA thermograms also exhibit differences between the samples prepared by BM/TSE and SD/WS (Fig. 4b). TGA of **chn-1-Co-NCS-H_2O** produced by SD/WS revealed 6.9 wt% loss before 100 °C, corresponding to loss of two aqua ligands per formula unit (calc. 6.9 wt%) and the formation of **sql-1-Co-NCS**, while BM/TSE products did not fully transform until 120 °C. This could be attributable to the compacted nature and agglomeration of the BM and TSE particles.

In order to determine if the intermediate **chn-1-Co-NCS-H_2O** prepared from different methods and conditions could impact the gas sorption properties of **sql-1-Co-NCS**, 195 K CO_2 sorption isotherms were collected on each sample after activation at 50 °C *in vacuo* for 10 h (Fig. 5). For the SD sample, it exhibited the expected switching isotherm with a steep adsorption step at 10 kPa as observed in our previous study.[35] The WS sample exhibited almost the same CO_2 uptake (138 cm^3 g^{-1}) but it showed a more gradual adsorption curve

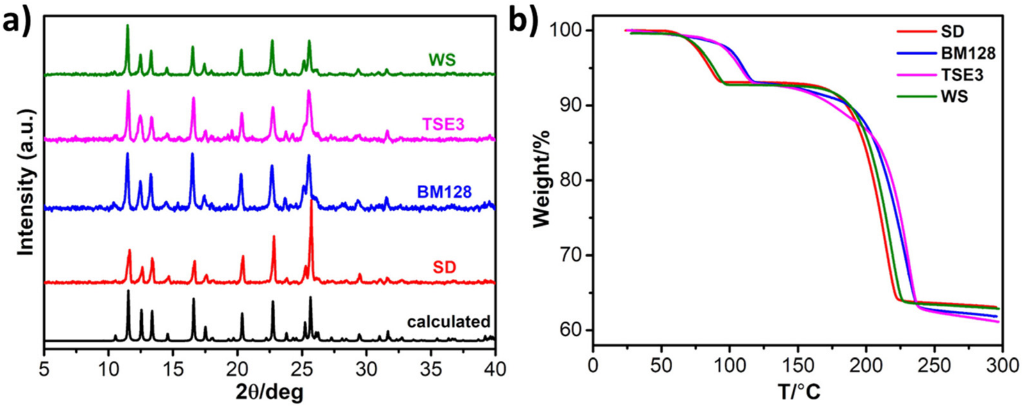

Fig. 4 (a) PXRD and (b) TGA profiles of SD, BM, TSE and WS products.

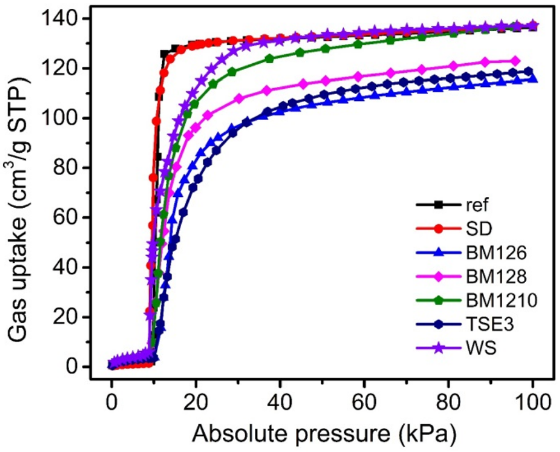

Fig. 5 195 K CO_2 adsorption isotherms of SD, BM, TSE and WS samples.

after the sharp gate opening. As a result, the WS sample did not reach full CO_2 uptake until *ca.* 30 kPa. Notably, some mechanochemical samples (*e.g.*, BM126, BM128 and TSE3) showed not only even more gradual sorption curves, but also lower CO_2 uptakes (*ca.* 115–123 cm^3 g^{-1}). This could be attributable to differences in crystallinity and/or particle size.[56–58] It can be addressed by adding larger water aliquots into the mechanosynthesis (*e.g.*, BM1210). It is reasonable to assert that stress caused by mechanical forces may affect the crystal quality of BM and TSE samples and may also induce some defects and mechanical damage in the coordination networks. This may require *in situ* monitoring techniques for more in-depth insights.[59–61]

Conclusions

Whereas it is recognized that the profiles (*e.g.*, shape and uptake) of gas sorption isotherms can vary to some extent for the same CNs prepared by different methods or the same methods under different conditions,[61–63] it is reasonable to note that flexible/switching CNs such as **sql-1-Co-NCS** might be more sensitive than rigid CNs to the particle size and morphology.[56–58] In this study, milder conditions and methods such as WS were found to retain more comparable sorption performance to their single-crystal counterparts. In addition, this work suggests that it is unsuitable to estimate product quality of sorbents just based on PXRD and/or TGA. Rather, gas sorption testing offered a more quantitative approach to estimate the overall quality of products obtained. Further, we found that neat BM and TSE methods were ineffective whereas water-assisted mechanosynthesis required an appropriate amount of water otherwise CO_2 sorption performance was compromised. Considering elapsed time, ease of operation, yield and waste, WS is at least in this case a promising alternative, apart from mechanosynthesis, for the scale-up preparation of **chn-1-Co-NCS-H_2O** and its analogue materials. Indeed, the Fe and Ni variants of **chn-1-Co-NCS-H_2O** were also prepared even using three ingredients ($FeSO_4$/$NiSO_4$, NaSCN, and bpy) *via* the WS method.[39] Further studies to explore WS and mechanochemical methods for other CN systems are in progress.

Author contributions

Shi-Qiang Wang: methodology, investigation, formal analysis, writing – original draft; Shaza Darwish: methodology, investigation, writing – review & editing; Michael J. Zaworotko: supervision, funding acquisition, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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