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ARTICLE

Mechanochemical synthetic strategy of isoreticular flexible metal-organic frameworks with pre-designed mixed metal clusters

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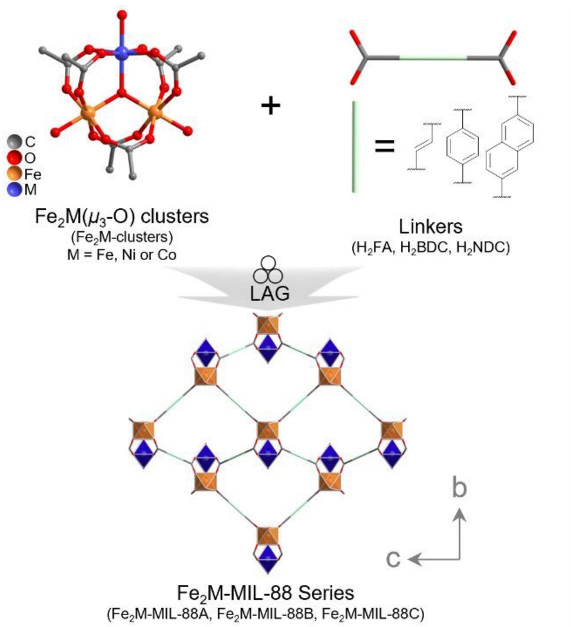
Mechanochemistry has emerged as a sustainable alternative to traditional solvothermal methods for synthesizing metal-organic frameworks (MOFs), offering reduced solvent usage, shorter reaction times, and scalability. However, the synthesis of flexible MOFs, such as the MIL-88 series, remains challenging due to the difficulty in forming secondary building units (SBUs) under mechanochemical conditions. Herein, we present a novel strategy for the mechanochemical synthesis of the MIL-88 series using pre-assembled mixed-metal clusters as precursors. This approach effectively overcomes limitations in controlling metal ratios and suppressing undesired phase mixtures, enabling the efficient and rapid formation of MIL-88 frameworks under mild conditions. The synthesized MIL-88s, including mixed-metal variants, were comprehensively characterized to confirm phase purity, structural fidelity, and tunable metal compositions. This strategy not only facilitates access to flexible MOFs that were previously difficult to synthesize mechanochemically but also demonstrates the feasibility of precisely controlling metal ratios in mixed-metal systems. These advancements underscore the significant potential of this approach for further expanding the scope and applications of mechanochemical synthesis.

Introduction

Among the various synthetic methods of metal-organic frameworks (MOFs),[1] mechanochemistry has emerged as a sustainable alternative to traditional solvothermal and hydrothermal approaches.[2] It offers significant advantages, including reduced solvent usage, shorter reaction times, scalability, and alignment with green chemistry principles.[3-6] Mechanochemical methods have successfully synthesized well-known MOFs such as MOF-74,[7] MOF-5,[8] UiO-66,[9] HKUST-1,[10] and ZIF-8,[11] highlighting their potential in MOF synthesis.[12-14] However, synthesizing flexible MOFs via mechanochemistry remains a challenge. For MOFs like MIL-88 and MIL-53, conventional mechanochemical methods typically require additional solvothermal steps after grinding, which diminishes the environmental and operational benefits of mechanochemistry.[15-17] Recently, the isoreticular MIL-53 series was successfully synthesized without additional heating steps by employing basic modulators such as sodium hydroxide.[18] This method was effective not only for aluminium-based MIL-53 but also for gallium- and indium-based analogues. In contrast, the direct mechanochemical synthesis of MIL-88 remains difficult. This challenge arises from the inherent complexity of forming $M_3(\mu_3\text{-}O)$ clusters–the secondary building units (SBUs) of MIL-88–under mechanochemical conditions.[15] unlike their well-established solvothermal synthesis, the mechanochemical synthesis of these clusters has not been reported, limiting the diversity of MOFs accessible through this approach.[19-21]

To overcome these challenges, this study employs pre-assembled $M_3(\mu_3\text{-}O)$, as tailored precursors for the direct mechanochemical synthesis of flexible MOFs. The use of pre-synthesized cluster as precursors has previously been demonstrated for the synthesis of Zr-based



Scheme 1 Schematic representation of the mechanochemical synthesis of Fe_2M-MIL-88 series using pre-designed mixed metal clusters and organic linkers.

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MOFs, a challenging series due to the difficulty of forming Zr SBUs under mechanochemical conditions.[22-25] This approach provided the rapid and efficient synthesis of Zr-based MOFs through direct mechanochemical reactions.

Building on this concept, we demonstrate the successful mechanochemical synthesis of the MIL-88 series, achieving efficient production of flexible MOFs without post-treatment. Moreover, this strategy extends to the synthesis of multivariate MIL-88 MOFs with mixed-metal cluster systems, incorporating combinations of nickel or cobalt with iron. Conventional one-pot solvothermal synthesis of mixed-metal MOFs often struggles to control metal ratios and is prone to forming undesired mixed phases.[26] In contrast, our approach offers a fast and straightforward method to precisely control metal ratios while suppressing phase impurity, ensuring the formation of targeted structures. Finally, the scalability and adaptability of this method are showcased through the successful synthesis of isoreticular MIL-88A, MIL-88B, and MIL-88C.

Experimental

Materials and characterization methods

All reagents are commercially available (Sigma Aldrich, TCI, Dae Jung, and Samchun) and used without any purification. All of metal clusters were synthesized by modifying previous reported methods.[27] Powder X-ray diffraction (PXRD) data were collected on a Bruker D2 phaser diffractometer at 10 mA and 30 kV for Cu Kα (wavelength = 1.5406 Å), with a 0.02 degree of increment. Thermogravimetric analysis (TGA) was measured under N2 flow at a ramp rate of 10 °C/min, using a TA instrument TGA Q50. Fourier-transform infrared spectra (FT-IR) and diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy were measured with a ThermoFisher Scientific iS10 FT-IR spectrometer. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) were obtained with a JEOL JSM-7610 at the Basic Science Research Institute of Ewha Womans University. Nitrogen (77 K) sorption data were collected using a Microtrac BEL Corp BELSORP-max. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed with Agilent 5110 at the Yonsei Center for Research Facilities of Yonsei University. Mechanochemical reactions were conducted with Retsch MM400 shaker mill. All mechanochemical reactions were achieved by milling for 90 min at a rate of 30 Hz in a 15 mL Teflon jar with two 7 mm steel balls.

Synthesis of Fe_3-cluster ($[Fe_3(\mu_3\text{-}O)(OAc)_6(H_2O)_3][Fe_3(\mu_3\text{-}O)(OAc)_{7.5}]_2\cdot 7H_2O$) Sodium acetate (8.16 g, 0.06 mol) and $FeCl_3\cdot 6H_2O$ (8.11 g, 0.03 mol) were dissolved in 10 mL of hot deionized water. Sodium and iron solutions were combined and stirred for 10 min. The mixed solution was left and exposed to air for crystallizations. After several days, the crystals were filtered and washed with small amounts of ethanol (EtOH) and diethyl ether. The product was dried in the air.

Synthesis of Fe_2Co-cluster ($[Fe_2Co(\mu_3\text{-}O)(OAc)_6(H_2O)_3]$) and Fe_2Ni-cluster ($[Fe_2Ni(\mu_3\text{-}O)(OAc)_6(H_2O)_3]$) Sodium acetate (12.31 g, 0.15 mol), $Fe(NO_3)_3\cdot 9H_2O$ (2.42 g, 0.01 mol) and $Co(NO_3)_2\cdot 6H_2O$ (8.73 g, 0.03 mol) (or $Ni(NO_3)_2\cdot 6H_2O$ (8.72 g, 0.03 mol)) were dissolved in 10 mL of deionized water. The mixed solutions were stirred for 24 h at RT. The product was washed with small amount of water and EtOH. The product was dried with vacuum at RT.

Synthesis of Fe_3-MIL-88B Fe_3-cluster (179.0 mg, 0.1 mmol), terephthalic acid (H_2BDC) (149.4 mg, 0.9 mmol) were milled with 140 μL of methanol (MeOH) and 40 μL of *N,N*-diisopropylethylamine (DIPEA). The product was washed with MeOH and *N,N*-dimethylformamide (DMF). The product was dried with vacuum filtration and yielded after drying at 65 °C vacuum oven overnight.

Synthesis of Fe_2Co-MIL-88B and Fe_2Ni-MIL-88B Fe_2Co-cluster (115.4 mg, 0.2 mmol) or Fe_2Ni-cluster (115.3 mg, 0.2 mmol), H_2BDC (99.6 mg, 0.6 mmol) were milled with 150 μL of MeOH and DIPEA mixed solution in a 7:2 ratio. The product was washed with MeOH and DMF. The product was dried with vacuum filtration and yielded after drying at 65 °C vacuum oven overnight.

Synthesis of Fe_3-MIL-88A Fe_3-cluster (179.0 mg, 0.1 mmol), fumaric acid (H_2FA) (104.5 mg, 0.9 mmol) were milled with 120 μL of EtOH and 30 μL of DIPEA. The product was washed with MeOH and DMF. The product was dried with vacuum filtration and yielded after drying at 65 °C vacuum oven overnight.

Synthesis of Fe_2Co-MIL-88A and Fe_2Ni-MIL-88A Fe_2Co-cluster (173.1 mg, 0.3 mmol) or Fe_2Ni-cluster (173.0 mg, 0.3 mmol), H_2FA (104.5 mg, 0.9 mmol) were milled with 120 μL of EtOH and 30 μL of DIPEA. The product was washed with MeOH and DMF. The product was dried with vacuum filtration and yielded after drying at 65 °C vacuum oven overnight.

Synthesis of Fe_3-MIL-88C Fe_3-cluster (179.0 mg, 0.1 mmol) and 2,6-naphthalenedicarboxylic acid (H_2NDC) (194.5 mg, 0.9 mmol) were milled with 50 μL of MeOH and 20 μL of DIPEA. The product was washed with DMF. The product was dried with vacuum filtration and yielded after drying at 65 °C vacuum oven overnight.

Synthesis of Fe_2Co-MIL-88C and Fe_2Ni-MIL-88C Fe_2Co-cluster (173.1 mg, 0.3 mmol) (or Fe_2Ni-cluster (173.0 mg, 0.3 mmol)) and H_2NDC (194.5 mg, 0.9 mmol) were milled with 50 μL of MeOH and 20 μL of DIPEA. The product was dried with vacuum filtration and yielded after drying at 65 °C vacuum oven overnight.

Results and discussions

As the first synthetic step of MIL-88 series, we prepared the trimeric clusters, $M_3(\mu_3\text{-}O)$, capped with six acetate groups (OAc), which act as SBU precursors in the synthesis of MOFs. Following previously reported methods,[27] sodium acetate and metal nitrate hydrates were dissolved in deionized water to produce three types of crystalline metal clusters: $[Fe_3(\mu_3\text{-}O)(OAc)_6(H_2O)_3][Fe_3(\mu_3\text{-}O)(OAc)_{7.5}]_2\cdot 7H_2O$ (Fe_3-cluster), $[Fe_2Co(\mu_3\text{-}O)(OAc)_6(H_2O)_3]$ (Fe_2Co-cluster), and $[Fe_2Ni(\mu_3\text{-}O)(OAc)_6(H_2O)_3]$ (Fe_2Ni-cluster). Notably, the Fe_3-cluster, which have a different formula compared to the Fe_2Co-cluster and Fe_2Ni-cluster, exhibits a network structure rather than discrete clusters; however, the $M_3(\mu_3\text{-}O)$ core remains identical. The synthesized clusters were characterized using DRIFT spectroscopy, SEM-EDX, ICP-OES, and PXRD. DRIFT

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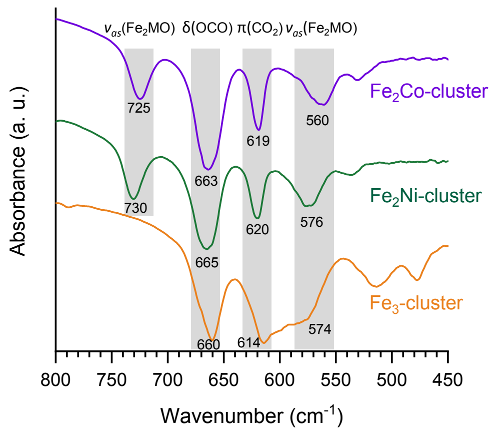

Fig. 1 DRIFT spectra of Fe_3-cluster, Fe_2Ni-cluster, and Fe_2Co-cluster. asymmetric stretching bands at 730 cm^{-1} for Fe_2Ni-cluster and 725 cm^{-1} for Fe_2Co-cluster, which were absent in the Fe_3-cluster. Asymmetric stretching bands were originated from the degeneracy of asymmetric vibration of $Fe_2M(\mu_3\text{-}O)$ moiety resulting from geometry reduction from D_{3h} to C_{2v}.

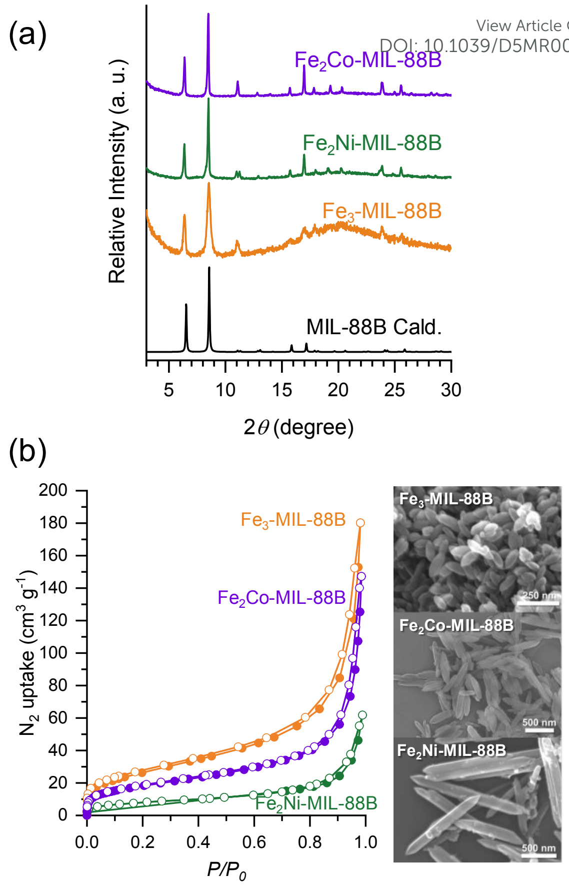

Fig. 2 (a) PXRD patterns of Fe_3-MIL-88B, Fe_2Co-MIL-88B, and Fe_2Ni-MIL-88B collected after isolation from DMF. (b) Nitrogen isotherms at 77 K and SEM images of Fe_3-MIL-88B, Fe_2Co-MIL-88B, and Fe_2Ni-MIL-88B.

spectroscopy showed distinct asymmetric stretching bands (730 cm^{-1} for Fe_2Ni-cluster, 725 cm^{-1} for Fe_2Co-cluster) absent in the Fe_3-cluster, confirming mixed-metal incorporation (Fig. 1 and Table S1).[28,29] EDX and ICP-OES confirmed a 2:1 molar ratio of iron to nickel or cobalt in the mixed-metal clusters (Fig. S1). PXRD patterns of three clusters were matched with previously reported data, verifying the same packing structures of $M_3(\mu_3$-O) clusters (Fig. S2).[30,31] These results demonstrate the successful synthesis of mixed-metal trimeric clusters, enabling the development of MIL-88s.

The synthesis of MIL-88B, the most extensively studied MOF in this series, featuring BDC ligands, was investigated first. The mechanochemical conditions for MIL-88B were optimized based on a previously reported solvothermal method utilizing metal clusters. In this mechanochemical synthesis, MeOH was added as an additive liquid for liquid-assisted grinding (LAG). DIPEA was also introduced for a dual purpose as a base for MOF formation and as a liquid for LAG. For MIL-88B with Fe_3 clusters (Fe_3-MIL-88B), the optimized synthesis involved milling 0.1 mmol of Fe_3-clusters and 0.9 mmol of H_2BDC with 140 μL of MeOH and 40 μL of DIPEA. For mixed-metal MIL-88B containing cobalt or nickel (Fe_2Co-MIL-88B or Fe_2Ni-MIL-88B), 0.2 mmol of Fe_2Co or Fe_2Ni clusters and 0.6 mmol of H_2BDC were milled with 150 μL of a solvent mixture MeOH and DIPEA in a 2:7 ratio. All mechanochemical reactions were conducted at 30 Hz for 90 min in a 15 mL Teflon jar containing two 7 mm stainless steel balls. The products were isolated using MeOH and further washed with MeOH and DMF. Compared to solvothermal methods, which require over a day of reaction time, the mechanochemical approach significantly shortens the process to just 90 min while still achieving the successful synthesis of MIL-88B.

To confirm the successful synthesis of MIL-88Bs, the PXRD patterns of MIL-88Bs were collected after isolating from DMF. The observed patterns were well matched with the calculated pattern of the open structure of MIL-88B (Fig. 2a).[32] Further detailed characterization was performed on the MIL-88B series for comprehensive analysis. FT-IR spectra confirmed the coordination between the deprotonated organic linkers and the metal clusters, as evidenced by asymmetric and symmetric vibrations of the carboxylate groups (Fig. S3). Fe_2Co-MIL-88B and Fe_2Ni-MIL-88B exhibited distinct asymmetric stretching bands at approximately 715 cm^{-1}, absent in Fe_3-MIL-88B. It indicated that Fe_2Co-MIL-88B and Mil-88B-Ni were well-constructed with mixed metal cluster systems (Fig. S4).[33-35] This was further confirmed through EDX analysis, which revealed that iron and cobalt or nickel were present in Fe_2Co-MIL-88B and Fe_2Ni-MIL-88B at an approximate molar ratio of 1:2 (Fig. S5). TGA showed that all MIL-88Bs displayed an initial weight loss below 200 °C, corresponding to the removal of guest molecules, followed by a second weight loss around 350 °C, attributed to the framework degradation (Fig. S6). The N_2 sorption measurements of MIL-88Bs exhibited a type 2 isotherm, indicating their non-porous and non-flexible nature toward N_2 (Fig. 2b).[27] This behavior is attributed to the dense phase of dried MIL-88Bs, which maintains narrow pores upon N_2 adsorption. The nitrogen uptake was observed to decrease in the order of Fe_3-MIL-88B, Fe_2Co-MIL-88B, and Fe_2Ni-MIL-88B, suggesting that the introduction of a mixed-metal system affects the dried structure. One possible explanation is the presence of a coordinating anion in Fe_3-MIL-88B, which is absent in the M^{2+}-containing Fe_2Co-MIL-88B and Fe_2Ni-MIL-88B.

However, further investigation is still required to fully understand this phenomenon.

To compare the products synthesized mechanochemically to their solvothermal counterparts, Fe_3-MIL-88B was synthesized using a previously reported solvothermal method with pre-assembled iron clusters. The PXRD patterns of the Fe_3-MIL-88B synthesized via solvothermal reactions (Fe_3-MIL-88B-Solvo) were identical to the mechanochemically synthesized Fe_3-MIL-88B (Fig. S7).[36] The textual properties of Fe_3-MIL-88B and Fe_3-MIL-88B-Solvo were studied with nitrogen sorption isotherms measured at 77 K (Fig. 2b and S8). At the low pressure region, both Fe_3-MIL-88B and Fe_3-MIL-88B-Solvo exhibited similar sorption behavior. However, at higher relative pressures (0.8–1.0), Fe_3-MIL-88B demonstrated greater nitrogen uptake compared to Fe_3-MIL-88B-Solvo. This behavior was likely influenced by the difference in crystal sizes between the two samples. SEM images revealed that Fe_3-MIL-88B-Solvo featured microcrystals with an average size exceeding 5 μm, whereas Fe_3-MIL-88B displayed smaller nanocrystals with an average size of around 100 nm (Fig. 2b and S9). The nano-sized crystals of Fe_3-MIL-88B might contribute to the presence of intercrystalline voids, resulting in mesoporosity.[37] Overall, these results confirm the successful mechanochemical synthesis of the MIL-88B series with properties comparable to solvothermal MIL-88Bs. Therefore, the well-designed mechanochemical synthetic strategy, with its shorter reaction time and higher yield, offers relatively greater efficiency and presents a promising alternative to solvothermal methods.

To extend our strategy, we attempted to synthesize the isoreticular series of MIL-88B, MIL-88A and MIL-88C. The mechanochemical syntheses of Fe_3-MIL-88A, Fe_2Co-MIL-88A, and Fe_2Ni-MIL-88A were processed with H_2FA under the similar conditions with MIL-88B synthesis. The successful synthesis of series of MIL-88A was confirmed with the PXRD patterns of these materials by comparing with the calculated patterns of MIL-88A (Fig. 3a). While Fe_3-MIL-88A exhibited slight deviations from the calculated patterns, this was attributed to the small crystal size, approximately 50 nm, which caused peak broadening, as well as the inherent flexibility of MIL-88A. In contrast, Fe_2Co-MIL-88A and Fe_2Ni-MIL-88A displayed crystal sizes of approximately 500 nm, as observed in SEM images, and exhibited the characteristic spindle-like morphology commonly associated with MIL-88A. Additionally, the minor peaks observed below 10° in all three MOFs resulted from air exposure during PXRD measurements, which caused a slight transition from the dried phase to a partially open phase. This phenomenon is commonly observed in previously reported MIL-88A samples.[38] To confirm the incorporation of mixed metals into Fe_2Co-MIL-88A and Fe_2Ni-MIL-88A, EDX analysis was conducted, revealing molar ratio of Fe and Co or Ni in approximately 2:1 within the frameworks (Fig. S10). Furthermore, consistent with observations in MIL-88B, the FT-IR spectra displayed a characteristic band at 730 cm^{-1}, attributed to the incorporation of mixed-metal clusters (Fig. S11). These results conclusively demonstrate the successful synthesis of MIL-88A and validate the effectiveness of the proposed strategy for designing isoreticular MOFs. Furthermore,

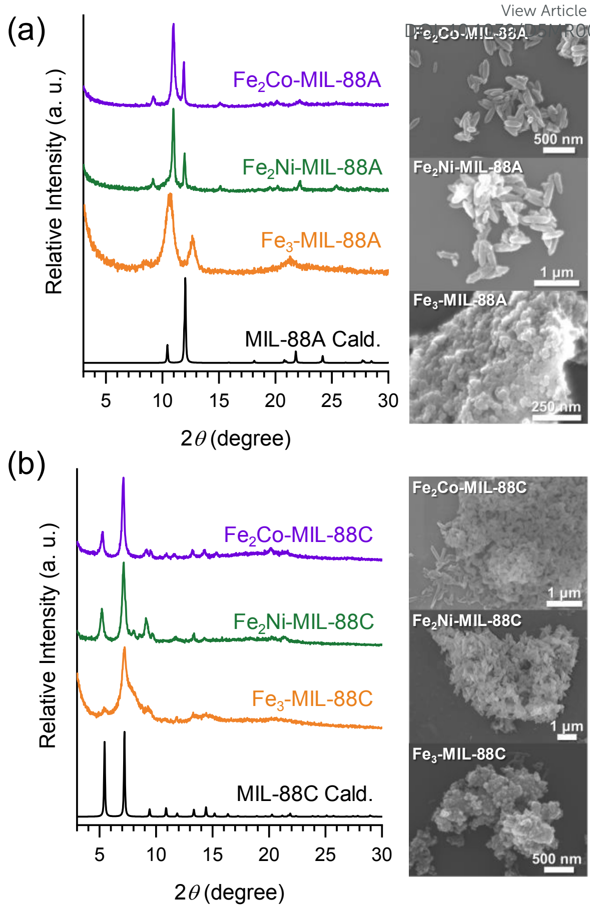

Fig. 3 (a) PXRD patterns and SEM images of Fe_2Co-MIL-88A, Fe_2Ni-MIL-88A, and Fe_3-MIL-88A after drying. (b) PXRD patterns and SEM images of Fe_2Co-MIL-88C, Fe_2Ni-MIL-88C, and Fe_3-MIL-88C after drying.

this approach could be extended to MIL-88C, which features a longer and symmetrically mismatched linker (H_2NDC). The synthetic conditions for MIL-88C are identical to those for MIL-88A, and the only differences lie in the amount of liquid additives. Comprehensive characterization using PXRD, SEM, EDX, and FT-IR confirmed the successful synthesis of MIL-88C (Fig. 3b and S12).

These findings demonstrate the high scalability of the mechanochemical strategy employing pre-designed clusters for the rational design and synthesis of isoreticular MOFs. We believe it will open new possibilities for accessing novel MOF structures and broadening the scope of mechanochemical MOF synthesis.

Conclusions

In this study, we introduced a mechanochemical strategy for synthesizing the MIL-88 series, using pre-assembled mixed-metal clusters. This approach effectively addresses the challenges associated with constructing SBUs under mechanochemical conditions. By utilizing these pre-designed clusters, we successfully synthesized MIL-88A, MIL-88B, and MIL-88C with precise control over metal ratios and phase purity, even in mixed-metal systems. The synthesized MOFs exhibited structural and functional properties comparable to those obtained via traditional solvothermal methods, while providing significant advantages such as shorter reaction times and reduced solvent use. Furthermore, this approach enables the precise introduction of well-regulated mixed-metal systems into MOFs by controlling the metal ratios in mixed-metal clusters. This method reduces the formation of side products commonly observed in conventional salt-based solvothermal or mechanochemical syntheses of mixed-metal MOFs. These findings demonstrate the high scalability of the mechanochemical strategy employing pre-designed clusters for the rational design and synthesis of isoreticular MOFs. We believe it will open new possibilities for accessing novel MOF structures and broadening the scope of mechanochemical MOF synthesis.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data generated or analyzed during this study are included in this published article and the part of ESI.

Acknowledgements

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Data availability statements:

All data generated or analyzed during this study are included in this published article and the part of ESI.