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Mechanochemistry of Group 4 Element-Based Metal–Organic Frameworks

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ABSTRACT: Mechanochemical synthesis is emerging as an environmentally friendly yet efficient approach to preparing metal–organic frameworks (MOFs). Herein, we report our systematic investigation on the mechanochemical syntheses of Group 4 element-based MOFs. The developed mechanochemistry allows us to synthesize a family of $Hf_4O_4(OH)_4(OOC)_{12}$-based MOFs. Integrating $[Zr_6O_4(OH)_4(OAc)_{12}]_2$ and $[Hf_6O_4(OH)_4(OAc)_{12}]_2$ under the mechanochemical conditions leads to a unique family of cluster-precise multimetallic MOFs that cannot be accessed by the conventional solvothermal synthesis. Extensive efforts have not yielded an effective pathway for preparing Ti^{IV}-derived MOFs, tentatively because of the relatively low Ti–O bond dissociation energy.

Metal–organic frameworks (MOFs),[1,2] a type of crystalline porous materials, have garnered significant attention because of their structural modularity and potential applications in gas storage,[3,4] separation,[5−7] catalysis,[8−11] and others.[12,13] Among them, Group 4 element-based MOFs, including tetravalent Ti-,[14−20] Zr-,[21,22] and Hf-based ones,[23−25] are some of the well-investigated families of MOFs, in part given by their superior chemical stability.[26] Conventional methods to obtain crystalline MOFs have to involve the reversible formation of coordination bonds, which typically relies on solvothermal reactions at high temperature for an extended period of time in the presence of excessive amounts of toxic solvents, e.g., *N*,*N*-dimethylformamide (DMF).

Mechanochemical synthesis has emerged as an alternative environmentally friendly approach to preparing MOFs in a short time.[27−33] Zr^{IV}-based MOFs, such as UiO-66,[34−37] UiO-67,[38,39] and MOF-804,[35] have been established by mechanochemical syntheses of $[Zr_6O_4(OH)_4(OOCR)_{12}]$ [R = $C(CH_3)$=CH_2 or C_6H_5] or $[Zr_6O_4(OH)_4(OOCCH_3)_{12}]_2$ molecular complexes and the corresponding ligands (Figure 1a). Thus far, there have been no reports about mechanochemical syntheses of MOFs based on other elements in Group 4. Herein we report our systematic efforts on the development of mechanochemical syntheses for Group 4 element-based MOFs. A family of Hf^{IV}-based MOFs has been successfully synthesized by the mechanochemical method based on a molecular precursor of $[Hf_6O_4(OH)_4(OOCCH_3)_{12}]_2$ (Figure 1b). The mechanochemical method also allows us to prepare a unique family of cluster-precise multimetallic MOFs derived from $Zr_6O_4(OH)_4$ and $Hf_6O_4(OH)_4$ secondary building units (SBUs; Figure 1c), which cannot be prepared by the conventional solvothermal method. Extensive attempts have not afforded any Ti-derived MOFs, presumably attributed to the low Ti–O bond enthalpy.

Inspired by the facile ligand substitution of $[Zr_6O_4(OH)_4(OOCCH_3)_{12}]_2$ generating $Zr_6O_4(OH)_4$-based MOFs under mechanochemical conditions, we initiated our investigation by preparing a molecular compound with a formula of $[Hf_6O_4(OH)_4(OOCCH_3)_{12}]_2$.[40] The phase purity of the molecular Hf complex is confirmed by powder X-ray diffraction (PXRD) analysis (Figure S1). The complex of $[Hf_6O_4(OH)_4(OOCCH_3)_{12}]_2$ (Figure 1b), isostructural to $[Zr_6O_4(OH)_4(OOCCH_3)_{12}]_2$, is composed of two Hf_6 subunits, which are connected by four acetate bridges. Given that $Hf_6O_4(OH)_4(OOC)_{12}$ is a commonly encountered SBU in Hf-based MOFs, we started to examine the role of $[Hf_6O_4(OH)_4(OOCCH_3)_{12}]_2$ as a molecular precursor for the mechanochemical synthesis of relevant MOFs.

Aiming at Hf-UiO-66, we chose 1,4-benzenedicarboxylic acid (H_2bdc) as the ligand in the initial mechanical syntheses. Ball milling a 1:12 mixture of $[Hf_6O_4(OH)_4(OOCCH_3)_{12}]_2$ and H_2bdc in the presence of added DMF (η = 0.67 μL/mg) afforded white crystalline solids, which did not dissolve in DMF or methanol. PXRD analysis reveals that the obtained materials match both the calculated PXRD patterns of Hf-UiO-66 and those of solvothermally synthesized Hf-UiO-66 (Figure S2a,b). The completeness of the mechanochemical reaction is monitored through infrared (IR) spectroscopy by examining the disappearance of carbonyl stretching from free carboxylic acid groups at 1674 cm^{-1} (Figure S3). The presence of DMF and its amount employed as the assisting liquid during the

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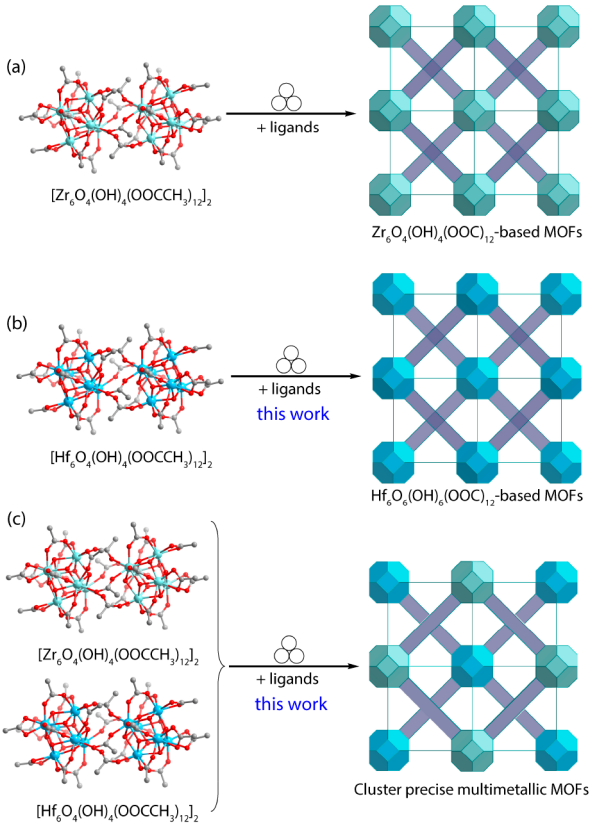

Figure 1. (a) Reported mechanochemistry accessing $[Zr_6O_4(OH)_4(OOC)_{12}]$-based MOFs. (b) $[Hf_6O_4(OH)_4(OOC)_{12}]$-based MOFs reported in this work to be accessible by mechanochemistry. (c) Family of cluster-precise multimetallic MOFs highlighted in this work to be only accessible by mechanochemistry rather than solvothermal methods.

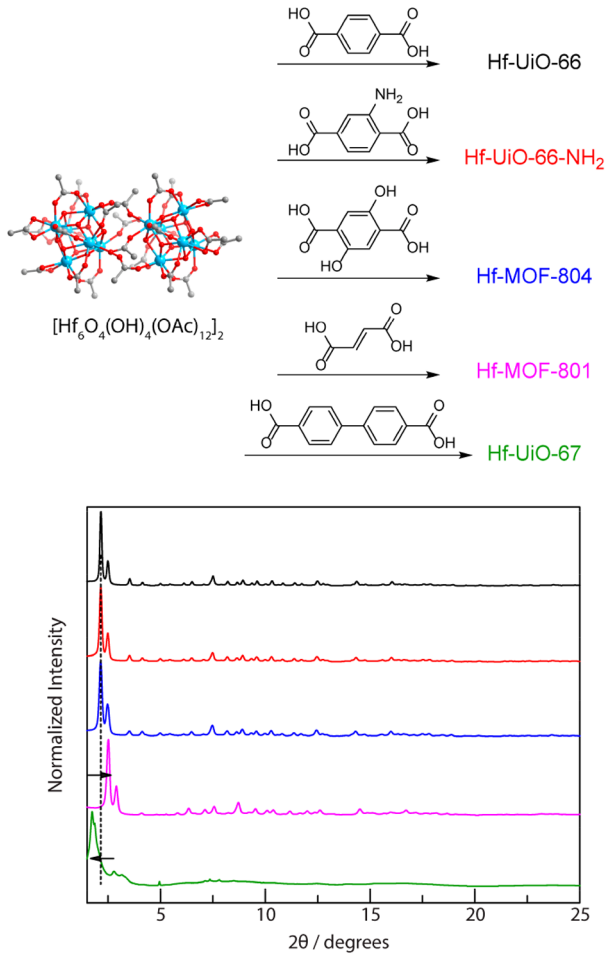

Figure 2. Mechanochemistry affording a family of Hf^{IV}-based MOFs. The PXRD patterns of the mechanochemically prepared Hf-UiO-66 (black —; λ = 0.45191 Å), Hf-UiO-66-NH_2 (red —; λ = 0.45174 Å), Hf-MOF-804 (blue —; λ = 0.45174 Å), Hf-MOF-801(pink —; λ = 0.45174 Å), and Hf-UiO-67 (green —; λ = 0.45191 Å) are presented.

synthesis are crucial, which is highlighted by control experiments: (1) Milling a 1:12 mixture of $[Hf_6O_4(OH)_4(OOCCH_3)_{12}]_2$ and H_2bdc under neat conditions or in the presence of water did not generate any crystalline phase of Hf-UiO-66 (Figure S4a). (2) The impact of the DMF amount on the mechanochemical synthesis was systemically explored, as shown in Figure S2c. The DMF loading of η = 0.67 μL/mg affords the best crystallinity. The permanent porosity of the mechanochemically synthesized Hf-UiO-66 was characterized by the N_2 adsorption isotherm at 77 K (Figure S4b). Hf-UiO-66 has a measured Brunauer–Emmett–Teller (BET) surface area of 944 m^2/g (P/P_0 = 0.02–0.15), which is comparable to the reported BET surface area value (940 m^2/g) of the solvothermally prepared Hf-UiO-66.[23]

To generalize the developed mechanochemical synthetic method, we successfully prepared a family of $Hf_6O_4(OH)_4(OOC)_{12}$-based MOFs under similar reaction conditions, including Hf-UiO-66-NH_2, Hf-MOF-804, Hf-MOF-801, and Hf-UiO-67, based on 2-aminoterephthalic acid, 2,5-dihydroxyterephthalic acid, fumaric acid, and biphenyl-4,4′-dicarboxylic acid, respectively (see details in the Supporting Information, SI). Their crystalline phases were characterized by PXRD analysis (Figures 2 and S5–S7), and the surface area values were evaluated based on the N_2 adsorption isotherms at 77 K (Figure S8a and Table S2). The linker extension from fumaric acid to biphenyl-4,4′-dicarboxylic acid leads to the corresponding peaks in the PXRD patterns shifting toward the lower angle direction, which is consistent with the increasing cavity space.

The developed mechanochemical synthesis also provides access to a family of multimetallic MOF materials. By employing $[Zr_6O_4(OH)_4(OOCH_3)_{12}]_2$ and $[Hf_6O_4(OH)_4(OOCCH_3)_{12}]_2$ as molecular precursors with tunable ratios (e.g., 1:4, 1:1, and 4:1) as well as the H_2bdc ligand, we synthesized a family of Hf_xZr_y-based mixed-metal MOF materials mechanochemically. These materials were characterized by PXRD analysis (Figures 3a and S9), which indicates that they are isostructural to Zr-UiO-66 and Hf-UiO-66. Meanwhile, the metal ratios of Hf/Zr were evaluated by energy-dispersive spectroscopy and inductively coupled plasma mass spectrometry (ICP-MS) of samples digested with nitric acid (see details in the SI). Both techniques provide consistent Hf/Zr ratios, which are comparable to the initial loading ratio of the mechanochemical syntheses (Table S3). The increasing Zr content in the mixed-metal MOFs results in a slight shift of the corresponding peaks in the PXRD patterns toward the lower-angle direction (Figure S9b), which is caused by the slightly larger ionic radius of Zr^{IV} (79 pm) than of Hf^{IV} (78 pm). Their scanning electron microscopy (SEM) images are shown in Figure S10, and the BET surface areas derived from the N_2 adsorption isotherms at 77 K are reported in Figure S11 and Table S4.

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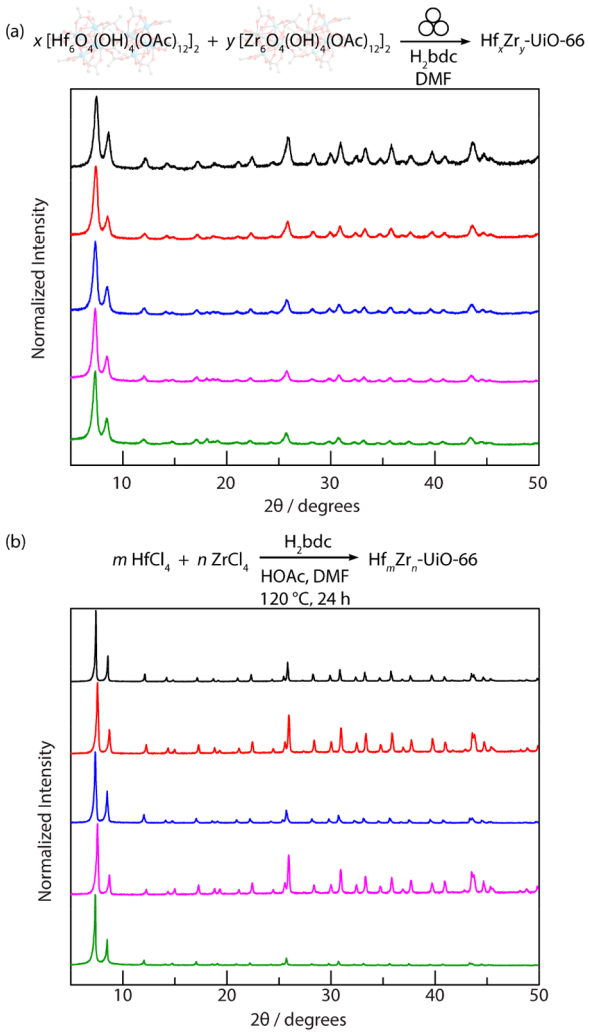

Figure 3. (a) Developed mechanochemistry accessing a family of multimetallic MOFs. The PXRD patterns of the mechanochemically prepared Hf-UiO-66 (black —), Hf_4Zr-UiO-66 (red —), HfZr-UiO-66 (blue —), $HfZr_4$-UiO-66 (pink —), and Zr-UiO-66 (green —) were collected. (b) Solvothermal reactions also afford a family of multimetallic MOFs. The PXRD patterns of the solvothermally synthesized Hf-UiO-66 (black —), Hf_4Zr-UiO-66 (red —), HfZr-UiO-66 (blue —), $HfZr_4$-UiO-66 (pink —), and Zr-UiO-66 (green —) were collected.

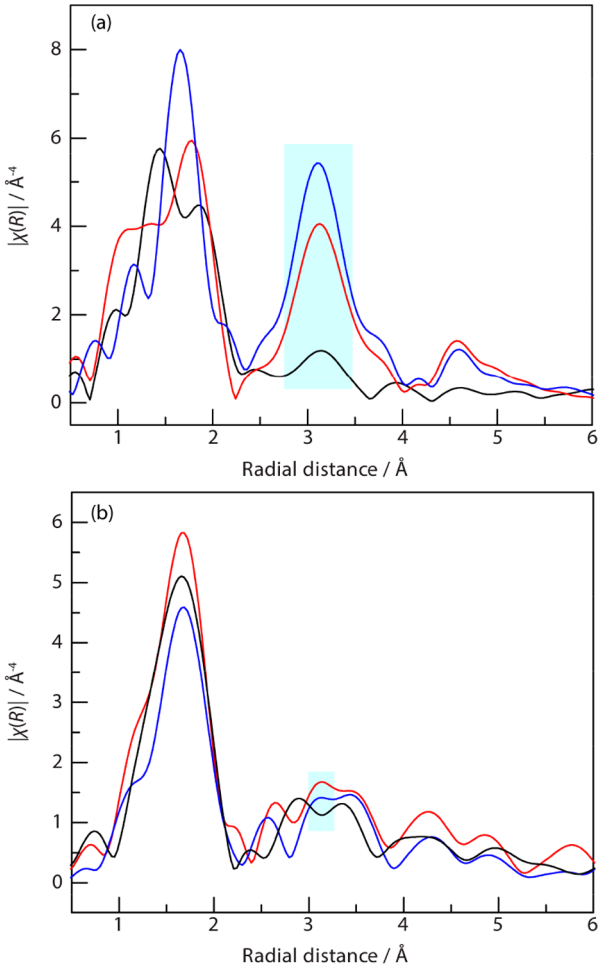

Figure 4. (a) Zr K-edge EXAFS data in *R* space shown for HfZr-UiO-66(mechano) (red —), Zr-UiO-66 (blue —), and HfZr-UiO-66(solvo) (black —). The M−M scattering around 3.1 Å is highlighted. (b) Hf L_3-edge EXAFS data in *R* space shown for HfZr-UiO-66(mechano) (red —), Hf-UiO-66 (blue —), and HfZr-UiO-66(solvo) (blcak —). The M−M scattering around 3.1 Å is highlighted.

Meanwhile, solvothermal reactions employing both $HfCl_4$ and $ZrCl_4$ with the addition of H_2bdc, excessive DMF, and acetic acid as the modulator at 120 °C for 24 h also provide crystalline mixed-metal MOF materials (see details in the SI), isostructural to UiO-66 (Figure 3b). For instance, the equimolar loading of $HfCl_4$ and $ZrCl_4$ under solvothermal conditions provides a crystalline multimetallic MOF, characterized by PXRD (Figure 3b) and the N_2 adsorption isotherm at 77 K (Figure S12a and Table S5). The metal ratio of 1:1 was confirmed by ICP-MS (Table S6).

X-ray absorption near-edge structure data for Zr and Hf (Figure S13) indicate that Zr and Hf from the solvothermally prepared and mechanochemically synthesized multimetallic materials retain the Zr^{IV} and Hf^{IV} oxidation states, respectively, similar to that of Zr-UiO-66 and Hf-UiO-66. Moreover, Zr K-edge extended X-ray absorption final structure (EXAFS) data collected for the mechanochemically synthesized HfZr-UiO-66(mechano) (see details in Figures 4a and S14a,c and Table S7) suggest that $Zr_6O_4(OH)_4(OOC)_{12}$ represents the Zr-containing cluster within the multimetallic framework, which is consistent with the observation of the singular metal MOF Zr-UiO-66 (see details in Figures 4a and S14b,c and Table S7). However, the Zr K-edge EXAFS spectrum of the solvothermally prepared HfZr-UiO-66(solvo) shows a much weaker and less distinguishable peak around 3.1 Å in *R* space (Figure 4a) than those of Zr-UiO-66 and HfZr-UiO-66(mechano), which is attributed to less Zr−Zr scattering[41] in HfZr-UiO-66(solvo). Thus, the mixed-metal cluster composed of both Zr^{IV} and Hf^{IV} is expected in the solvothermally prepared HfZr-UiO-66(solvo).

This is further evidenced by examination of the Hf L_3-edge EXAFS data (see details in Figures 4b and S15 and Table S8) collected for HfZr-UiO-66(mechano), HfZr-UiO-66(solvo), and Hf-UiO-66. They indicate that HfZr-UiO-66(mechano) retains the single-metal cluster of $Hf_6O_4(OH)_4(OOC)_{12}$, similar to that of Hf-UiO-66, which is a significant departure from that of HfZr-UiO-66(solvo) (Figure 4b). Therefore, two types of single-metal clusters, $Zr_6O_4(OH)_4(OOC)_{12}$ and $Hf_6O_4(OH)_4(OOC)_{12}$, are observed in the multimetallic

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materials prepared by the mechanochemistry. In comparison, the conventional solvothermal method affords mixed metals in the individual cluster.

The observed ligand substitution of Hf^{IV} and Zr^{IV} under mechanochemical conditions generates extended corresponding MOFs. This drove us to examine the possibility of preparing Ti^{IV}-derived MOFs by mechanochemistry. Aiming at PCN-415, a known MOF based on $Ti_8Zr_2O_{12}(OOC)_{16}$ and H_2bdc,[42] we prepared a molecular complex with a formula of $[Ti_8Zr_2O_{12}(OOCCH_3)_{16}]\cdot 0.33H_2O$ (see details in the SI) for mechanochemical syntheses. This complex was characterized by single-crystal X-ray diffraction (SCXRD; Table S9 and Figure S16) and PXRD (Figure S17) analyses. SCXRD analysis reveals that the metal cluster consists of a Ti_8 cube capped by two Zr^{IV} cations on the top and bottom. All 18 acetate ligands in the complex participate in the bridging of two adjacent metal cations. Extensive trials using $[Ti_8Zr_2O_{12}(OOCCH_3)_{16}]\cdot 0.33H_2O$ as the molecular precursor and H_2bdc have been attempted to build PCN-415 under mechanochemical conditions without any success (Table S1 and Figure S18). This is tentatively explained by the difference of the bond enthalpy values: 662 kJ/mol of Ti−O, 760 kJ/mol of Zr−O, and 791 kJ/mol of Hf−O.[43] The relatively low bond energy in the Ti−O bond possibly leads to rapid aggregation of the molecular clusters by themselves under mechanochemical conditions, observed from milling $[Ti_8Zr_2O_{12}(OOCCH_3)_{16}]\cdot 0.33H_2O$ alone without any H_2bdc or solvents (Figure S18).

Overall, we not only report an effective mechanochemical method to synthesize $Hf_6O_4(OH)_4$-based MOFs but also demonstrate the mechanochemistry that provides a unique family of cluster-precise multimetallic materials. In contrast to the solvothermally prepared MOFs exhibiting mixed metals in the individual metal cluster, the mechanochemically synthesized multimetallic materials demonstrate two types of single-metal clusters. Although extensive attempts fail to deliver the mechanochemical synthesis of Ti-derived MOFs, we expect our systematic investigation on the mechanochemical syntheses of Group 4 element-based MOFs to be an alternative yet unparalleled synthetic method for multimetallic materials with controllable metal compositions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c02704.

General considerations, synthesis and characterization, and supporting data (PDF)

Accession Codes

CCDC 2090486 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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