

Metal–Organic Framework@Microporous Organic Network: Hydrophobic Adsorbents with a Crystalline Inner Porosity

Jiseul Chun,[†] Sungah Kang,[†] Nojin Park,[†] Eun Ji Park,[†] Xing Jin,[†] Kwang-Dae Kim,[†] Hyun Ook Seo,[†] Sang Moon Lee,[†] Hae Jin Kim,[‡] Woo Hyun Kwon,[§] Young-Kwon Park,[§] Ji Man Kim,^{*,†} Young Dok Kim,^{*,†} and Seung Uk Son^{*,†}

[†]Department of Chemistry and Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea

[‡]Korea Basic Science Institute, Daejeon 350-333, Korea

[§]Graduate School of Energy and Environmental System Engineering, University of Seoul, Seoul 130-743, Korea

Supporting Information

ABSTRACT: This work reports the synthesis and application of metal–organic framework (MOF)@microporous organic network (MON) hybrid materials. Coating a MOF, UiO-66-NH₂, with MONs forms hybrid microporous materials with hydrophobic surfaces. The original UiO-66-NH₂ shows good wettability in water. In comparison, the MOF@MON hybrid materials float on water and show excellent performance for adsorption of a model organic compound, toluene, in water. Chemical etching of the MOF results in the formation of hollow MON materials.

Microporous materials with pores <2 nm have been applied for diverse purposes such as gas capture, catalysis, and separation.^{1–12} Among the microporous materials, metal–organic frameworks (MOFs) assembled with various organic building blocks and metal ions show very large surface areas and chemical diversity.² For example, UiO-66(Zr)-based MOFs have been prepared using dicarboxylic acids and zirconium ions.³ Their excellent stability^{3a,b,4} attracted the attention of scientists and widened the field for their possible applications. Recently, the adsorption properties of UiO-66(Zr)-based MOFs have been extensively studied.⁵ Beyond their well-defined crystalline pore structure, the introduction of additional polar groups in building blocks induces better adsorption performance toward small target molecules.⁶ However, competitive moisture adsorption can hamper the target adsorption under conventional conditions. The water affinity of UiO-66(Zr)-based MOFs is a critical parameter in their application as environmental adsorbents for organic pollutants on water (such as an oil spill in the sea). Thus, for efficient adsorption of organic adsorbates in water, chemical control of the surface properties of adsorbents must be achieved. In our test, UiO-66(Zr)-based MOFs such as UiO-66-I with I groups and UiO-66-NH₂ with NH₂ groups showed excellent stability and good wettability in water, as reported in the literature,⁷ possibly due to their polar Zr-carboxylate bonds. Notably, despite having lower densities than water, many MOFs, including the UiO-66 series, sink in water upon wetting.

Similar to the synthesis of MOFs, microporous organic networks (MONs) have been recently prepared by assembling various organic building blocks with organic connectors via

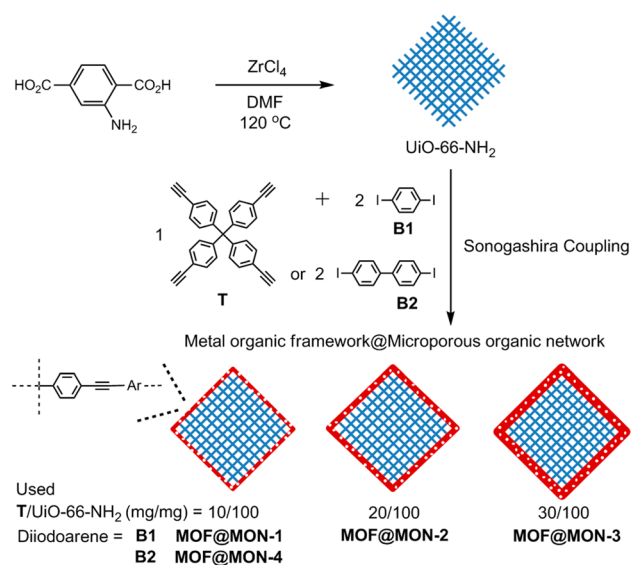


Figure 1. Synthesis of MOF@MON hybrid materials.

coupling reactions.⁸ MONs would be expected to have properties distinct from those of MOFs; the unique properties of MONs and MOFs can be judiciously combined by chemical hybridization of the two materials. In addition, the MOF in hybrid materials can be used as a template¹⁰ for the synthesis of hollow MONs. Although MOF@MOF core/shell hybrid materials were recently reported,¹¹ as far as we are aware, there is no report on MOF@MON hybrid materials. Our research group has studied separately the functional MOFs¹² and MONs.¹³ In this work, we report the synthesis of MON-coated UiO-66(Zr)-based MOFs and their chemical conversion to a hydrophobic surface for the adsorption of organic compounds floating on water.

Figure 1 shows a synthesis scheme for the MON-coated UiO-66-NH₂.¹⁴ First, UiO-66-NH₂ was prepared by the literature method.^{3,6} The MOF was coated by the MON via Sonogashira coupling of tetra(4-ethynylphenyl)methane with 1,4-diiodobenzene or 4,4'-diiodobiphenyl.

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In conventional synthesis, white UiO-66-NH₂ powders were well dispersed in a mixture of toluene and triethylamine. Catalytic amounts of bis(triphenylphosphine)palladium dichloride and copper(I) iodide were added. The reaction mixture was stirred for 1 h. Tetra(4-ethynylphenyl)methane and 2 equiv of diiodoarene were added. The reaction mixture was heated at 90 °C for 24 h. The pale yellow solid materials were retrieved by centrifugation, washed with methanol, acetone, and methylene chloride, and then dried under vacuum. To control the MON thickness on UiO-66-NH₂, the amount of tetra(4-ethynylphenyl)methane used was gradually increased from 10 to 20 to 30 mg with 2 equiv of 1,4-diiodobenzene and a fixed amount (100 mg) of UiO-66-NH₂; the resultant materials are denoted as MOF@MON-1, MOF@MON-2, and MOF@MON-3, respectively. Instead of 1,4-diiodobenzene, 4,4'-diiodobiphenyl was used for pore structure variation, forming MOF@MON-4 (Figure 1; see Supporting Information (SI) for details). The obtained MOF@MON materials were investigated by scanning and transmission electron microscopy (SEM and TEM, Figure 2).

As can be seen in Figure 2d, SEM of pristine UiO-66-NH₂ showed angulated particles with an average size of 200 nm and a smooth surface. As the amount of organic building blocks increased, the surface of MOF@MON became gradually rougher (Figure 2a–c). The outer shape of MOF@MON-4 was similar to that of MOF@MON-1 (Figure 2a,e). TEM analysis of MOF@MON-4 revealed that the surface of the MOF is coated with ultrathin (~9 nm thickness) MON materials (Figure 2f). The MON coating in the TEM images can be distinguished by a lighter contrast than that of the inner MOF. The coating thickness of MONs in MOF@MONs was 8–30 nm.

It was reported that the UiO-66(Zr)-based MOF can be disassembled in HF solution.¹⁵ A homogeneous coating of MON on UiO-66-NH₂ was confirmed by chemical etching of UiO-66-NH₂ (Figure 2g). Pale yellow powders, H-MON-1, H-MON-2, H-MON-3, and H-MON-4, were obtained by chemical etching of the MOFs in MOF@MON-1–4, respectively. The resultant materials were investigated by TEM (Figure 2h–m). As shown in Figure 2h–j,l,m, hollow structures were clearly observed. The size and shape of the inner hollow space matched well with those of the original UiO-66-NH₂ (Figure 2k,l). As expected, the shell thickness of MON gradually increased from H-MON-1 (8 nm) to H-MON-2 (15 nm) to H-MON-3 (25 nm). The shell thickness of H-MON-4 (9 nm) was similar to that of H-MON-1 (Figure 2h,i).

To study any change that may have occurred in the inner crystalline MOF structure, powder X-ray diffraction (PXRD) studies were conducted on the MOF@MON hybrid materials. As reported in the literature for the MON materials prepared by Sonogashira coupling,^{16,17} the H-MONs showed an amorphous character (Figure S1a in the SI). The inner crystalline structure of the MOF in the MOF@MON materials was completely retained after MON coating (Figure S1a). Thermogravimetric analysis showed that MOF@MONs and H-MONs are stable up to ~230 and ~250 °C, respectively (Figure S1e).

The solid-phase ¹³C NMR spectroscopy on the MOF@MON-1 showed new peaks at 65 (benzyl carbon), 90 (internal alkynes), 131, and 145 ppm (aromatic parts) due to the MON shells, in addition to those at 171 (carbonyl), 123, and 138 ppm (aromatic parts) from the MOF, supporting the hybrid chemical components (Figure S1b). As expected, the relative intensity of ¹³C peaks from the MON (red asterisks in Figure S1b) compared with those from the inner MOF (blue asterisks in Figure S1b)

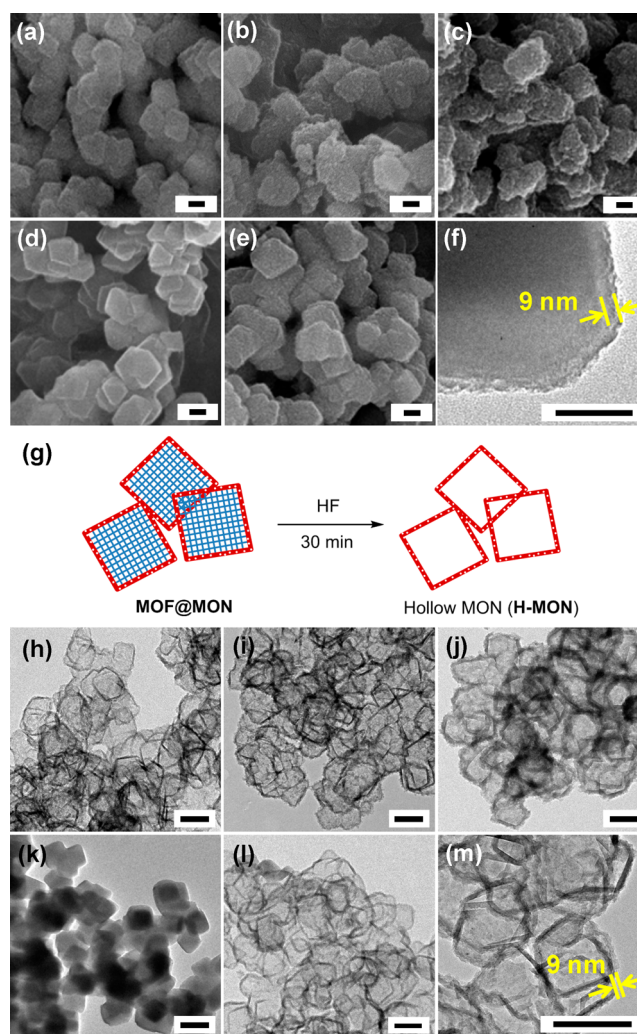


Figure 2. (a–e) SEM images of MOF@MON-1 (a), MOF@MON-2 (b), MOF@MON-3 (c), UiO-66-NH₂ (d), and MOF@MON-4 (e). (f) TEM image of MOF@MON-4. (g) Synthetic scheme for hollow MONs (H-MONs) via MOF etching from MOF@MON. (h–m) TEM images of H-MON-1 (h), H-MON-2 (i), H-MON-3 (j), and H-MON-4 (l,m) obtained from MOF@MON-1–4, respectively, and of UiO-66-NH₂ (k). Scale bars in panels a–e, f, and h–m = 100, 50, and 200 nm, respectively.

increased gradually from MOF@MON-1 to MOF@MON-2 to MOF@MON-3. The ¹³C NMR spectrum of MOF@MON-4 showed a new peak at 125 ppm, compared with that of MOF@MON-1, indicating that the diphenyl moieties were successfully introduced into MOF@MON-4. Elemental analysis showed that the nitrogen content gradually decreased from UiO-66-NH₂ (2.86 mmol/g) to MOF@MON-1 (2.41 mmol/g), MOF@MON-2 (2.18 mmol/g), and MOF@MON-3 (2.09 mmol/g). The nitrogen content of MOF@MON-4 (2.46 mmol/g) was similar to that of MOF@MON-1 (Table S1).

The N₂ sorption isotherms were analyzed by Brunauer–Emmett–Teller method, and the surface areas of MOF@MON-1–4 were measured as 795, 711, 703, and 809 m²/g, respectively (Figure S1c). As the MON component increased, the surface area slightly decreased. UiO-66-NH₂ in this study showed a 1070 m²/g surface area, similar to that reported in the literature.^{3,6} The MONs prepared by Sonogashira coupling had surface areas of ~510–1600 m²/g in the literature.¹⁶ The surface areas of H-MON-1 and H-MON-4 were measured as 1138 and 866 m²/g,

respectively (Table S1). Considering these results, the reduced surface areas of MOF@MONs, compared with those of the original MOF and MON shells, can be attributed to the inclusion of MONs in the pores of the MOF. Density functional theory (DFT) study of the pore size distributions of MOF@MON-1–3 showed the major pore sizes to be 0.7 and 1.3 nm, between those of UiO-66-NH₂ and H-MON-1 (Figure S1d). The nanopore distribution of H-MON-4 shifted slightly more to a larger value than that of H-MON-1, implying easier accessibility of guest molecules in MOF@MON-4 than MOF@MON-1 (Figure S2).

Chemical changes of the surface properties of MOF@MONs, compared with the original MOF, were studied by water contact angle measurement using pellets of each material. UiO-66-NH₂ showed complete water wetting (Figure 3a). The water drop was

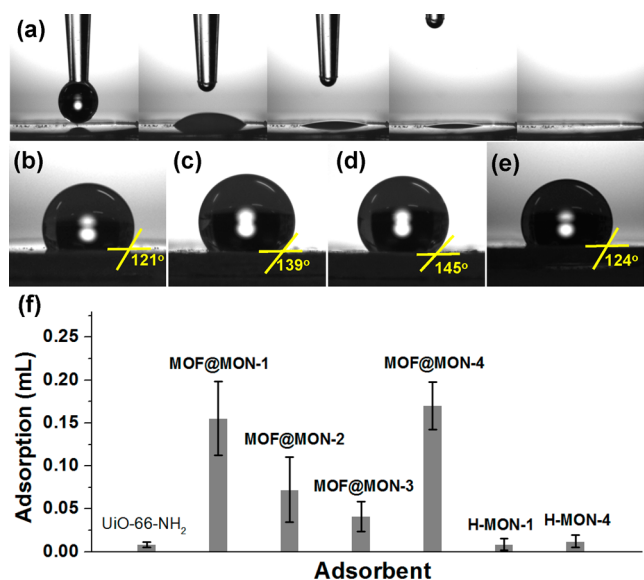


Figure 3. (a–e) Water contact angle measurement of UiO-66-NH₂ (a), MOF@MON-1 (b), MOF@MON-2 (c), MOF@MON-3 (d), and MOF@MON-4 (e) using pellets of each material at room temperature. (f) Toluene adsorption (average values of three sets; see SI for details) with UiO-66-NH₂ and MOF@MON-1–4 (30 mg of adsorbents used). For control tests, H-MON-1 and H-MON-4, obtained from 30 mg of MOF@MON-1 and MOF@MON-4, respectively, through HF etching of MOF were used.

smoothly adsorbed into MOF. As shown in Figure 3b–d, the water contact angles gradually increased from 121° (MOF@MON-1) to 139° (MOF@MON-2) to 145° (MOF@MON-3), depending on the thickness of the MON on the MOF. MOF@MON-4 showed a 124° contact angle (Figure 3e). The MOF@MONs float on water even after vigorous shaking or standing for a week.¹⁸ (Figure S3) In comparison, UiO-66-NH₂ gradually wets and sinks into the water. PXRD studies confirmed that the inner crystalline structure of MOF@MON-1 was maintained after exposure to water for a week (Figure S4).

Separation of organic compounds from contaminated water is an environmentally important issue.^{19–23} Recently, tailored porous adsorbents with hydrophobic coatings have been prepared for selective removal of organic adsorbates.^{19,20} In this regard, the adsorption properties of MOF@MONs toward a model organic compound, toluene, on water were studied.^{20–22}

A fixed amount of Oil Red O dye was dissolved in toluene (0.010 M, 0.20 mL), added to water, and located on the surface of the water. After the adsorbents (30 mg) were added, the red-

colored adsorbents were separated from the reaction mixtures. After the adsorbents were dried and the dye was dissolved in methylene chloride, the amounts of Oil Red O and toluene were analyzed by UV/vis absorption spectroscopy. Figure 3f summarizes the results.

UiO-66-NH₂ showed poor adsorption (8.6×10^{-3} mL) for toluene due to complete wetting in water. In comparison, MOF@MON-1 showed good adsorption. The amount of toluene adsorbed decreased gradually from MOF@MON-1 (0.15 ± 0.04 mL) to MOF@MON-2 (0.072 ± 0.038 mL) to MOF@MON-3 (0.041 ± 0.017 mL). MOF@MON-4 (0.17 ± 0.03 mL) showed slightly higher adsorption behavior than MOF@MON-1. It is noteworthy that both MOF@MON-1 and UiO-66-NH₂ can be dispersed in toluene (Figure S5). UiO-66-NH₂ showed more favorable adsorption behavior in both adsorption isotherms of water and pure component toluene, compared with those of MOF@MON-1 (Figure S6). In addition, UiO-66-NH₂ showed relatively faster adsorption kinetics for toluene gas than MOF@MON-1 (Figure S7). Thus, the observed adsorption trend can be interpreted on the basis of the relative amount of MOF and MON in materials and the surface areas. The chemical accessibility of guest molecules to the inner MOF in MOF@MON-1 was verified by the post-synthetic approach reported recently by Cohen et al.¹⁵ The NH₂ group in the inner MOF was successfully converted to acetamide by reaction with acetic anhydride in toluene at room temperature (Figure S8).

After etching of the MOF in MOF@MON-1 and MOF@MON-4, the obtained H-MON-1 and H-MON-4 showed poor adsorption properties, implying that the inner crystalline MOFs play a key role in adsorption performance.²⁴ It should be noted that the amount of toluene adsorbed exceeds the total pore volume of MOF@MON adsorbents by 4–14 times (4–12 times weight of adsorbents; see Table S1), which is common in adsorption studies for the model system of an oil spill on water.²³ For example, 9–16 times weight adsorptions of aromatic adsorbates such as benzene, toluene, and nitrobenzene by porous hydrophobic adsorbents were reported.^{20,21} It can be reasoned that the capillary action effect²⁰ of nanopores induces efficient adsorption of adsorbates and the excess adsorbates accompany the adsorbed molecules in pores through additional intermolecular interactions.

In conclusion, this work shows that the surface properties of MOFs can be chemically controlled to have hydrophobic character by homogeneous coating with MONs, enabling the MOFs to be applied as adsorbents of organic compounds on water. In addition, chemical etching of the inner MOF resulted in the formation of hollow MONs, implying that the MOF can be used as a template¹⁰ for shape-controlled synthesis of MONs. We believe that, based on this strategy, a new class of functional porous hybrid materials can be prepared by tailored design of new organic building blocks for the inner MOF and outer MON.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details, Table S1, and Figures S1–S9. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

jimankim@skku.edu; ydkim91@skku.edu; sson@skku.edu

Notes

The authors declare no competing financial interest.

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