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Highly Chemically Stable MOFs with Trifluoromethyl Groups: Effect of Position of Trifluoromethyl Groups on Chemical Stability

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S Supporting Information

ABSTRACT: Metal-organic frameworks (MOFs) are a class of advanced porous crystalline materials. However, numerous MOFs have poor chemical stability, significantly restricting their industrial application. The introduction of trifluoromethyl groups around clusters of MOFs results in a shielding effect caused by their hydrophobicity and bulkiness, thus preventing guest molecules from attacking the coordination bonds. To prove such a shielding effect, the position of the trifluoromethyl groups is rationally adjusted, with trifluoromethyl groups at the ortho positions of carboxyl groups significantly improving the



chemical stability of UiO-67. The prepared UiO-67-o-2CF₃ remains intact after treatment with boiling water, 8 M HCl, 10 mM NaOH, and 50 ppm of NaF aqueous solutions. As the control experiment, trifluoromethyl groups at the meta positions of carboxyl groups have no shielding effect; hence, UiO-67-m-2CF₃ has a stability that is lower than that of UiO-67-o-2CF₃. In addition, the shielding effect is also applied to other MOFs, including DUT-5-o-2CF₃ and Al-TPDC-o-2CF₃, confirming the universality of this strategy.

1. INTRODUCTION

Metal-organic frameworks (MOFs) are widely studied functional porous materials, consisting of metal ions (or metal clusters) and organic linkers which are linked through coordination bonds to form extended porous crystalline frameworks.¹⁻³ High surface areas, proper pore structures, and a variety of chemical compositions make MOFs extremely attractive for an array of applications, such as gas storage,² separation,⁵ sensing,⁶ catalysis,⁷ and energy storage/conversion.⁸ However, the application of MOFs in chemical engineering is severely restricted by their poor chemical stability.9

To enhance the chemical stability of MOFs, five strategies have been proposed.¹⁰⁻¹⁴ (I) Improve coordination bond strength by applying hard/soft acid/base rule. For example, high oxidation state metals such as Zr⁴⁺, Cr³⁺, and Fe³⁺, as hard acids, can form strong coordination bonds with carboxylate ligands (as hard bases).^{15,16} (II) Introduction of hydrophobic groups such as an alkyl group into MOF structures.^{17,18} (III) Coat the external surfaces of MOFs with hydrophobic materials.^{19,20} For example, water-sensitive MOFs, including MOF-5, HKUST-1, and ZnBT, are coated with hydrophobic

polydimethysiloxane to enhance water stability.¹⁹ (IV) Generate framework interpenetration.²¹ (V) Prepare MOF composites such as CNT@MOF-5 and MOF-5@SBA-15.^{22,23}

Compared with other methods, the incorporations of high oxidation state metals and hydrophobic groups are the most facile and effective methods. The successful adoption of high oxidation state metals generates highly chemically stable MOFs such as UiO-66(Zr),²⁴ MIL-53(Cr),²⁵ and MIL-100(Fe).²⁶ However, the method is not applicable to all MOFs. For example, ZrMOF-BIPY is even sensitive toward acetone and chloroform.²⁷ As an alternative method, the introduction of hydrophobic groups into MOFs can enhance the water stability of the frameworks. For example, MOF-5 instability toward moisture in air is easily rectified via the introduction of methyl groups.¹⁷ However, compared with methyl groups, trifluoromethyl groups are more hydrophobic and bulkier, which increases their effectiveness in repelling water and their steric hindrance.^{28,29} In addition, we envisage that the position of the trifluoromethyl groups has significant influence on MOF

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Scheme 1. Shielding Effect of the Hydrophobic Groups in the Framework on Coordination Bonds of MOFs^a



 $a^{\prime}(a)$ Unfunctionalized MOFs decompose after coordination bonds are attacked by guest molecules. (b) MOFs bearing hydrophobic groups far from the coordination bonds decompose after attack by guest molecules (c) MOFs bearing hydrophobic groups close to the coordination bonds remain intact after attack by guest molecules.

stability.¹⁴ Moreover, the addition of such groups not only improves hydrophobicity, but causes a shielding effect that blocks destructive water molecules from MOF coordination bonds, thereby effectively enhancing framework stability.

Therefore, in order to study the shielding effect of hydrophobic groups, we designed a series of proof-of-concept experiments. Since the UiO series of MOFs were pioneered by Lillerud's group in 2008,²⁴ Zr-MOFs, especially UiO-66, have attracted increasing interest due to their excellent stability. As a Zr-MOF, UiO-67 has been intensively studied, showing excellent performance in many areas including wastewater treatment, catalysis, and drug delivery.³⁰⁻³² However, in contrast to UiO-66, UiO-67 possesses poor water stability due to its reduced kinetic stability. Therefore, UiO-67 was chosen as the model MOF material for our study. Herein, we designed and synthesized two trifluoromethyl modified ligands, 3,3'-bis(trifluoromethyl)-4,4'-biphenyldicarboxylic acid $(H_2BPDC-o-2CF_3)$ and $2_2'$ -bis(trifluoromethyl)-4,4'-biphenyldicarboxylic acid (H₂BPDC-m-2CF₃). H₂BPDC, H₂BPDC-o-2CF₃, and H₂BPDC-m-2CF₃, as organic ligands, were coordinated with Zr(IV) clusters to form UiO-67, UiO-67-o-2CF₃, and UiO-67-m-2CF₃, respectively. The chemical stability of these materials was examined and compared systematically and the shielding effect of the trifluoromethyl groups proved. In order to further confirm the versatility of the shielding effect, 3,3''-bis(trifluoromethyl)-[1,1':4',1''-terphenyl]-4,4"-dicarboxylic acid (H₂TPDC-*o*-2CF₃) was synthesized. H₂BPDC-o-2CF₃ and H₂TPDC-o-2CF₃ were used to obtain two chemically stable Al-MOFs containing trifluoromethyl groups at the ortho positions of carboxylate groups. Thus, the shielding effect of the trifluoromethyl groups in MOFs can be used to design and construct stable MOFs, which is ideal for utilization under harsh conditions in chemical engineering.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Ligands. H₂BPDC-*o*-2CF₃, H₂BPDC-*m*-2CF₃, and H₂TPDC-*o*-2CF₃ were synthesized according to previously

reported methods.^{33–35} The detailed synthetic procedures and characterization data are presented in the Supporting Information.

2.2. Synthesis of UiO-67. $ZrCl_4$ (0.117 g, 0.5 mmol), H_2BPDC (0.121 g, 0.5 mmol), benzoic acid (1.832 g, 15.0 mmol), and DMF (20 mL) were added to a Teflon liner (100 mL). After 10 min of sonication, the reaction mixture was kept at 120 °C for 24 h and then cooled to room temperature. The resulting UiO-67 was collected by centrifugation, washed with DMF and acetone five times, and dried under vacuum at 120 °C for 12 h (0.115 g, yield: 65.3%).

2.3. Synthesis of UiO-67-o-2CF₃. ZrCl₄ (0.117 g, 0.5 mmol), H₂BPDC-o-2CF₃ (0.190 g, 0.5 mmol), benzoic acid (0.610 g, 5.0 mmol), and DMF (20 mL) were added to a Teflon liner (100 mL). After 10 min of sonication, the reaction mixture was kept at 120 °C for 24 h and then cooled to room temperature. The resulting UiO-67-o-2CF₃ was collected by centrifugation, washed with DMF and acetone five times, and dried under vacuum at 120 °C for 12 h (0.168 g, yield: 68.5%).

2.4. Synthesis of UiO-67-m-2CF₃. UiO-67-m-2CF₃ was synthesized analogously by replacing H₂BPDC-o-2CF₃ with the equivalent molar amount of H₂BPDC-m-2CF₃ (0.169 g, yield: 69.1%).

2.5. Synthesis of DUT-5. H_2BPDC (0.260 g, 1.07 mmol), $Al(NO_3)_3 \cdot 9H_2O$ (0.525 g, 1.4 mmol), and DMF (30 mL) were added to a Teflon liner (100 mL). After 10 min of sonication, the reaction mixture was kept at 120 °C for 24 h and then cooled to room temperature. The resulting DUT-5 was collected by centrifugation, washed with DMF and acetone five times, and dried under vacuum at 120 °C for 12 h (0.283 g, yield: 93.2%).

2.6. Synthesis of DUT-5-*o*-2CF₃, Al-TPDC, and Al-TPDC-*o*-2CF₃. DUT-5-*o*-2CF₃ (0.408 g, yield: 90.6%), Al-TPDC (0.351 g, yield: 90.9%), and Al-TPDC-*o*-2CF₃ (0.480 g, yield: 90.3%) were synthesized in a similar way to DUT-5 by replacing H₂BPDC with the equivalent molar amount of H₂BPDC-*o*-2CF₃, [1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (H₂TPDC), and H₂TPDC-*o*-2CF₃, respectively

3. RESULTS AND DISCUSSION

As shown in Scheme 1, the shielding effect may depend on the distance between hydrophobic groups and coordination bonds in MOFs. Once a limited distance between the hydrophobic groups and coordination bonds is reached, the shielding effect is not observed. Their paternal and functionalized frameworks permit attack from guest molecules (Scheme 1a,b). However,



Figure 1. Structures of (a) UiO-67, (b) UiO-67-*m*-2CF₃, and (c) UiO-67-*o*-2CF₃. Structures of (d) DUT-5-*o*-2CF₃ viewed along the *b*-axis and *c*-axis, and (e) Al-TPDC-*o*-2CF₃ viewed along the *a*-axis and *c*-axis. Zr, green; Al, blue; C, black; O, red; H, white; F, turquoise.

as this distance is reduced, the hydrophobic groups can effectively hinder guest molecules and consequently enhance chemical stability (Scheme 1c). To prove this hypothesis, we designed and synthesized trifluoromethyl-functionalized UiO-67. As shown in Figure 1a, UiO-67 possesses $Zr_6O_4(OH)_4$ clusters interconnected with 12 4,4'-biphenyldicarboxylate (BPDC) linker molecules, generating octahedral and tetrahedral micropores. By incorporating H₂BPDC-*o*-2CF₃ and H₂BPDC-*m*-2CF₃ instead of H₂BPDC, two trifluoromethyl-functionalized MOFs, labeled UiO-67-*o*-2CF₃ and UiO-67-*m*-2CF₃, were obtained, respectively. The yields of UiO-67, UiO-67-*o*-2CF₃, and UiO-67-*m*-2CF₃ were 65.3%, 68.5%, and 69.1%, respectively, which indicates that the trifluoromethyl groups have no significant effect on MOF yields. Unfortu-

nately, even though numerous attempts were made, a single crystal of UiO-67-o-2CF₃ and UiO-67-m-2CF₃ was not obtained. To confirm the crystal structures of UiO-67, UiO-67-o-2CF₃, and UiO-67-m-2CF₃, they were characterized by powder X-ray diffraction (PXRD). UiO-67-o-2CF₃ and UiO-67-m-2CF₃ structures (Figure 1b,c) were determined by Rietveld refinement (Figures S16 and S17). Their initial models were obtained by functionalizing the UiO-67 framework in Materials Studio software.³⁶ This approach has been widely applied by many groups.^{18,37} Figure S18 shows that the trifluoromethyl group's fluorine atoms are near oxygen atoms of the carboxylate groups; hence, the Zr metal sites are not covered up.



Figure 2. (a) PXRD patterns of UiO-67, UiO-67-o-2CF₃, and UiO-67-m-2CF₃. PXRD patterns of (b) UiO-67 treated with water, 1 M HCl, and 10 mM NaOH (pH = 12) for 1 day; PXRD patterns of (c) UiO-67-o-2CF₃ and (d) UiO-67-m-2CF₃ treated with water, 1 M HCl, and 10 mM NaOH (pH = 12) for 1 day and treated with water for 60 days.



Figure 3. PXRD patterns of (a) UiO-67-o-2CF₃ and (b) UiO-67-m-2CF₃ treated with boiling water, 4 M HCl, 8 M HCl, and 50 ppm of NaF aqueous solutions for 1 day. N₂ adsorption-desorption isotherms at 77 K for (c) UiO-67-o-2CF₃ and (d) UiO-67-m-2CF₃ treated with boiling water, 4 M HCl, 8 M HCl, and 50 ppm of NaF aqueous solutions for 1 day.

As shown in Figure 2a, the similarity between the experimental and simulated patterns of UiO-67 confirms its formation. Meanwhile, the PXRD patterns of UiO-67-o-2CF₃ and UiO-67-m-2CF₃ are in good agreement with those of UiO-67. In the case of UiO-67-o-2CF₃, an obscure shoulder peak at 10.8 degrees overlapped partially by the intense and broad peak at 11.2 degrees is observed. The consistency of PXRD patterns shows that UiO-67, UiO-67-o-2CF₃, and UiO-67-m-2CF₃ are topologically equivalent. This phenomenon of functioned Zr-MOFs maintaining parent structures has been

observed in the literature.^{38,39} In addition, no redundant peak is observed in the PXRD patterns, indicating that the MOFs are pure crystals. To confirm retention of the trifluoromethyl groups in the frameworks, UiO-67-o-2CF₃ and UiO-67-m-2CF₃ were characterized by FT-IR. As shown in Figure S19, the absorption peaks at 1129 and 1137 cm⁻¹ for UiO-67-o-2CF₃ and UiO-67-m-2CF₃, respectively, are attributed to C–F stretching vibrations of the trifluoromethyl groups.⁴⁰

To study their porosity, UiO-67, UiO-67-o-2CF₃, and UiO-67-m-2CF₃ were characterized by N₂ adsorption at 77 K



Figure 4. SEM images of UiO-67-o-2CF₃ treated with water, boiling water, 1 M HCl, 4 M HCl, 8 M HCl, 10 mM NaOH (pH = 12), and 50 ppm of NaF aqueous solutions for 1 day and treated with water for 60 days.

(Figure S20). At the adsorption branch, with an increase in relative pressure, the N₂ adsorption amounts on all three MOFs rapidly reach equilibrium $(P/P_0 < 0.05)$, which indicates that they are microporous materials.⁴¹ The surface areas of the studied materials were obtained using the Brunauer-Emmett-Teller (BET) method (Table S3). The BET surface areas of UiO-67-o-2CF₃ and UiO-67-m-2CF₃ are 1198 and 1193 m² g⁻¹, respectively, and their total pore volumes calculated from their adsorption isotherms at P/P_0 = 0.95, are 0.53 and 0.50 cm³ g⁻¹, respectively. Similar surface area and pore volume values of UiO-67-o-2CF₃ and UiO-67-m-2CF₃ are attributed to their comparable ligand length, same functional groups, and topological structures. Furthermore, these values are much lower than those of UiO-67 (BET surface area of 1857 m² g⁻¹; total pore volume of 0.79 cm³ g^{-1}), which is due to the bulk size of trifluoromethyl groups in the frameworks, leading to reduced free space and increased framework weight.

To study the effect of the trifluoromethyl groups on chemical stability, UiO-67, UiO-67-o-2CF₃, and UiO-67-m-2CF3 were immersed in water, 1 M HCl, and 10 mM NaOH (pH = 12) for 1 day. After which, they were characterized by PXRD to assess their stability. As shown in Figure 2b, the structure of UiO-67 completely collapses when exposed to these conditions, resulting in amorphous solids. However, UiO-67-o-2CF3 and UiO-67-m-2CF3 PXRD patterns remain unchanged (Figure 2c,d), confirming their stability. More importantly, when UiO-67-o-2CF₃ and UiO-67-m-2CF₃ are immersed in water for 60 days, their structural integrity remains unaffected. The enhanced chemical stability is attributed to the hydrophobicity of trifluoromethyl groups, which is consistent with the literature.^{42,43} Figure S21 shows that the contact angles of water in UiO-67-o-2CF₃, UiO-67-m-2CF₃, and UiO-67 are 142.4°, 135.3°, and 43.3°, respectively. However, the position of the trifluoromethyl groups may lead to variations in MOF stability even though they have similar hydrophobicity.

To prove the presence of the shielding effect of trifluoromethyl groups, UiO-67-0-2CF₃ and UiO-67-m-2CF₃ were immersed in boiling water, 50 ppm of NaF, 4 M HCl, and 8 M HCl for 1 day. As shown in Figure 3, after these treatments, PXRD peak intensities of UiO-67-m-2CF₃ significantly decrease due to structure decomposition and loss of crystallinity. However, PXRD peak intensities of treated UiO-67-0-2CF₃ are still comparable with those of untreated MOF (Figure 3a), which highlights UiO-67-o-2CF₃ undeterred crystallinity under the same conditions. In addition, in order to determine whether the surface areas of MOFs decrease after exposure to these conditions, treated UiO-67-o-2CF₃ and UiO-67-m-2CF₃ were characterized by N₂ adsorption at 77 K. As shown in Figure 3c, Figure S22, and Table S4, UiO-67-0-2CF₃ retains its surface area after these treatments. Meanwhile, the crystallite surfaces of treated UiO-67-o-2CF₃ are still smooth (Figure 4). In the case of UiO-67-m-2CF₃, after treatment with water, 1 M HCl, and 10 mM NaOH, the BET surface area and crystallite surface remain practically unchanged (Figures S23 and S24). However, after treatment with boiling water, 4 M HCl, 8 M HCl, and 50 ppm of NaF aqueous solutions, the BET surface area significantly drops from 1193 to 383, 423, 354, and 163 m² g⁻¹, respectively (Figure 3d and Table S4). Moreover, the crystallite surfaces of the treated MOFs are severely corrupted (Figure S24), which indicates that UiO-67m-2CF₃ is unstable toward such harsh conditions. These results are consistent with PXRD analysis. Although UiO-67-o-2CF₃ and UiO-67-m-2CF₃ have similar hydrophobicity, UiO-67-o-2CF₃ has enhanced chemical stability, which is attributed to the position of trifluoromethyl groups, which are closer to Zr-O bonds between Zr(IV) and carboxylate groups effectively blocking guest molecules (such as H_2O , H^+ , and F^{-}) from attacking the coordination bonds (Scheme 2a). In the case of UiO-67-m-2CF₃, although UiO-67-m-2CF₃ is stable toward water and 1 M HCl, the trifluoromethyl groups are far from the coordination bonds, leaving them unprotected and open to attack in boiling water, 4 M HCl, 8 M HCl, and 50

Scheme 2. The Maintenance of the UiO-67-o-2CF₃ Structure and the Collapse of the UiO-67-m-2CF₃ Structure^a



^{*a*}(a) The maintenance of the UiO-67-o-2CF₃ structure after treatment with boiling water, 4 M HCl, 8 M HCl, and 50 ppm of NaF aqueous solutions; (b) the collapse of the UiO-67-m-2CF₃ structure after treatment with boiling water. Zr, green; C, gray; O, red; H, white; F, light blue.

ppm of NaF. Once the coordination bonds cleave, Zr metal sites are exposed, which may coordinate H_2O molecules in boiling water (Scheme 2b). In 4 M (8 M) HCl and 50 ppm of NaF, chlorine and fluorine atoms provide charge compensation after coordination bond cleavage (Schemes S1 and S2).²⁷

To confirm that the shielding effect is valid for MOFs with other metal ions and ligands, we further increased the ligand length to generate H2TPDC-o-2CF3. H2BPDC, H2BPDC-o-2CF₃, H₂TPDC, and H₂TPDC-o-2CF₃ were used to synthesize isoreticular Al-based MOFs, namely, DUT-5 (Al(OH)-(BPDC)), DUT-5-o-2CF₃ (Al(OH)(BPDC-o-2CF₃), BPDC $o-2CF_3 = 3,3'-bis(trifluoromethyl)-4,4'-biphenyldicarboxy$ late), Al-TPDC (Al(OH)(TPDC), TPDC = [1,1':4',1''terphenyl]-4,4"-dicarboxylate), and Al-TPDC-o-2CF₃ (Al-(OH) (TPDC-o-2CF₃), TPDC-o-2CF₃ = 3,3''-bis-(trifluoromethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate), respectively. The yields of DUT-5, DUT-5-o-2CF₃, Al-TPDC, and Al-TPDC-o-2CF₃ based on the ligands are 93.2%, 90.6%, 90.9%, and 90.3%, respectively. In accordance with the DUT-5 structure, the initial structures of DUT-5-o-2CF₃ and Al-TPDC-0-2CF₃ were obtained by substituting BPDC with BPDC-o-2CF₃ and TPDC-o-2CF₃ linkers in Materials Studio software followed by geometry optimization.³⁶ Then, the structures of DUT-5-o-2CF₃ and Al-TPDC-o-2CF₃ were determined by Rietveld refinement. The final profile fits show good agreement with the observed diffraction patterns,

with final R_{wp} values of 5.02% and 4.34% for DUT-5-o-2CF₃ and Al-TPDC-o-2CF₃, respectively (Figures S25 and S26). As shown in Figure 1d,e and Figure S27, in the frameworks, every Al atom is linked to six O atoms, forming a distorted octahedral structure. The Al chains are connected by BPDC, BPDC-o-2CF₃, TPDC, and TPDC-o-2CF₃ linkers to obtain three-dimensional frameworks, namely, DUT-5, DUT-5-o-2CF₃, Al-TPDC, and Al-TPDC-o-2CF₃, respectively. As shown in Figure S28, the PXRD pattern of DUT-5-0-2CF₃ is in good agreement with that of DUT-5, which demonstrates that DUT-5-0-2CF₃ is topologically equivalent to DUT-5. As shown in Figure S29, the PXRD pattern of Al-TPDC-o-2CF₃ is in good agreement with that of Al-TPDC. To study their porosity, the N₂ adsorption-desorption isotherms at 77 K were measured (Figures S30-S32). The BET surface areas of DUT-5, DUT-5-o-2CF₃, Al-TPDC, and Al-TPDC-o-2CF₃ are 1479, 1366, 553, and 1203 m² g⁻¹, respectively.

To confirm the excellent chemical stability of DUT-5-o-2CF₃ and Al-TPDC-o-2CF₃, they were immersed in water, 10 mM HCl (pH = 2), and 1 mM NaOH (pH = 11) for 1 day. As shown in Figure 5, after treatment, the PXRD patterns of DUT-5-o-2CF₃ and Al-TPDC-o-2CF₃ remain practically unchanged. PXRD peaks of treated Al-TPDC-o-2CF₃ at high angle are broad, which may be attributed to a decrease in This phenomenon was previously reparticle sizes.44 ported.^{37,45,46} In addition, a reduction in N₂ uptake of the treated samples at 77 K is not observed (Figures S41 and S42). However, even when treated with water, DUT-5 and Al-TPDC structures decompose (Figures S43 and S44). For DUT-5-o-2CF₃ and Al-TPDC-o-2CF₃, the enhanced chemical stability is attributed to the trifluoromethyl groups at the ortho positions of the carboxyl groups. These results reveal that our strategy is effective in the synthesis of chemically stable MOFs viable under harsh conditions in chemical engineering. In addition, we speculate that tetra-trifluoromethyl groups at the ortho positions in the ligand can further enhance the chemical stability of MOFs. In the near future, the synthesis of MOFs with enhanced chemical stability will be examined.

4. CONCLUSION

By harnessing the advantageous hydrophobicity and bulkiness of trifluoromethyl groups, we synthesized trifluoromethyl-functionalized UiO-67 (namely, UiO-67-*o*-2CF₃ and UiO-67-*m*-2CF₃) to enhance the chemical stability of UiO-67. In contrast to UiO-67, UiO-67-*o*-2CF₃ and UiO-67-*m*-2CF₃ are stable toward water, 1 M HCl, and 10 mM NaOH. In addition, although UiO-67-*o*-2CF₃ and UiO-67-*m*-2CF₃ have similar



Figure 5. PXRD patterns of (a) DUT-5-*o*-2CF₃ and (b) Al-TPDC-*o*-2CF₃ before and after treatment with water, 10 mM HCl (pH = 2), and 1 mM NaOH (pH = 11).

hydrophobicity, due to the shielding effect of the trifluoromethyl groups at the ortho positions of the carboxyl groups, UiO-67-o-2CF₃ is more chemically stable. Moreover, we determined that the shielding effect is also valid for Al-based MOFs of varying ligand length. We believe that the shielding effect of the hydrophobic groups provides a promising opportunity to prepare chemically stable MOFs with industrial applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00088.

> Additional experimental procedures, characterization techniques, PXRD patterns, NMR spectra, SEM images, TGA data, nitrogen sorption isotherms, FT-IR spectra, contact angles of water, and structural data (PDF)

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Notes

The authors declare no competing financial interest.

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