Tailor-Made Stable Zr(IV)-Based Metal–Organic Frameworks for Laser Desorption/Ionization Mass Spectrometry Analysis of Small Molecules and Simultaneous Enrichment of Phosphopeptides

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ABSTRACT: Although thousands of metal–organic frameworks (MOFs) have been fabricated and widely applied in gas storage/separations, adsorption, catalysis, and so on, few kinds of MOFs have been used as adsorption materials while simultaneously serving as matrices to analyze small molecules for laser desorption/ionization mass spectrometry (LDI-MS). Herein, a new concept is introduced to design and synthesize MOFs as both adsorption materials and matrices according to the structure of ligands and common matrices. The proof of concept design was demonstrated by selection of 2,5-pyridinedicarboxylic acid (PDC) and 2,5-dihydroxyterephthalic acid (DHT) as ligands for synthesis of MOFs. Two Zr(IV)-based MOFs of UiO-66-PDC and UiO-66-(OH)₂ were synthesized and applied for the first time as new matrices for analysis of small molecules by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). Both of them showed low matrix interferences, high ionization efficiency, and good reproducibility when used as matrices. A variety of small molecules, including saccharides, amino acids, nucleosides, peptides, alkaline drugs, and natural products, were analyzed. In addition, UiO-66-(OH)₂ exhibited potential for application in the quantitative determination of glucose and pyridoxal 5′-phosphate. Furthermore, thanks to its intrinsically large surface area and highly ordered pores, UiO-66-(OH)₂ also showed sensitive and specific enrichment of phosphopeptides prior to MS analysis. These results demonstrated that this strategy can be used to efficiently screen tailor-made MOFs as matrices to analyze small molecules by MALDI-TOF-MS.

KEYWORDS: metal–organic frameworks, UiO-66-PDC, UiO-66-(OH)₂, LDI-MS, small molecules

INTRODUCTION

Metal–organic frameworks (MOFs), also known as coordination polymers, are crystalline materials constructed by joining metal-containing units with organic linkers, using strong bonds (reticular synthesis) to create multidimensional networks with permanent porosity. Since the pioneering work of Hoskins and Robson1,2 in the field, worldwide research began with the simple self-assembly of molecules with metallic centers, bringing the first generation of MOFs.3 The field then developed toward the use of secondary building units and the construction of large metal–organic polyhedral cages.4,5 MOFs occupy a special place among porous materials owing to their extraordinary surface areas, high porosity, topological diversity, and high functional tunability. As a consequence, their potential applications have been explored in a wide variety of areas, such as gas storage/separations, adsorption, catalysis, drug delivery, sensing, luminescence, and ionic/electronic conductivity.6–20

Recently, it was very interesting that a new application of MOFs emerged. MOFs were randomly selected as matrices to analyze small molecules for laser desorption/ionization mass spectrometry (LDI-MS). Huang’s group21 first utilized MIL-100(Fe) MOFs as matrices for analysis of polycyclic aromatic hydrocarbons (PAHs) in surface-assisted laser desorption/ionization mass spectrometry (SALDI-MS). However, MIL-100(Fe) is not suitable to analyze other small molecules. After that, only a few kinds of MOFs22,23 were successfully selected...
as matrices for LDI-MS and simultaneous extraction of small molecules in spite of the appearance of thousands of MOFs. Therefore, the exploration of new MOF-based matrices for various small molecules is urgently necessary.

Herein, a new concept was introduced to design and synthesize MOFs as both adsorption materials and matrices according to the structure of ligands and common matrices. The proof of concept design was demonstrated by selection of 2,5-pyridinedicarboxylic acid (PDC) and 2,5-dihydroxyterephthalic acid (DHT) as ligands for the synthesis of MOFs, whose structures are similar to those of 2-picolinic acid (PA) and 2,5-dihydroxybenzoic acid (DHB), respectively. Moreover, zirconium (Zr)-based MOFs have been shown great interest due to their particular physical and chemical properties, such as water- and acid-resistant stability and excellent thermal stability. Therefore, we designed and synthesized two kinds of MOFs with zirconium chloride (ZrCl4) as the metallic center and 2,5-pyridinedicarboxylic acid (PDC) and DHT as the organic linkers (as shown in Scheme 1).

Two kinds of Zr-MOFs, UiO-66-PDC (II) and UiO-66-(OH)2 (IV) (Scheme 1), were successfully obtained and also applied as matrices for LDI-MS. Various kinds of small molecules, including saccharides, amino acids, nucleosides, peptides, alkaline drugs, and natural products were successfully analyzed with the two designed MOFs as matrices. In addition, many exposed Zr−O clusters of UiO-66 present high affinity toward phosphoric groups and can uptake phosphor-bearing phosphates or phosphonates via the formation of Zr−O−P bonds. The MOF-IV was also applied to trap phosphopeptides from bovine serum albumin (BSA) digest prior to MS analysis.

**EXPERIMENTAL SECTION**

**Chemicals and Reagents.** ZrCl4, aluminum nitrate nonahydrate (Al(NO3)3·9H2O), DHB, PA, pyridoxal 5'-phosphate, oligosaccharides (glucose, sucrose, maltose, raffinose, ribose, lactose, and galactose), amino acids (arginine, lysine, glutamic acid, phenylalanine, asparagine, and glutamine), nucleosides (cytosine, cytidine, uridine, and guanosine), glutathione, β-casein, BSA, β-cyclodextrin (β-CD), and trifuoroacetic acid (TFA) were purchased from Sigma-Aldrich (St. Louis, MO). Atropine, carbachol, azetadrol, gastrodin, and 3-O-tigloylswietenolide were obtained from Aladdin (Shanghai, China). 1,4-Benzencarboxylic acid (BDC), PDC, DHT, and 2,5-diaminoterephthalic acid (DAT) were ordered from J&K Scientific Ltd. (Beijing, China). Standard peptides (angiotensin I, Ac-ALRISIYSDR, AEKLLTQHENIK, SHKQIYYSDK, ALKASALGHELEK, FEKLFT-QIYYSDY, and GQKGFIDLPFEPFGLEPRAEKLTTQHENIK) were obtained from China Peptides Co., Ltd. (Shanghai, China). Methanol, ethanol, N,N-dimethylformamide (DMF), acetonitrile (ACN), concentrated hydrochloric acid (HCl), and other solvents were at least analytical grade. The deionized water used in all experiments was purified by a Milli-Q system (Millipore Inc., Milford, MA). All of the above chemicals were used as received without further purification.

**Synthesis of Zr-MOFs.** Direct solvothermal synthesis and postsynthetic exchange (PSE) methods were adopted to fabricate several Zr-MOFs in this work. The detailed methods are shown in Table S1.

**Synthesis of UiO-66 via Solvothermal Approach.** UiO-66 was directly synthesized via a solvothermal approach according to previous literature. A 20 mL vial with a screw cap loaded with anhydrous ZrCl4 (0.54 mmol), concentrated HCl (1 mL), and DMF (15 mL) was sonicated until fully dissolved. BDC (0.74 mmol) was then added, and the mixture was sonicated for 10 min before being heated at 80 °C overnight. The resulting white powder sample was collected by centrifugation, successively washed with DMF (3 × 30 mL) and ethanol (3 × 30 mL), and then dried in a vacuum oven at 50 °C. UiO-66 was activated at 120 °C before further experiments.

**Synthesis of UiO-66-PDC (II) by Postsynthetic Exchange (PSE).** Twenty-eight milligrams of UiO-66, 167 mg (1.0 mmol) of PDC, and 6 mL of methanol were added to a Teflon-lined stainless steel autoclave and heated to 150 °C for 24 h. After being cooled to room temperature, the resulting II was separated by centrifugation and washed with fresh methanol (20 mL, 3 times per day over 3 days) and ethanol (20 mL, 3 times per day over 3 days). Finally, the product was dried at 70 °C overnight under vacuum.

**Synthesis of Al-PDC (III) by Solvothermal Approach.** The synthesis of Al-PDC was carried out with 0.9 mmol Al(NO3)3·9H2O, 0.9 mmol PDC, and 0.875 mmol sodium hydroxide dissolved in water (15 mL) was sonicated until fully dissolved. The ligand DHT (0.74 mmol) was then added, and the mixture was sonicated for 10 min before being heated at 80 °C overnight. The resulting yellow powder sample was collected by centrifugation, successively washed with DMF (3 × 30 mL) and ethanol (3 × 30 mL), and then dried in a vacuum oven at 100 °C overnight under vacuum.

**Synthesis of UiO-66-(OH)2 (IV) by Solvothermal Approach.** In a typical synthesis, a 20 mL vial with a screw cap loaded with anhydrous ZrCl4 (0.54 mmol), concentrated HCl (1 mL), and DMF (15 mL) was sonicated until fully dissolved. The ligand DHT (0.74 mmol) was then added, and the mixture was sonicated 10 min before being heated at 80 °C overnight. The resulting yellow powder sample was collected by centrifugation, successively washed with DMF (3 × 30 mL) and ethanol (3 × 30 mL), and then dried in a vacuum oven at 100 °C overnight under vacuum.

**Synthesis of UiO-66-(OH)2·PSE (V) by Solvothermal Approach.**
molecules for LDI-MS analysis. There was no basis for random selection of MOFs and application in LDI-MS analysis, which would be time-consuming. As a result, a concept was presented to design and synthesize MOFs according to the structure of ligands and common matrices. To serve as matrix, the materials should be able to absorb photons from a pulsed laser. As shown in Scheme 1, it is well-known that PA and DHB are commonly used organic matrices in MALDI-TOF/MS for biomolecule analysis and proteomics research, while two organic linkers, PDC and DHT, were widely used for synthesis of MOFs, which have one more carboxyl group, respectively. It was deduced that both PDC and DHT are possibly able to absorb photons from a pulsed laser. As shown in Figure S1A, the UV−visible spectra of PDC and DHT are similar to those of PA and DHB. It was further deduced that the MOFs synthesized with PDC and DHT could absorb photons from a pulsed laser. This inspired us to design MOFs as LDI-MS matrices, and we finally choose PDC and DHT as ligands for synthesis of MOFs.

**MOF Synthesis and Characterization.** As shown in Scheme 1, direct solvothermal synthesis of aqueous solution containing ZrCl4 and PDC did not afford an MOF material. Given the high structural analogy of BDC and PDC, the approach of PSE was employed as a strategy to introduce PA units into Zr-MOF. PSE was performed by incubating solid UiO-66 in a methanol solution of PDC for 24 h at 60 °C. The linker-exchanged material of UiO-66-PDC (II) was isolated by centrifugation, followed by extensive washing with fresh methanol and activation under vacuum. PXRD patterns (Figure 1A) and SEM images (Figure S2) of II confirmed retention of crystallization with high phase purity, and its average size was ∼260 nm. The presence of PDC in II was verified by elemental analysis (UiO-66-PDC: C = 32.79, H = 3.42, N = 6.04%; UiO-66: C = 36.80, H = 4.41, N = 0.00%). In addition, 1H NMR measurement was performed by digesting UiO-66-PDC with concentrated aqueous HCl. Chemical shifts (δ = 9.16, 8.44, 8.16 ppm, Figure S3F) indicated that PDC was successfully exchanged into MOF. The activated II had a high BET surface area of 1141 m2/g and a total pore volume of 0.726 cm3/g, which is comparable to those of UiO-66 (Figure S4, Table S2). For comparison, another MOF (III) was synthesized using PDC and Al(NO3)3·9H2O as precursors. The PXRD pattern is in agreement with the previously reported result49 (Figure 1B). The SEM image of III (Figure S2) shows that its average size was about 32−46 μm. It was deduced that III, with such a large size, could not be suitable as a LDI-MS matrix due to poor dispersity on the MALDI plate.

Another Zr-MOF with DHT as organic linker could be obtained via both direct solvothermal synthesis and PSE strategy. The resulting IV, fabricated by solvothermal synthesis, was highly crystalline and topologically identical to UiO-66, demonstrating IV was successfully prepared (Figure 1A). Moreover, the morphology of IV was quite uniform, and it possessed a characteristic cubic close-packed structure in agreement with the previous observation49 (Figure S2). The activated IV had a relatively high BET surface area of 557 m2/g and a total pore volume of 0.380 cm3/g (Figure S4, Table S2). In addition, V was afforded by the PSE strategy. To confirm the existence of DHT in V, 1H NMR was performed by digesting V with concentrated aqueous HCl. Two kinds of linkers, DHT and BDC, can be seen in Figure S3B, proving that ligand exchange indeed occurred in the process of PSE. The degree of functionalization was tunable between 40 and 71% using 2−10 equiv of DHT in the PSE solution. The PXRD pattern of V was
their high surface area and porosity, MOF II could evenly disperse analyte molecules, facilitating the formation of uniform cocrystals. This would contribute to an increase in the shot-to-shot reproducibility of the MALDI-TOF-MS analysis. The same phenomenon was also observed when investigating IV (Figures S5A and B).

The MALDI-TOF-MS spectra of II and IV were detected and presented in Figure S6. The MS spectrum presented interference-free background in the mass range of m/z 100–1000 in positive mode when spotting II onto the plate. As for IV (Figure S6D), there was only one obvious background noise signal (m/z 39) and a relatively low signal (m/z 23) was observed in the range of m/z 0–100, possibly caused by [K]⁺ and [Na]⁺, respectively. Metal cation adducts might originate from residual Na⁺ and K⁺, which were included in the reagents used for preparing MOFs and/or in the analyte sample solutions as impurities. In addition, they also might be produced by the ion source of the equipment. This phenomenon was also found in graphene and porous silicon matrixes. 37,38 These results strongly demonstrated that II and IV were possibly suitable as matrixes for the analysis of small molecules with MALDI-TOF-MS. Despite the existence of two interference peaks, the mass range below m/z 100 was no longer considered in the following experiments.

Zr-MOF-Assisted LDI-MS Analysis. To further investigate the performance in MALDI-TOF-MS analysis, II was used as a matrix for detection of azedarachol in positive ion mode (Figure 3C). Meanwhile, PA and III were also used as matrixes for comparison (Figures 3A and B). It can be easily seen from Figure 3A that interference ions almost dominated the spectra, making it difficult for identification, while Figure 3B exhibits a cleaner mass spectrum but with relatively low signal intensity. This may be assigned to nonuniform distribution of the matrix

Figure 2. Morphologies of (A) DHB crystal, (B) DHB-sample cocrystal, (C) UiO-66-PDC crystal, and (D) UiO-66-PDC-sample cocrystal on the MALDI target. Scale bar depicted is 20 μm. Pictures were obtained using a Leica DM2500 M microscope (Leica Instrument Co., Ltd., Germany).
caused by the large size of III. Interestingly, II provided a very clean mass spectrum with high signal intensities of 443.37 and 459.11, assigning to the Na⁺ and K⁺ adducts of the analyte, respectively (Figure 3C). It was deduced that Al-PDC-based MOFs with nanometer sizes would also generate a clean mass spectrum with low background noise peaks (Figures S7C and D). The di-sensitivity and clean mass spectra with low background noise of sucrose and atropine were successfully detected with high sensitivity and clean mass spectra with low background noise when analytes were oligosaccharides and natural products. It was not suitable to serve as matrix to analyze other small molecules such as alkaline drugs or nucleosides. In a word, the application range of UiO-66-(NH₂)₂ was not so wide as that of both UiO-66-PDC and UiO-66-(OH₂).

Effect of DHB Amount. IV exhibited excellent analytical performance for the analysis of small molecules (m/z < 1000), but as seen in Figure S9A, some interference appeared in the spectrum when analyzing the substances of m/z > 1000 (for example, β-CD). To solve this problem, some DHB was mixed with IV and selected as the dual matrix. It was found that the interference could be eliminated when mixing a few DHB in the IV suspension (1.5/1, w/w) (Figure S9B). However, the background noise of DHB emerged when the content of DHB (3/1, w/w) was continually increased (Figure S9C). As the content of DHB in the dual matrix (DHB/IV) further increased to 10/1 (w/w), strong background noises emerged, seriously suppressing the analyte signals (Figure S9D), which was almost the same as that using DHB as the matrix (Figure S9E). To probe the underlying cause, PXRD characterizations of IV cocrystallized with different amounts of DHB were performed, and the corresponding results are shown in Figure S10. When the mass ratio of DHB and IV was 1.5:1, the characteristic peaks (at 7.4 and 8.3) of IV still existed; particularly, an obvious new peak at 23 appeared, which were not assigned to either IV or DHB. When continually increasing DHB content (DHB/IV = 3:1, w/w), characteristic peaks of IV became weaker until they disappeared, while new peaks gradually increased. This result indicated that the cocrystal changed when adding DHB to the IV suspension. It was deduced that cocrystallization possibly occurred by mixing DHB and IV, causing crystal transformation. During the laser irradiation, this cocrystallization structure possibly enhances electromagnetic fields and charge interactions on the surface of the nanomaterials, further facilitating suppression of matrix interference when analyzing molecules of m/z > 1000. Another possible reason is that DHB has a strong absorption of UV light at around 355 nm. The addition of an appropriate amount of
DHB can largely increase desorption and ionization efficiency and thus enhance signal intensities.

The morphologies of different mass ratios of DHB and IV cocrystal were shown in Figures SSC, E, and G. It could be easily observed that a uniform cocrystal layer was obtained when the mass ratio of DHB and IV was 1.5:1 or 3:1 (Figures SSC and E). However, if the mass ratio is increased to 10:1, it presents a large branched cocrystal layer (Figure SSG), which was similar to that of the DHB crystal. Furthermore, the morphology of the cocrystal layer still remained after analyte solution was dropped onto it (Figures SSD, F, and H). These results indicated that adding a small amount of DHB to the IV suspension (DHB:IV = 1.5:1, w/w) did not have an influence on the formation of the uniform cocrystal layer. However, a “branched crystal” could be observed when a large amount of DHB was added to the IV suspension (DHB:IV = 10:1, w/w), which was the same as DHB used as sole matrix.

Analysis of Various Small Molecules. To further demonstrate the feasibility of the II and IV matrix in robust applications, various small molecules, including oligosaccharides, amino acids, alkaline drugs, nucleosides, natural products, and standard peptides, were investigated. The m/z values in these mass spectra with corresponding quasi-molecular ions are listed in Table S3. As shown in Figure S11, all analytes containing carbamazepine, guanosine, glutathione, gastrodin, azedarachol, and 3-O-tigloylswietenolide were detected with high sensitivity and clean spectra with little noise peaks when using II as the matrix. The limits of detection (LOD) of glutathione and 3-O-tigloylswietenolide reached 1.0 pmol. As one knows, analysis of neutral oligosaccharides is still a challenge because of low ionization efficiency. When IV is used, 7 oligosaccharides such as xylose, glucose, maltose, raffinose, ribose, galactose, and lactose were exclusively detected with clear sodium and potassium adduct ion peaks and with little matrix interference (Figure S12). The LODs of both maltose and raffinose could reach 1.0 pmol. Further, six amino acids and glutathione were also successfully detected with relatively high signal intensities (Figure S13). Though the matrix-related interference was slightly more serious than that of the oligosaccharides, it could be ignored in real analysis. Moreover, IV also exhibited good performance in analysis of the basic compounds. In this case, two important alkaline drugs (carbamazepine and atropine) were chosen. As shown in Figures S14A and B, strong analyte signals were observed in the form of [M + Na]+ and/or [M + K]+. The LODs of carbamazepine and atropine reached 5.0 and 3.0 pmol, respectively. Additionally, IV was used to analyze several natural products (Figures S14C–F) and nucleosides (Figure S15) and showed a high signal-to-noise (S/N) ratio around 3000–4000. Finally, six peptides were also analyzed using DHB and IV as a dual matrix. As shown in Figure S16, all peptide signals were observed in the form of intact molecular ion peaks with quite low background noise. These results demonstrated that IV is an effective matrix for analysis of various small molecules.

Except for the independent detection of these analytes, the mixtures of oligosaccharides, amino acids, and peptides were also analyzed. For comparison, the traditional DHB was also employed as the matrix under the same conditions. As shown in Figure 4, IV provided sufficient signals of these analytes in the ionization process. Figures S17A and B show mass spectra of oligosaccharides and amino acids obtained from DHB; the strong background signals correspond to the DHB-related ions’ strongly suppressed analyte signal. Although relatively obvious peptides signals were detected by DHB (Figure S17C), the resolution and signal-to-noise obtained with DHB were far lower than those with IV (Figure 4C).

Reproducibility and Quantitative Analysis of Glucose. Reproducibility is a commonly encountered problem in conventional MALDI-TOF-MS. For IV, for example, the relative standard deviations (RSDs) of signal intensities in five replicate analyses are displayed in Table S4. The RSD values of glucose and maltose were 4.0 and 5.2%, respectively. These results indicate better reproducibility compared to that in the previous literature. The reproducibility for amino acids, alkaline drugs, and natural products were not so good as that of oligosaccharides, indicating IV is more suitable for oligosaccharide analysis. Furthermore, a homogeneous crystal layer of

Figure 4. Mass spectra of (A) oligosaccharides containing xylose, glucose, maltose, and raffinose; (B) amino acids containing lysine, glutamic acid, phenylalanine, and arginine; and (C) peptides containing Ac-ALRSYSDR, AEKLLTQHENIK, FEKLFTQIYYSDR, GKQGFIDLPEFPFGLEPR, and angiotensin I with UiO-66-(OH)2 as the matrix.
IV-analyte (Figure S4) eliminated the necessity to search for the “sweet spot”, not only avoiding the variability of signal intensity across different locations on the target surface due to the heterogeneous crystals but also greatly improving spot-to-spot reproducibility.

Encouraged by the good reproducibility, we tried to perform quantitative analysis of analytes with a IV matrix. In this experiment, pyridoxal 5′-phosphate and glucose were selected as test compounds. As [M + Na]+ and [M + K]+ signals were produced in the positive ion mode MS, two options could be considered for quantitative analysis. Then, two calibration curves were plotted for each compound according to the signal intensities of [M + Na]+ and [M + K]+, respectively (Figure 5). Good linearity was obtained with R² > 0.99 in the range of 0.5−40 nmol, which provided the possibility of quantitative analysis for pyridoxal 5′-phosphate and glucose.

Selective Enrichment of Phosphopeptides. To realize the sensitive detection of LDI-MS, the pre-enrichment ability of the nanomaterial-based matrix is attractive because it can enhance the detection efficiency and avoid the complicated elution procedure during the conventional enrichment method prior to MALDI-TOF-MS analysis.43 Motivated by good affinity of UiO-66 toward phosphoric groups, IV could possibly serve as an adsorbent for enrichment of phosphoric-containing compounds. Then, selective enrichment of phosphopeptides from β-casein digest was performed, and the results are shown in Figure 6. The signals of phosphopeptides were too weak to be detected before enrichment owing to the interference of high-abundance nonphosphopeptides (Figure 6A). As expected, after treatment with IV, the targeted phosphopeptide peaks at m/z 2061, 2556, and 3122 and their dephosphorylated counterparts were easily observed with remarkably increased MS signals (Figure 6B). To examine its selective enrichment performance in a complex system, large amounts of BSA digest were added to β-casein digest (β-casein/BSA = 1:100) to construct a mimic biological sample. As shown in Figure 6D, a similar spectrum was obtained compared to Figure 6B, also indicating that IV can be used as an adsorbent to capture phosphopeptides.

**CONCLUSION**

In summary, two Zr-MOFs of UiO-66-PDC and UiO-66-(OH)₂ were designed and successfully exploited as novel MALDI matrices for small molecules analysis. The results demonstrated that these two Zr-MOFs exhibit good advantages, including low background interference, high desorption/ionization efficiency, and good signal reproducibility. Moreover, the quantitative analysis of small molecules could be potentially performed when using UiO-66-(OH)₂ as the matrix for LDI-MS. Particularly, UiO-66-(OH)₂ presents high affinity toward phosphoric groups via the formation of Zr−O−P bonds, and high selective enrichment for phosphopeptides prior to MS analysis could be performed. These merits make UiO-66-PDC and UiO-66-(OH)₂ promising matrixes to solve more analytical challenges by LDI-MS in the future. It should be pointed out that the linkers of PDC and DHT in UiO-66-PDC and UiO-66-(OH)₂ possess high structural analogy to PA and DHB, respectively. This plays a vitally important role as an effective matrix for MALDI-TOF-MS. The proof of concept design was successfully demonstrated, and we optimistically hypothesize that other nanometer-sized MOFs fabricated with PDC or DHT as the linkers and various metal clusters as the nodes can also serve as new matrices in LDI-MS.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b06225.
Synthesis scheme; UV–vis, mass, and 1H NMR spectra; SEM images; N2 isotherms; PXRD patterns; compound structures; experimental parameters; and table of BET surface areas and total pore volumes (PDF)

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Notes

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