Journal of Solid State Chemistry 223 (2015) 79–83

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Pore surface engineering in a zirconium metal–organic framework via thiol-ene reaction

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ARTICLE INFO

Article history:
Received 26 April 2014
Received in revised form
12 June 2014
Accepted 14 June 2014
Available online 23 June 2014

Keywords:
Metal–organic framework
Post-synthetic modification
Thiol-ene reaction
Zirconium-based
Photoaddition

ABSTRACT

A porous olefin-functionalized Zr(IV)-based metal–organic framework, denoted as UiO-68-allyl, has been constructed. Our results clearly demonstrated that the surface of UiO-68-allyl could be decorated with organic molecule (ethanethiol) via thiol-ene reaction. More importantly, the crystallinity of the framework were maintained during the post-synthetic modification process. However, the microporosity of the framework is retained but the surface area decreased, due to the grafting of ethylthio groups into the pores. From our studies, we can conclude that the strategy of post-synthetic modification of UiO-68-allyl via thiol-ene reaction may be general. Furthermore, we may anchor other desired functional group onto the pore walls in Zr-MOFs via thiol-ene reaction, enabling more potential applications.

1. Introduction

Metal–organic frameworks (MOFs) have attracted intensive attention over the past two decades, largely because of their porosity nature and promising applications in gas storage [1], separation [2], catalysis [3], sensors [4] and biology [5]. Compared to other porous materials, one of the most attractive aspects of MOFs is that the organic linker can be easily functionalized, which allows for structural and functional diversity. In principle, a variety of functional groups can be introduced into MOFs through two approaches - direct synthesis [6] or post-synthetic modification (PSM) [7]. For the former, however, many chemical functionalities are incompatible with the conditions for MOF assembly. As an alternative route, PSM has garnered increasing attention and has emerged as a powerful tool for anchoring functional groups onto MOFs. To date, several different types of organic reactions has been successfully utilized to chemically tailor the interiors of MOFs, such as click reaction [8], imine and hydrazone formation [9], deprotection reaction [10] and so on. For example, Zhou and co-workers recently reported the introducing of diverse functional groups into the MOF by using click reaction [11].

As a new type of click reaction, thiol-ene reaction has also gained intensive attention and been widely applied in many different areas [12]. This reaction is very efficient, high yielding, and tolerant of various solvents and functional groups. In principle, it can also be applied to covalently attach functional groups within the framework of MOFs. However, to our surprise, the thiol-ene reaction had only been utilized to chemically tailor the pore surface of an olefin-tagged Zn paddle-wheel MOF until recently [13]. In this manuscript, we reported the second example of the PSM of MOF through thiol-ene reaction. We chose Zr(IV)-based MOFs (Zr-MOFs) as the substrate, which are well-known for their robustness compared with common Zn/Cu-centered MOFs [14]. Our result clearly demonstrated that the olefin-functionalized Zr-MOF, denoted as UiO-68-allyl, can undergo a quantitative thiol-ene reaction with ethanethiol to form thioether group on the pore wall surfaces (Fig. 1).

2. Experimental section

2.1. Materials and general methods

4-Methoxyl carbonylphenylboronic acid (97%) was purchased from AK Scientific, Inc. Allyl bromide, ethanethiol and 2,2-dimethoxy-2-phenylacetophenone were purchased from TCI. $Pd(PPh_3)_4$ was bought from Aladdin. Zirconium (IV) chloride (99.5%) was purchased from Alfa Aesar. 1,4-dibromo-2,5-dimethoxybenzene was synthesized according to the literature [15]. ^1H and ^{13}C NMR spectra were measured on a Bruker Fourier 300 and 400 M spectrometer. High resolution mass spectra was collected on Bruker Daltonics Inc. APEXII FT-ICR mass spectrometer, which was equipped with EI, ESI and MALDI as ionization source. Powder X-ray diffraction (PXRD) data was collected

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http://dx.doi.org/10.1016/j.jssc.2014.06.023
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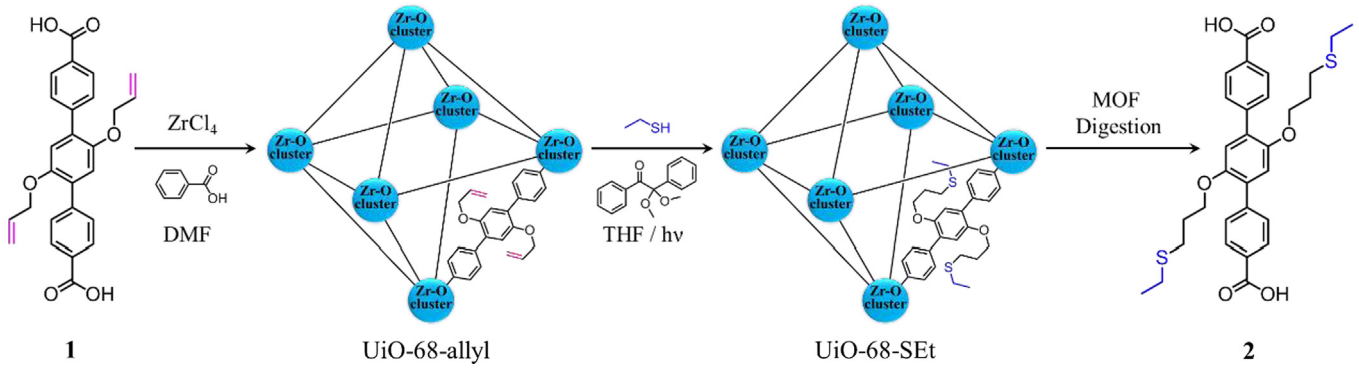

Fig. 1. Scheme for the post-synthetic modification of UiO-68-allyl. The topology is the same as for UiO-68-NH_2 and is shown in simplified form as an octahedron cage.

on PANalytical X'Pert PRO with Cu*K*α1 (λ=1.54056 Å) radiation operated at 40 kV and 40 mA, from 2θ=4.2° up to 50° with 0.02° increment. Thermogravimetric analysis from 50 to 800 °C was carried out on a DTA-60 Simultaneous DTG-TG Apparatus (Shimadzu) in air atmosphere using a 5 °C min^{-1} ramp without equilibration delay. For supercritical CO_2 activation, the solvent-exchanged MOFs were immersed in liquid CO_2, kept under supercritical CO_2 atmosphere, and then bled using a Tousimis Samdri PVT-3D critical point dryer. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Quantachrome Nova 4200e surface area and pore size analyzer. Before measurement, the samples were degassed in vacuum at room temperature for 12 h. The BET surface areas were determined by multi-point BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05 to 0.30. The crystal photographs were taken with an optical microscope (Olympus DX51).

2.2. Ligand synthesis

Synthesis of 3: 1,4-Dibromo-2,5-dimethoxybenzene (2.00 g, 6.76 mmol), 4-methoxyl carbonylphenyl boronic acid (3.04 g, 16.89 mmol), K_2CO_3 (2 M aqueous solution, 25 mL) and Pd $(PPh_3)_4$ (0.35 g, 3.5 mol%) were added to flask containing THF (50 mL). The reaction mixture was refluxed at 80 °C under N_2 for 15 h. After cooling down, DCM (100 mL) was added and the organic layer was washed with brine and dried over Na_2SO_4. After that, the solvents were evaporated under reduced pressure and the resulting residue was subjected to column chromatography [SiO_2:CH_2Cl_2/petroleum ether (4:1)]. The product **3** was isolated as a white gray solid (1.23 g, 45%, yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ=8.11 (d, J=7.9 Hz, 4*H*), 7.66 (d, J=7.9 Hz, 4*H*), 6.99 (s, 2*H*), 3.95 (s, 6*H*), 3.81 (s, 6*H*). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ=167.0, 150.7, 142.8, 130.0, 129.43, 129.39, 128.8, 114.5, 56.4, 52.1. HR-MS (MALDI): calcd for $C_{24}H_{22}O_6$: 406.1416; found, 406.1411.

Synthesis of 4: 10 mL of BBr_3 was slowly added to a solution of compound **3** (3.0 g) in 50 mL dry DCM under nitrogen atmosphere. The reaction was stirred at room temperature for 48 h. After that, H_2O (100 mL) was added. The precipitate was filtered, washed extensively with H_2O (1 L), and dried under vacuum. Compound **4** was isolated as a green yellow solid (2.5 g, 97%, yield). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 12.93 (s, 2*H*), 9.24 (s, 2*H*), 7.99 (d, J=8.4 Hz, 4*H*), 7.70 (d, J=8.4 Hz, 4*H*), 6.94 (s, 2*H*). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ=167.3, 147.3, 142.7, 129.1, 129.0, 128.8, 127.0, 117.5. HR-MS (ESI): calcd for $C_{20}H_{13}O_6$: 349.0790 $[M-H]^-$; found, 349.0717 $[M-H]^-$.

Synthesis of 5: A solution of compound **4** (253 mg, 0.72 mmol) in dry DMF (20 mL) was treated with potassium carbonate (540 mg, 3.9 mmol) and ally bromide (0.6 mL, 6.94 mmol) under N_2. The resulting reaction mixture was heated at 80 °C for 60 h before H_2O (50 mL) was added. The aqueous solution was extracted with DCM (3 × 50 mL), and the combined extracts were washed with saturated aqueous NaCl (2 × 50 mL), dried (Na_2SO_4) and concentrated in vacuum. The resulting residue was subjected to column chromatography [SiO_2:CH_2Cl_2/petroleum ether (1:1)] and compound **5** was isolated as a white solid (308 mg, 84%, yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ=8.13 (d, J=8.2 Hz, 4*H*), 7.68 (d, J=8.2 Hz, 4*H*), 7.01 (s, 2*H*), 6.18–5.84 (m, 4*H*), 5.55–5.08 (m, 8*H*), 4.86 (d, J=5.6 Hz, 4*H*), 4.51 (d, J=4.9 Hz, 4*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=166.2, 149.9, 142.8, 133.1, 132.3, 130.5, 129.5, 129.4, 128.7, 118.2, 117.2, 116.3, 70.2, 65.6. HR-MS (ESI): calcd for $C_{32}H_{30}O_6$: 533.1935 $[M+Na]^+$; found, 533.1935 $[M+Na]^+$.

Synthesis of 1: In a mixture of 10% NaOH aqueous solution (15 mL), MeOH (15 mL) and THF (15 mL), compound **5** (900 mg, 1.76 mmol) were added. The reaction mixture was refluxed for 6 h. After cooling to room temperature, MeOH and THF were evaporated under reduced pressure. Additional water (20 mL) were added and the mixture was heated until the solid was fully dissolved, then the solution was acidified with diluted HCl until no further precipitate was detected (PH ≈ 2). The precipitate was collected by filtration, washing with water and drying in vacuum. Compound **1** was isolated as a white solid (750 mg, 84%, yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ=13.01 (s, 2*H*), 8.01 (d, J=8.4 Hz, 4*H*), 7.74 (d, J=8.4 Hz, 4*H*), 7.15 (s, 2*H*), 6.22–5.73 (m, 2*H*), 5.39–5.11 (m, 4*H*), 4.62 (d, J=4.8 Hz, 4*H*). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ=167.2, 149.3, 142.1, 133.8, 129.6, 129.4, 129.3, 129.0, 116.7, 115.9, 69.3. HR-MS (ESI): calcd for $C_{26}H_{21}O_6$: 429.1344 $[M-H]^-$; found, 429.1341 $[M-H]^-$.

2.3. MOFs synthesis

Synthesis of UiO-68-allyl: $ZrCl_4$ (19.1 mg), ligand **1** (24.5 mg) and benzoic acid (185 mg) were ultrasonically dissolved in DMF (2 mL) and placed in a preheated 130 °C oven for 24 h. Single crystals in octahedral shape were harvested with yield of ~19 mg. The as-synthesized UiO-68-allyl was rinsed with DMF overnight to remove unreacted starting materials and trapped benzoic acid. After that, the sample was allowed to immerse in anhydrous EtOH for 3 days to exchange and remove DMF. During this period, anhydrous EtOH was freshly exchanged three times per day. The crystal samples were kept in EtOH for further modification. In addition, samples not undergoing subsequent modification were activated with a supercritical CO_2 activation protocol.

Synthesis of UiO-68-SEt: The crystal samples of UiO-68-allyl (~15 mg) was exchanged with THF for 3 times before being placed in a Pyrex glass tube, which was then charged with THF (1.5 mL), ethanethiol (1.5 mL) and 2,2-dimethoxy-2-phenylacetophenone (60 mg) as the photoinitiator. The reaction mixture was degassed, sealed and then irradiated under UV light (365 nm) for 14 h. The resultant solid product of UiO-68-SEt (with little change in appearance from the pristine crystals of UiO-68-allyl) was rinsed DCM for several times and then allowed to immerse in anhydrous