Zr-based metal-organic framework with dual Brønsted acid-base functions

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Abstract. Design and synthesis of metal-organic frameworks (MOFs) with multi-functionality have attracted a lot of attention since the different functional groups can enhance the cooperative effect providing properties superior to those found in mono-functional MOFs. The efficiency and selectivity of the reactions can be improved by the simultaneous activation of multi-functional catalysts. Herein, a series of Brønsted acid-base bifunctional UiO-66 bearing acidic sulfo- and basic amino- functional groups were successfully prepared via a simple one-pot solvothermal method. PXRD patterns of the bifunctional frameworks were similar to that of simulated UiO-66. The existence of sulfo- and amino- functional groups was investigated by IR and H1-NMR. The bifunctional frameworks showed high thermal stability up to 300°C examined by TGA. By varying the molar ratios of ligands, the proportions of acidic and basic moieties in the framework were successfully tuned. The amount of functional groups anchoring in resulting frameworks was determined by 1H-NMR. This bifunctional UiO-66 was tested for CO2 capture.

1. Introduction
Metal-organic frameworks (MOFs), also called porous coordination polymers (PCPs), are porous crystalline solids assembled from metal ions and organic ligands. MOFs have generated considerable interest due to their high surface area, the diverse design for pore sizes and shapes, and the possibility for chemical functionalization [1, 2]. To use MOFs as materials for specific applications, MOFs were functionalized generally in three strategies, e.g., trapping active guests into the framework cavities, modulating metal ions in the framework to obtain coordinatively unsaturated metal sites (CUSs), and employing organic ligands which have pendant functionalized groups [3].

MOFs have been demonstrated in various applications such as gas storage, gas separation, sensing and catalysis [1-3]. CO2 capture using MOFs as adsorbents is one interesting studied area [4]. Many MOFs were investigated for CO2 capture and separation from flue gas mixtures which is released into the atmosphere (1 atm). The CO2 partial pressure (<0.15 atm) is relatively low in such conditions. The strong interaction between CO2 and MOF frameworks is essential to increase the CO2 uptake [4]. Linear CO2 has a permanent electrical quadrupole moment that can enhance strong interactions with polar molecules by the quadrupole-dipole interaction. The introduction of polar functional groups into the frameworks such as amino- (NH2), sulfo- (SO3H), and carboxylic- (COOH) is one promising strategy to increase CO2 and MOF interaction aiming for efficient CO2 capture [5-7]. Amino and amine-derivative functional MOFs have demonstrated a great performance of CO2 capture evaluated.
from the CO₂ heat of adsorption [8-10]. For instance, ethylenediamine, pendant alkylamine species, was incorporated into the CUSs of H₃[(CuCl)₃(BTTri)₈] (H₃BTTri = 1,3,5-tris(1H-1,2,3-triazol-5-yl)benzene). It showed a higher value of the CO₂ heat of adsorption (90 kJ mol⁻¹) compared with a non-functionalized framework (21 kJ mol⁻¹) [8].

Recently, multi-functional MOFs bearing more than one functional group have attracted much attention. Having multi-functional groups in the frameworks can provide synergistic behaviors which contribute to some properties superior to those found in mono-functional MOFs [11]. For example, the catalytic performance of USTC-253–TFA (USTC = University of Science and Technology of China, TFA = trifluoroacacetate), a sulfone functionalized MOF, for the CO₂ cycloaddition of epoxides was investigated [12]. USTC-253-TFA contains different kinds of active sites, i.e., sulfone groups, Brønsted acid from bridging OH groups, and Lewis acid from CUSs (introduced by TFA). TFA has been used to generate structural defects in MOFs causing Lewis acid sites [13-15]. The Lewis acid CUSs and sulfone functional groups exhibit strong interaction with CO₂ molecules. Also, Brønsted and Lewis acid sites were used to activate the epoxides. The cooperative manners of the mentioned functional groups in USTC-253-TFA contributed to improved CO₂ storage capacity at 298 K (64.6 cm³ g⁻¹) compared to un-functional EL-MIL-53 (27.5 cm³ g⁻¹) and sulfone only functional USTC-257 (47.8 cm³ g⁻¹) [12]. Also, USTC-253-TFA exhibited high CO₂ conversion (81.3% with propylene oxide), and catalytic recyclability [12].

In the present work, a series of Brønsted acid-base bifunctional UiO-66 (UiO = University of Oslo) bearing acidic sulfo- and basic amino- functional groups were successfully prepared via a simple one-pot solvothermal method. UiO-66 (Zr₄O₈(OH)₆(1,4-bdc)₈, 1.4-bdc = 1,4-benzenedicarboxylate) is Zr based MOFs assembled from hexanuclear [Zr₄O₈(OH)₆]¹²⁺ metal ions and twelve 1,4-bdc ligands [16]. The three-dimensional framework of UiO-66 possesses two different kinds of cages, a large octahedral cage (pore size of ~12 Å) encompassed with eight smaller tetrahedral cages (pore size of ~8 Å). UiO-66 has many advantages to design and synthesize MOFs for particular applications due to its high thermal and chemical stability [16]. Sulfo- and amino- functional groups were selected because the polar functional groups are expected to interact strongly with CO₂ molecules [5]. Moreover, the presence of such antagonistic acid-base functional groups in the framework aims the study at the synergistic effects of CO₂ capture.

2. Experimental

2.1. Materials

Zirconium (IV) chloride (ZrCl₄, Merck, ≥98%), 2-aminobenzene-1,4-dicarboxylate (NH₂-bdc, TCI, ≥98%), sodium 4-carboxy-2-sulfobenzoate (SO₃Na-bdc, TCI, >98.0%), 1,4-benzenedicarboxylate (1,4-bdc, Sigma-Aldrich, 98%) acetic acid (Sigma-Aldrich, 99.8%), dimethylformamide (DMF, Qrec, 99.8%), and deionized water (d.i. H₂O, 18.2 MΩ).

2.2. Preparation of parent MOFs UiO-66-SO₃H and UiO-66-NH₂

UiO-66-SO₃H was prepared following the previous report [17]. Note that UiO-66-SO₃H consists of mixed ligands: 1,4-bdc and SO₃Na-bdc. 789 mg (3.3 mmol) of ZrCl₄, 122 mg (0.7 mmol) of 1,4-bdc, and 726 mg (2.7 mmol) of SO₃Na-bdc were dissolved into 45 ml of DMF in a 100 ml glass reactor. Then, 10 ml of concentrated acetic acid was added. The mixture was heated at 120°C for 30 h, yielding a white powder. The product was washed three times with DMF and acetone. The resulting solids were activated by water and acetone under refluxing and then dried at 100°C for 5 h in a vacuum oven. The actual mole percent of sulfonic functional groups in UiO-66-SO₃H was 50% as determined by ¹H-NMR.

UiO-66-NH₂ was synthesized by adding 315 mg (1.35 mmol) of ZrCl₄ and 240 mg (1.35 mmol) of NH₂-bdc, 0.02 ml of water and 50 ml of DMF into a 100 ml glass reactor [18]. The mixture was heated at 120°C for 24 h, resulting in a yellow powder. The product was washed three times with DMF and
acetone. The resulting powder was activated in refluxing water and then dried at 100°C for 5 h in a vacuum oven.

2.3. Preparation of UiO-66-SO$_3$H-NH$_2$

A series of UiO-66-SO$_3$H-NH$_2$ were synthesized by dissolving 466 mg (2 mmol) of ZrCl$_4$, various molar ratios of SO$_3$Na-bdc and NH$_2$-bdc in 38 ml of DMF. Then, 8 ml of concentrated acetic acid was added. The molar ratios of SO$_3$H-bdc and NH$_2$-bdc were denoted as UiO-66-(x)SO$_3$H-(100-x)NH$_2$, where x was the mole percent of SO$_3$H-bdc. The amounts of SO$_3$Na-bdc and NH$_2$-bdc linkers were varied for UiO-66-(25)SO$_3$H-(75)NH$_2$ = 134 mg (0.5 mmol) of SO$_3$Na-bdc, 270 mg (1.5 mmol) of NH$_2$-bdc, UiO-66-(50)SO$_3$H-(50)NH$_2$ = 268 mg (1 mmol) of SO$_3$Na-bdc, 180 mg (1 mmol) of NH$_2$-bdc, and UiO-66-(75)SO$_3$H-(25)NH$_2$ = 402 mg (1.5 mmol) of SO$_3$Na-bdc, 90 mg (0.5 mmol) of NH$_2$-bdc. The mixtures were heated at 120°C for 30 h obtaining a pale-yellow powder. The product was washed three times with DMF and acetone. The resulting solids were activated in refluxing water and dried at 100°C for 5 h in a vacuum oven.

2.4. Characterizations

The powder X-ray diffraction (PXRD) patterns were obtained from a Bruker D8 Advance X-ray powder diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at a scan rate of 0.02 deg s$^{-1}$. Thermogravimetric analysis (TGA) experiments were examined by a Linseis STA PT1600 under nitrogen gas with a flow rate of 100 cm$^3$ min$^{-1}$. The samples were heated at the rate of 5°C min$^{-1}$ up to 700°C. Quantitative analysis of linker was measured by proton nuclear magnetic resonance (H-NMR) using a Bruker Advance III HD (600 MHz). Before $^1$H-NMR measurement, 20 mg of MOF was digested in 600 μL of a 1 M NaOH-D$_2$O solution [19]. Attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) were recorded on a Perkin Elmer Universal-ATR. The samples were measured over the wavenumber range 400—4000 cm$^{-1}$ with 4 cm$^{-1}$ resolution and 32 scans. CO$_2$ sorption isotherms of the parent UiO-66 and the bifunctional frameworks measured at 298 K were obtained from a BELSORP-mini II. Before gas sorption measurement, MOF samples were activated again at 100°C for 5 h under vacuum conditions.

3. Results and discussion

Structure and purity of UiO-66-SO$_3$H-NH$_2$ samples with various ligand ratios were confirmed by PXRD analysis. The PXRD patterns of UiO-66-(25)SO$_3$H-(75)NH$_2$, UiO-66-(50)SO$_3$H-(50)NH$_2$, and UiO-66-(75)SO$_3$H-(25)NH$_2$ were similar to that of the simulated parent UiO-66 as shown in Figure 1 [16]. The results indicated that all synthesized UiO-66-SO$_3$H-NH$_2$ frameworks shared the same structure with the parent UiO-66.

![Figure 1. PXRD patterns of simulated UiO-66 (black), as-synthesized UiO-66-(25)SO$_3$H-(75)NH$_2$ (red), UiO-66-(50)SO$_3$H-(50)NH$_2$ (blue), and UiO-66-(75)SO$_3$H-(25)NH$_2$ (green).](image-url)
The coexisting of SO$_3$H-bdc and NH$_2$-bdc in UiO-66-SO$_3$H-NH$_2$ was determined by IR and $^1$H-NMR. Figure 2 shows the IR spectrum of UiO-66-(50)SO$_3$H-(50)NH$_2$ which presented the characteristic stretching peaks of N-H (primary amine) at 3471 and 3358 cm$^{-1}$, O=S=O at 1253 and 1167 cm$^{-1}$ and S-O at 1074 and 1024 cm$^{-1}$ [17, 20, 21]. These results confirmed the existence of acid and base functional groups in the bifunctional frameworks.

![Figure 2. IR spectrum of as-synthesized UiO-66-(50)SO$_3$H-(50)NH$_2$ possessing sulfo- and amino-functional groups.](image)

The $^1$H-NMR spectra of the digested UiO-66-SO$_3$H-NH$_2$ in NaOH/D$_2$O solution also confirmed the coexistence of acidic SO$_3$H-bdc and basic NH$_2$-bdc ligands as shown in Figure 3. The proportions of acid and base moieties in the bifunctional frameworks were successfully tuned. The SO$_3$H-bdc and NH$_2$-bdc peaks of all UiO-66-SO$_3$H-NH$_2$ samples were measured to calculate the actual percentages of acid and base moieties in each bifunctional framework. Table 1 presents percentages of SO$_3$H functions from the molar ratio of ligands and $^1$H-NMR results after synthesis. The $^1$H-NMR results show that all bifunctional frameworks have slightly less percentage of acidic moieties than the original molar ratio of ligands.

![Figure 3. $^1$H-NMR spectra of as-synthesized UiO-66-(25)SO$_3$H-(75)NH$_2$ (red), UiO-66-(50)SO$_3$H-(50)NH$_2$ (green), and UiO-66-(75)SO$_3$H-(25)NH$_2$ (blue).](image)
Table 1. The percentages of SO$_3$H-bdc from the molar ratio of ligands at preparation and $^1$H-NMR results of UiO-66-(25)SO$_3$H-(75)NH$_2$, UiO-66-(50)SO$_3$H-(50)NH$_2$, and UiO-66-(75)SO$_3$H-(25)NH$_2$.

| MOF                      | The percentage of SO$_3$H-bdc | Molar ratio of ligands | $^1$H-NMR results |
|--------------------------|-------------------------------|------------------------|-------------------|
| UiO-66-(25)SO$_3$H-(75)NH$_2$ | 25                            | 25                     | 17                |
| UiO-66-(50)SO$_3$H-(50)NH$_2$   | 50                            | 50                     | 41                |
| UiO-66-(75)SO$_3$H-(25)NH$_2$   | 75                            | 75                     | 68                |

Thermal stability of UiO-66-(50)SO$_3$H-(50)NH$_2$ was examined by TGA. Figure 4 shows the TGA profile with two steps of weight loss. In the first step, the weight loss of 23.3% for temperatures up to 225 °C corresponded to the evaporation of the water solvent. The second weight loss starting from 300 °C was due to the decomposition of the framework. This result confirmed that the bifunctional framework was thermally stable up to 300°C.

![TGA profile](image)

**Figure 4.** TGA of UiO-66-(50)SO$_3$H-(50)NH$_2$ which has thermal stability up to 300°C.

The UiO-66-SO$_3$H-NH$_2$ frameworks were tested for CO$_2$ capture. Figure 5 and Table 2 show CO$_2$ sorption isotherms and storage capacity of UiO-66-NH$_2$, UiO-66-SO$_3$H (50% of sulfonic groups), UiO-66-(25)SO$_3$H-(75)NH$_2$, UiO-66-(50)SO$_3$H-(50)NH$_2$, and UiO-66-(75)SO$_3$H-(25)NH$_2$ at 298 K. UiO-66-NH$_2$ exhibited CO$_2$ storage capacity of 43 cm$^3$ g$^{-1}$, lower than reported in the literature (c.a. 67 cm$^3$ g$^{-1}$) [22]. UiO-66-(25)SO$_3$H-(75)NH$_2$ showed the highest CO$_2$ storage capacity (57 cm$^3$ g$^{-1}$) while UiO-66-SO$_3$H exhibited the lowest capacity (14 cm$^3$ g$^{-1}$).
Figure 5. CO$_2$ sorption isotherms at 298 K, adsorption (filled circles) and desorption (open circles) of UiO-66-SO$_3$H (blue), UiO-66-NH$_2$ (black), UiO-66-(25)SO$_3$H-(75)NH$_2$ (pink), UiO-66-(50)SO$_3$H-(50)NH$_2$ (green), and UiO-66-(75)SO$_3$H-(25)NH$_2$ (red).

Table 2. CO$_2$ storage capacity of UiO-66-SO$_3$H, UiO-66-NH$_2$, UiO-66-(25)SO$_3$H-(75)NH$_2$, UiO-66-(50)SO$_3$H-(50)NH$_2$, and UiO-66-(75)SO$_3$H-(25)NH$_2$ at 298 K.

| MOF                      | CO$_2$ storage capacity (cm$^3$ g$^{-1}$) |
|--------------------------|------------------------------------------|
| UiO-66-SO$_3$H            | 14                                       |
| UiO-66-NH$_2$             | 43                                       |
| UiO-66-(25)SO$_3$H-(75)NH$_2$ | 57                                       |
| UiO-66-(50)SO$_3$H-(50)NH$_2$ | 21                                       |
| UiO-66-(75)SO$_3$H-(25)NH$_2$ | 26                                       |

4. Conclusion
A series of Brønsted acid-base bifunctional UiO-66 MOFs carrying acidic sulfo- and basic amino functional groups were successfully synthesized via a one-pot solvothermal procedure. PXRD results confirmed that the structures of the bifunctional frameworks shared the same structure as the parent UiO-66. The existence of sulfo- and amino- ligands in the bifunctional frameworks was examined by IR and $^1$H-NMR. The proportions of acid and base moieties were successfully tuned by changing molar ratios of the ligands before synthesis. TGA analysis showed the bifunctional framework had high thermal stability up to 300°C. The bifunctional UiO-66 with ~17% of SO$_3$H (25% original molar ratio) showed improvement of CO$_2$ storage capacity compared with the parent MOFs, acidic and basic UiO-66.
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