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Synthesis of Secondary and Tertiary Amine-Containing MOFs: C-N Bond Cleavage during MOF Synthesis

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Secondary and tertiary amine-containing metal-organic frameworks (MOFs) have been synthesized, and unprecedented C-N bond cleavage phenomena were observed during MOF formation. Utilizing the secondary amine-containing ligand (BDC-NHMe), three new MOFs have been prepared, two of which are zinc(II)-based, IRMOF-NHMe(IRMOF = isoreticular MOF) and DMOF-1-NHMe(DMOF = dabco MOF), in addition to the zirconium(IV)-based UiO-66-NHMe (UiO = University of Oslo). The tertiary amine-containing ligand (BDC-NMe_2) was converted to the secondary amine-containing ligand (BDC-NHMe) during both IRMOF and UiO-66 synthesis conditions, indicating an *in situ* C-N bond cleavage of ligand during MOF formation. In contrast, the tertiary amine-containing DMOF-1-NMe_2 was successfully synthesized and studied for CO_2 adsorption experiments.

Introduction

Metal-organic frameworks (MOFs) are organic-inorganic hybrid materials constructed by the combination of a metal ion or cluster and organic linker molecules. Various applications of MOFs have been developed utilizing their high porosity, thermal stability, and structural diversity for gas storage,[1,2] gas separation,[3] sensor,[4] and catalysis.[5] Indeed, the organic linker of MOFs can be modified with a variety of organic functional groups, such as an amino group (NH_2), halogens (F, Cl, Br, I), alkyl ether chains, etc.[6] Among them, the amino group has been widely used for the synthesis of functional group-containing MOFs. Amino groups are polar and have Lewis basic characteristics due to the lone pair of electrons on the nitrogen atom. Additionally, the N-H bond can form hydrogen bonds or be used for various organic transformations such as conversions to amides or azido groups.[6]

Once the amino group has been successively introduced into the MOF pore, it can undergo solid-state functionalization methods. The Cohen group demonstrated the postsynthetic modification (PSM) strategy to introduce a series of amide moiety into MOF pores, starting from a single, homogeneous, aminated MOF material, in a solid-state manner.[7] Subsequently, this PSM technique, starting from the amino group, has been widely used for introducing various new functional groups into the MOF pores. To highlight a few, metal-binding groups and fluorescence probe molecules have been successively incorporated into MOF pores using amide and urea groups.[8,9] Additionally, imine groups have been introduced into MOF pores using a PSM technique.[10-12] Although chemical transformations of amines have been intensively explored, the properties of the amino group itself, inside the MOF pores, and direct alkylation of amines are rarely studied.

In 2012, both the Stock and Wang groups independently reported direct and postsynthetic routes for the methylation of amino groups inside MOFs.[13,14] During the synthesis of the aluminium-based MOF, CAU-1-NH_2, the methylation of BDC-NH_2 (BDC = 1,4-benzene dicarboxylic acid) was observed. Methanol was used as a solvent for the CAU-1-NH_2 synthesis, and it was also the methylation reagent of the amino groups. Interestingly, the percent of methylation was controlled via reaction conditions and vessel choice. The mono-methylated ligand, secondary amino group (BDC-NHMe), was incorporated into CAU-1-NH_2 using a microwave-assisted synthesis in a teflon-lined steel autoclave with 12% conversion. By changing the reaction vessel to a glass autoclave, 52% of mono-methylated, secondary amino group (BDC-NHMe) and 22% of di-methylated, tertiary amino group (BDC-NMe_2) was observed by ^{1}H NMR analysis. The Stock group revealed that the amino group could also be methylated during the MOF formation and, depending on the solvothermal conditions, affected the ratio of methylation.[13]

In contrast, the Wang group performed methylation of the amino group in a definite PSM fashion. NH_2-functionalized

zinc-based IRMOF-3 (IRMOF = isoreticular metal-organic framework) was synthesized and treated with iodomethane for 4 days at room temperature to effect the methylation reaction. FT-IR spectrum of the methylated material suggested that quaternary ammonium salts were synthesized by this postsynthetic treatment. The ratio of functionalization was reported using iodine content, and not determined by ^{1}H NMR analysis.[14]

The secondary amine-containing MOF syntheses were also achieved through a PSM type imine reduction,[10] ring-opening of aziridine,[15] and benzylation of the amine.[16] In these studies, the conversion or degree of methylation was difficult to control. In this contribution, we synthesized the secondary and tertiary amine-containing 1,4-benzene dicarboxylic acid ligands (BDC-NHMe and BDC-NMe_2) and utilized them in various amine-containing MOF syntheses to systematically explore the differences between these molecules when incorporated into MOFs.

Experimental methods

General

Concentration of solution was carried out by using a rotary evaporator with a water aspirator, and generally followed by removal of residual solvents on a vacuum line held at 0.1–1 torr. Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on FT AM 400 or 500 (400 MHz or 500 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, J, were reported in Hertz unit (Hz). Carbon 13 nuclear magnetic resonance spectroscopy (^{13}C NMR) was recorded on FT AM 400 or 500 (100 MHz or 125 MHz) and was fully decoupled by broad band decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-d and a septet at 39.52 ppm of DMSO-d_6.

Ligand synthesis

*Dimethyl-2-(methylamino)terephthalate **(1)***: Dimethyl-2-aminoterephthalate (1 g, 5 mmol) and potassium carbonate (2.07 g, 15 mmol), dimethyl sulfate (1.4 mL, 15 mmol) were dissolved in acetone (15 mL). The mixture was stirred under reflux condition (60 ^{o}C) for overnight. Once conversion was complete (by TLC), the solvent was evaporated. And then water was added to dissolve all of the inorganic salt. The solution was three times extracted with ethyl acetate. The solution was then dried using $MgSO_4$, filtered, and evaporated of ethyl acetate. The solid mixture was separated by silica gel column chromatography (10% EtOAc/n-Hexane) and the desired compound, dimethyl 2-(methylamino)terephthalate (**1**, 560 mg, 50%), were obtained as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 7.93 (1H, d, J = 8.3 Hz), 7.35 (1H, d, J = 1.5 Hz), 7.21 (1H, dd, J = 8.3, 1.6 Hz), 3.91 (s, 3H), 3.89 (s, 3H), 2.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 168.6, 167.0, 151.5, 135.3, 131.8, 115.2, 113.4, 112.4, 52.4, 51.9, 29.9. ESI-MS(+) m/z calcd. For $C_{11}H_{14}NO_4$ $[M+H]^+$: 224.0917, found $[M+H]^+$: 224.0917.

*Dimethyl-2-(dimethylamino)terephthalate **(2)***: Sodium hydride (1 g of 60% suspension in oil, 25 mmol) was washed with hexanes and suspended in DMF (2.5 mL) at 0 ^{o}C under nitrogen atmosphere. A solution of **1** (1.12 g, 5 mmol) in DMF (5 mL) was then added drop-wise and the reaction mixture was stirred at 0 ^{o}C for 1 h. Methyl iodide (1.6 mL, 25 mmol) was then added and stirring continued at room temperature for 4 h. The reaction was quenched by addition of water and the resulting mixture was extracted with EtOAc. The organic phase was washed with brine. The solution was then dried using $MgSO_4$, filtered, and evaporated of ethyl acetate. The solid mixture was separated by silica gel column chromatography (10% EtOAc/n-Hexane) and the desired compound, dimethyl 2-(dimethylamino)terephthalate (**2**, 1.07 g, 90%), were obtained as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 7.70 (1H, d, J = 8.0 Hz), 7.68 (1H, s), 7.53 (1H, dd, J = 8.0, 1.1 Hz), 3.93 (s, 3H), 3.92 (s, 3H), 2.92 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 168.7, 166.9, 152.0, 133.3, 131.6, 124.5, 119.2, 117.8, 52.4, 43.5, 29.8. ESI-MS(+) m/z calcd. For $C_{12}H_{16}NO_4$ $[M+H]^+$: 238.1074, found $[M+H]^+$: 238.1074.

*2-(Methylamino)terephthalic acid **(3)***: **1** (558 mg, 2.5 mmol) was dissolved in 12.5 mL of THF. To this, 12.5 mL of a 4% KOH aqueous solution was added drop-wise. The mixture was stirred under reflux condition (66 ^{o}C) for 3 h. Once conversion was complete (by TLC), THF was removed by evaporation and the mixture was acidified with a 1.0 M HCl aqueous solution. The precipitate was collected by filtration, and washed with water. The desired compound was obtained by air drying (**3**, 460 mg, 93%) as a yellow solid.

^{1}H NMR (DMSO-d_6, 400MHz, ppm.): δ 7.86 (1H, d, J = 8.2 Hz), 7.21 (1H, d, J = 1.4 Hz), 7.09 (1H, dd, J = 8.2, 1.5 Hz), 2.87 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 169.5, 167.3, 151.4, 135.9, 132.0, 114.4, 113.2, 111.5, 29.3 . ESI-MS(+) m/z calcd. For $C_9H_{10}NO_4$ $[M+H]^+$: 196.0604, found $[M+H]^+$: 196.0604.

*2-(Dimethylamino)terephthalic acid **(4)***: **2** (475 mg, 2 mmol) was dissolved in 10 mL of THF. To this, 10 mL of a 4% KOH aqueous solution was added drop-wise. The mixture was stirred under reflux condition (66 ^{o}C) for 3 h. Once conversion was complete (by TLC), THF was removed by evaporation and the mixture was acidified with a 1.0 M HCl aqueous solution. The solution was stored overnight in a refrigerator. The precipitate

was collected by filtration, and washed with water. The desired compound was obtained by air drying (**4**, 300 mg, 71%) as a pale yellow solid.
^{1}H NMR (DMSO-d_6, 400 MHz, ppm.): δ 8.03 (1H, d, J = 1.4 Hz), 7.95 (1H, d, J = 8.0 Hz), 7.76 (1H, dd, J = 8.0, 1.5 Hz), 2.9 (s, 6H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 167.2, 166.4, 150.3, 134.9, 131.0, 127.3, 125.0, 121.0, 39.5. ESI-MS(+) m/z calcd. For $C_{10}H_{12}NO_4$ $[M+H]^+$: 210.0761, found $[M+H]^+$: 210.0761.

MOF synthesis

IRMOF-3-NHMe: **4** (16 mg, 0.082 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (65 mg, 0.22 mmol) were dissolved in 2 mL of DMF. The solution was then transferred to a scintillation vial and heated at a rate of 2.5 °C/min from room temperature to 100 °C. The temperature was then held for 18 h and then cooled to room temperature at a rate of 2.5 °C/min. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with chloroform (5 mL) over three days, replacing the old chloroform with fresh chloroform every 24h.

UiO-66-NHMe: **4** (68 mg, 0.35 mmol) and $ZrCl_4$ (82 mg, 0.35 mmol) and DMF (4 mL) were placed in a Teflon lined autoclave and heated at 120 °C for 24 h. The microcrystalline powders were then isolated by centrifugation and residual DMF and ligand precursors were removed from the material by washing with 10 mL DMF three times. Then the solid was soaked with fresh 10 mL methanol. This process was repeated for three days.

DMOF-1-NHMe: **4** (98 mg, 0.5 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (149 mg, 0.5 mmol) were dissolved in 12.5 mL of DMF. To this mixture, dabco (90 mg, 0.8 mmol) was added. Upon adding, a white precipitate formed. This precipitate was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a scintillation vial and heated at a rate of 1 °C/min from room temperature to 100 °C. The temperature was then held for 12 h and then cooled to room temperature at a rate of 1 °C/min. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with chloroform (5 mL) over three days, replacing the old chloroform with fresh chloroform every 24 h.

DMOF-1-NMe$_2$: **5** (105 mg, 0.5 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (149 mg, 0.5 mmol) were dissolved in 12.5 mL of DMF. To this mixture, dabco (90 mg, 0.8 mmol) was added. Upon adding, a white precipitate formed. This precipitate was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a scintillation vial and heated at a rate of 2.5 °C/min from room temperature to 100 °C. The temperature was then held for 12 h and then cooled to temperature at a rate of 2.5 °C/min. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with chloroform (5 mL) over three days, replacing the old chloroform with fresh chloroform every 24 h.

MOF Characterization

Digestion and Analysis by ^{1}H NMR of IRMOF-3 and DMOF-1 Series: Approximately 10 mg of IRMOF-3 or DMOF-1 material was dried under vacuum and digested with sonication in 590 μL of DMSO-d_6 and 10 μL of DCl.

Digestion and Analysis by ^{1}H NMR of UiO-66 Series: Approximately 10 mg of UiO-66 material was dried under vacuum and digested with sonication in 500 μL of CD_3OD-d_4, 85 μL of DMSO-d_6 and 15 μL of HF (48% aqueous solution).

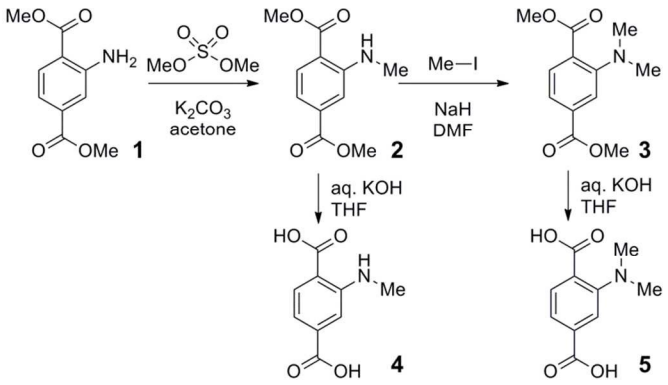
Thermal Analysis: Approximately 10 mg of DMOF was used for TGA measurements, after BET analysis (activated). Sample was analyzed under a stream of N_2 using a TGA/DSC 1 running from room temperature to 1000 °C with a scan rate of 10 °C/min.

Powder X-ray Diffraction: Approximately 10 mg of IRMOF, UiO-66 or DMOF-1 was air-dried for 1 min prior to PXRD analysis. PXRD data was collected at ambient temperature on a Bruker D8 Discover at 40 kV, 40 mA for CuKa (1 = 1.5406 Å), with a scan speed of 1 sec/step, a step size of 0.02° in 2θ, and a 2θ range of 5-55°.

BET Surface Area Analysis: Approximately 30-50 mg of DMOF-1 sample was evacuated under vacuum for a moment at room temperature. Samples were transferred to a pre-weighed sample tube and degassed at room temperature on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 μmHg/min. The sample tube was re-weighted to obtain a consistent mass for the degassed MOF materials. BET surface area (m^2/g) measurements were collected at 77K by N_2 on a Micromeritics ASAP 2020 Adsorption Analyzer using a volumetric technique.

Result and Discussion

Methylation of the amino group was undertaken starting from dimethyl-2-amino terephthalate (**1**) and using dimethyl sulfate as the methylation reagent. Dimethyl-2-(methylamino) terephthalate (**2**) was obtained in 50% yield. Although iodomethane demonstrated very low conversion, in comparison to dimethyl sulfate, for the first methylation, the second methylation was successively achieved using an excess of iodomethane. Dimethyl-2-(dimethylamino) terephthalate (**3**) was obtained, in 90% yield, by using sodium hydride as the base. The desired BDC ligands were synthesized by hydrolysis of **2** and **3** (BDC-NHMe (**4**, 93%), BDC-NMe$_2$ (**5**, 71%), Scheme 1).



Scheme 1 Preparation of secondary and tertiary amino group-containing BDC ligands.

Using both secondary and tertiary amine-containing ligands, syntheses of IRMOF, DMOF and UiO-66 (DMOF = Dabco MOF, UiO = University of Oslo, dabco = 1,4-diazabicyclo[2,2,2]octane) were carried out (Scheme 2). IRMOF is one of the most well-known MOF materials with the empirical formula $Zn_4O(BDC)_3$. IRMOF-3-NHMe and IRMOF-3-NMe_2 were synthesized by combining the amino BDC ligand **4** or **5** with $Zn(NO_3)_2$ in *N*,*N*-dimethylformamide (DMF) and heating the mixture to 100 °C or 120 °C for 18 h. Block shaped yellow crystals were obtained from the solvothermal synthesis and were shown to possess the same lattice parameters as IRMOF-3 as evidenced by power X-ray diffraction (PXRD and Figure S1†).[7] However, ^{1}H NMR spectra analysis, after acid digestion of the MOFs, indicates that the tertiary amino group had been converted to the secondary amino group (80%, Table 1, and Figure S2†). Since ligand **5** remained intact after exposure to the acid digestion, we assumed that C-N bond dissociation must have occurred during the solvothermal synthesis. Importantly, the C-N bond in ligand **4** (*i.e.,* C-N bond in the secondary amine) was unaltered and had not demethylated to the starting BDC-NH_2 ligand. In this synthetic condition, only the tertiary amine was demethylated back to a secondary amine. Alkyl groups, such as a methyl substituent, should provide an electron-donating effect. We attribute the differences in the C-N bond cleavage to the difference in nucleophilicity of the nitrogen atom of the amine or amide and the impact this has on the zinc-mediated C-N bond cleavage during solvothermal synthesis.

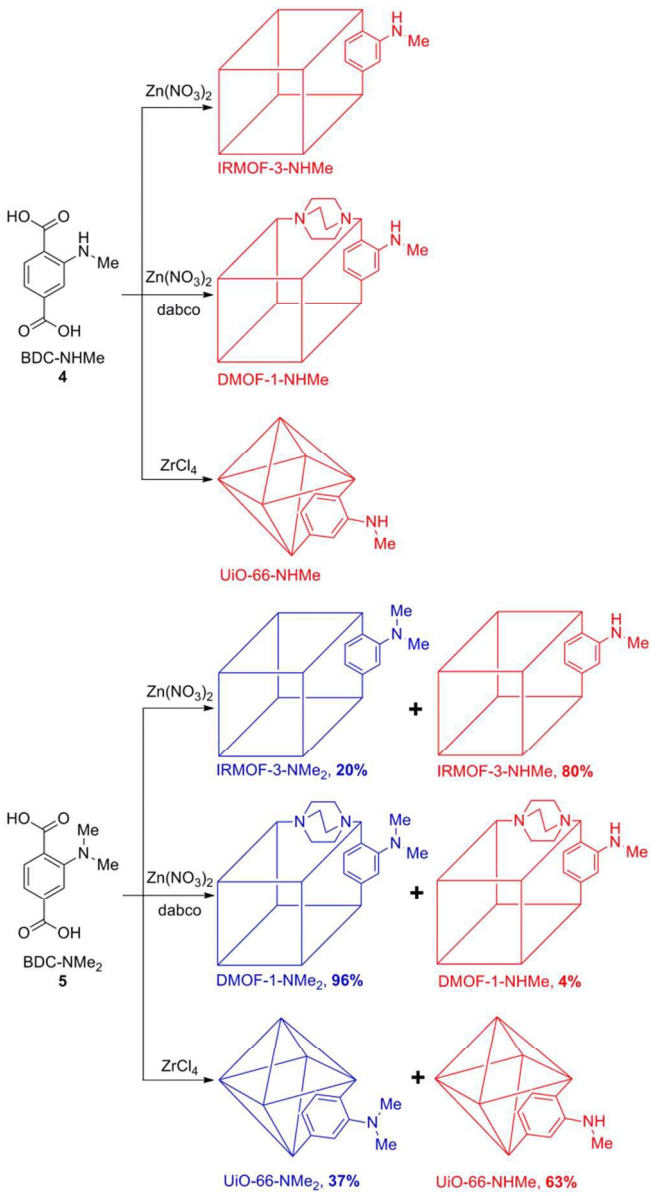
Table 1 C-N bond cleavage ratio during MOF synthesis using BDC-NMe_2 ligand[a]

Entry	MOF	Condition	Ratio of ligand (%)	
			BDC-NMe_2	BDC-NHMe
1	IRMOF-3	120 °C, 18 h	20	80
2	UiO-66	120 °C, 24 h	37	63
3	DMOF-1	100 °C, 12 h	96	4
4	DMOF-1	120 °C, 12 h	92	8
5	DMOF-1	120 °C, 72 h	84	16

[a] Ratio was determined by 1H NMR analysis after digestion of the materials, and is reported as an average from two independent samples.

The cleavage between a C-N bond is a useful organic transformation to build new C-C architectures or introduce free amine/amide functional groups.[17-23] Several synthetic methods of amine C-N bond cleavage have been reported including late transition metal-catalyzed conditions such as ruthenium,[24-26] iron,[27,28] and copper.[29,30] Thus, to obtain mechanistic clues, the detailed C-N bond cleavage using zinc was carried out. When the tertiary amine-containing carboxylic ester ligand **3** was treated with 10 mol% of $Zn(NO_3)_2$ in DMF and stirred at 120 °C for 18 h (identical conditions to the IRMOF synthesis), only trace amount of C-N bond cleavage was detected by TLC. Thus, we concluded that the 80% of C-N bond cleavage seen had occurred because of more than just the presence of a zinc salt in solvothermal conditions. Moreover, similar selectivity was reported in the late-transition metal catalytic systems. In several cases, only tertiary amines were converted to secondary amine and no conversion was observed for secondary amine moieties.

A different metal salt based MOF (zirconium) was also attempted with the tertiary amine-containing ligand in the MOF synthesis. The UiO-66 series also showed a similar C-N bond cleavage of the tertiary amine during the synthesis. UiO-66-NHMe and UiO-66-NMe_2 were synthesized following a previously reported UiO-66-NH_2 synthesis,[31] and PXRD displayed a high degree of crystallinity and indicated that they contained the same topology of new materials (Figure S3†). However, ^{1}H NMR analysis after HF digestion indicated that 63% (Table 1) of the tertiary e were converted to the secondary amine during UiO-66-NMe_2 synthesis. UiO-66-NHMe was successively formed without C-N bond cleavage (Scheme 2 and Figure S4†).



Scheme 2 Synthesis of the secondary and tertiary amino group-containing MOFs.

DMOF-1 is another widely studied zinc(II)-based MOF, which has a paddle-wheel type secondary building unit (SBU).[32] DMOF-1-NH_2 has also been studied for various amide formation using PSM and is synthesized by combining BDC and dabco ligands with $Zn(NO_3)_2$ in a DMF solution followed by heating at 120 °C for 12 h.[26] Both the new DMOF-1-NHMe and DMOF-1-NMe_2 were readily obtained under solvothermal conditions as evidenced by PXRD (Figure 1). The ^{1}H NMR spectra analysis after acid digestion of the MOFs show that both amine-containing ligands and dabco were present in both DMOF-1 samples with the ratio between the BDC and dabco ligands confirmed to be 2:1 in each case (Figure 2 and S5†). Importantly, the tertiary amine could be successfully incorporated into DMOF-1 with over 96% of ligands being unaltered. Only 4% of C-N bond cleavage was observed by ^{1}H NMR after digestion (Table 1). The ratio of C-N Bond cleavage could be increased by elongating the reaction time and increasing the synthesis temperature. Around 16% of the tertiary amines were converted to the secondary amines at 120 °C after 72 h (Table 1 and Figure S5†). Since the only difference between IRMOF and DMOF synthetic conditions is the addition of a 'basic' dabco ligand, we assumed that the acidity of mixture solution is a major factor for metal-mediated C-N bond cleavage reaction. Litmus paper indicated that the solution of DMOF is less acidic than in the case of IRMOF or UiO-66(Figure S6†). The acid effect on transition metal-catalyzed C-N bond cleavage reactions have been studied with both amines and amides.[33,34] In the C-N bond cleavage of amines, the existing H^+ in solution could accelerate the protonation of the secondary amine products. Indeed, the BDC-NMe_2 ligand needs to bind first with the metal center for C-N bond cleavage to occur and the dabco ligand could in competition to create metal-nitrogen bonding and coordination complexes.

Thermogravimetric analysis (TGA) also verified the composition and thermal stability of the new MOFs (Figure S7†). Finally, Brunauer-Emmett-Teller (BET) surface area measurements, obtained from N_2 adsorption isotherms (Figure 3), confirmed the high porosity of these DMOF-1 derivatives. In this study, the non-methylated DMOF-1-NH_2 has a BET surface area of 1295 m^2/g which is well matched with previously reported number by Cohen et al. (1510 m^2/g).[35] As expected, introducing one or more methyl groups decreases the BET surface area since the accessible surface area should be diminished. Surface areas of 995 and 951 m^2/g BET were confirmed for DMOF-1-NHMe and DMOF-1-NMe_2, respectively. In the N_2 adsorption isotherm, a small hysteresis at $P/P_0 > 0.5$ could be attributed to capillary condensation within mesoscale features or the presence of crystal defects (Figure 3).[36-38] These phenomena were also observed in DMOF-1, DMOF-1-NH_2, and amide-containing DMOF series.[38]

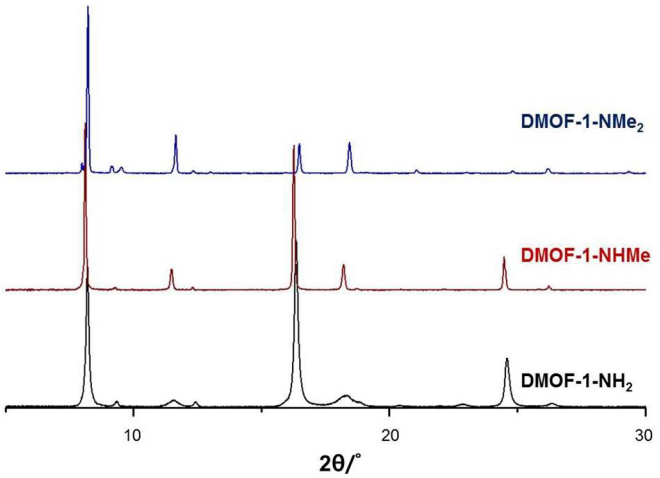


Figure 1 PXRD patterns and ^{1}H NMR spectra of DMOF-1-NH_2, -NHMe and -NMe_2.

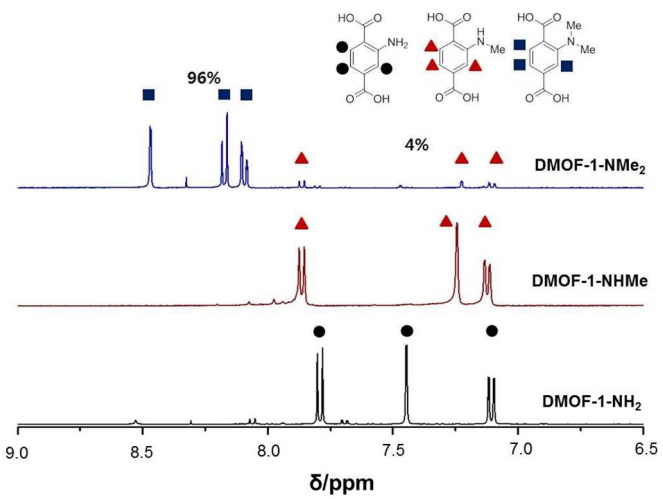


Figure 2 ^{1}H NMR spectra of DMOF-1-NH_2, -NHMe and -NMe_2.

Altering the degree of alkylation potentially affected the nucleophilicity of the nitrogen atom of the amino groups so we investigated the carbon dioxide adsorption of both secondary and tertiary amine-containing DMOFs at 298 K (Figure 4). Approximately, 3.14 mmol of CO_2 was captured by 1 g of DMOF-1-NHMe and 2.48 mmol of CO_2 for DMOF-1-NMe_2, which is 9% and 28% lower than parent MOF (DMOF-1-NH_2, 3.44 mmol/g). For DMOF-1-NHMe, while 23% of the surface area was decreased, only 9% of its CO_2 capturing ability was reduced. It was hypothesized that by introducing a variable nucleophilic moiety into a MOF pore could affect its capability for gas sorption, however, the surface area and pore size seem to have more significant effects on the CO_2 adsorption.

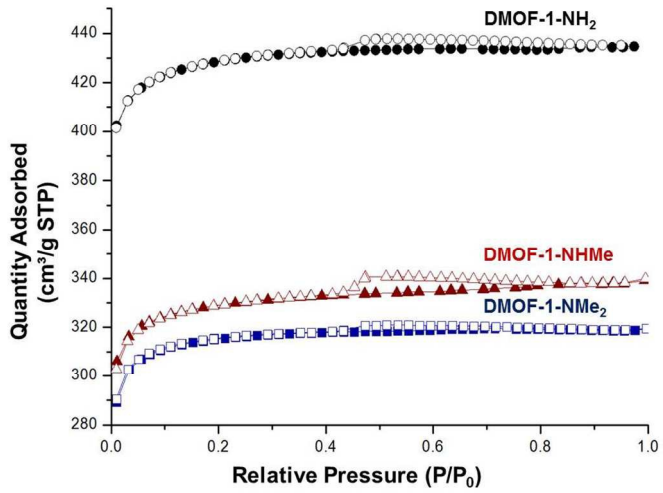


Figure 3 N_2 isotherms (77 K) of DMOF-1-NH_2 (circle, black), -NHMe (triangle, red) and -NMe_2 (square, blue). Adsorption and desorption traces are indicated by filled and open symbols, respectively.

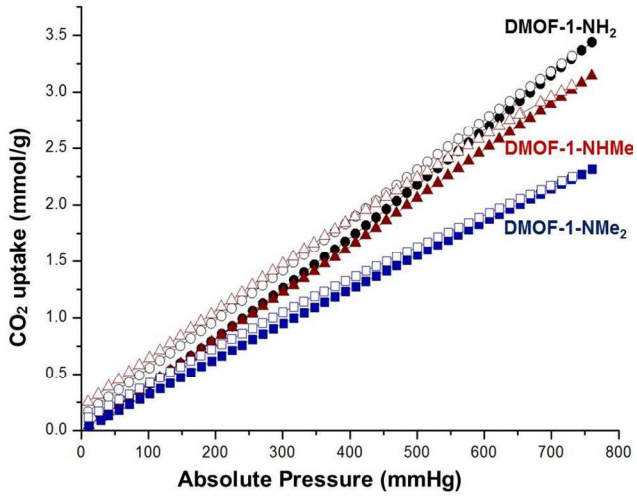


Figure 4 CO_2 isotherms (298 K) of DMOF-1-NH_2 (circle, black), -NHMe (triangle, red) and -NMe_2 (square, blue). Adsorption and desorption traces are indicated by filled and open symbols, respectively.

Conclusions

In conclusion, we synthesized secondary and tertiary e-containing BDC ligands and exposed them to a variety of MOF syntheses to control the nucleophilicity of the amine functional group within the MOF pores. The N-CH_3 bond of the tertiary amine largely dissociated in solvothermal MOF synthetic conditions. The ratio of C-N bond cleavage depended on the metal salt, reaction time and temperature. In contrast, the secondary amino group was fully retained in IRMOF, UiO-66 and DMOF-1 syntheses. Surprisingly, the tertiary amine was successfully incorporated into DMOF-1. DMOFs containing either secondary or tertiary amino groups were fully characterized with PXRD, TGA, ^{1}H NMR after digestion, and gas adsorption. Our study indicates that the nucleophilicity of functional groups may be an important parameter in enhancing interactions between the framework and guest molecules and also in the preparation of new materials.

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† Electronic supplementary information (ESI) available: Detailed synthetic procedures and characterization of ligands and materials. Fig. S1–S8, For ESI other electronic format see DOI:

‡ H. Hahm and H. Ha are equally contributed to this work.

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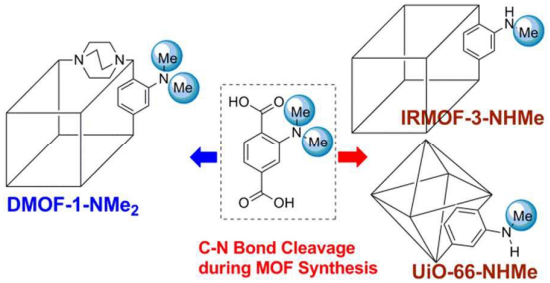

The secondary and tertiary amine-containing MOFs have been synthesized, and interesting C-N bond cleavage of amine was revealed during MOF synthesis.