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Synthesis, characterization and CO₂ adsorption studies of DABCO based pillared Zn-BDC and Co-BDC metal organic frameworks

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Abstract

This study focuses on pre-synthetic functionalized MOF material normally known as pillared layer MOFs. An additional component DABCO (1,4-diazabicyclo[2.2.2] octane) is added to the MOFs which works as a pillar to produce 3D structured MOFs. Zn-BDC-DABCO and Co-BDC-DABCO were studied for their performance in CO₂ capture application. The addition of DABCO turns the 2D-layered metal-BDC lattice into a 3D structure with enhanced performance for CO₂ capture. The MOFs were characterized using XRD, SEM, TGA, FTIR, and BET, and the CO₂ capture capacity was tested at 25 °C and 0–25 bar. Zn-BDC-DABCO and Co-BDC-DABCO showed a maximum adsorption capacity of 6.3 and 4.4 mmol g⁻¹ CO₂.

1. Introduction

The excessive use and dependence of humans on fossil fuels have led to an enhanced buildup of CO₂ and other harmful greenhouse gases in the atmosphere which is considered the biggest source of global warming and climatic change. Carbon capture and storage methods are therefore being investigated at a rapid rate and are currently being used to reduce CO₂ emissions in the atmosphere [1]. Different techniques that include capture from industrial exhausts and then storage in geological reservoirs or under the deep ocean and other similar storage sites have been reported for CO₂ capture [2, 3]. However, most of the currently researched techniques have risks that affect ocean life or the fertility of the land, etc and other major environmental issues. This makes Carbon Capture and Utilization (CCU), the process in which carbon is captured and utilized to produce other useful products, the most interesting topic in carbon-reduction studies today [4]. Adsorption of CO₂ using different materials has received a lot of attention due to its low energy consumption and cost effectiveness. Various different adsorbents are used for CO₂ capture including zeolites, molecular sieves, nano materials, metal organic frameworks, silica, and covalent organic framework materials etc [5–7]. These porous materials are preferred for CO₂ capture because of their diverse attractive characteristics such as porosity that allows fast flow rates and high separation and adsorption rates [8], added affinity to Carbon dioxide [9], low cost [10], low regeneration energy requirements [11], and stability in moistorous conditions [12].

Metal-organic frameworks [MOFs] because of their ultra-high porosity, strong crystal structure, and functionalizability have been reported as promising and efficient candidates for CO₂ adsorption. Their unique properties such as high surface area, high stability, open channels, and permanent porosity, make them suitable for CO₂ capture. Due to the additional features, MOFs stand out in comparison to other adsorbent materials as it greatly enhances the efficiency of CO₂ capture. [13–22]. Two main approaches are used for the synthesis and functionalization of specialized MOFs for CO₂ capture. These are (i) pre-synthetic functionalization, in which the functional group is already present in the final synthesized product, and (ii) post-synthetic functionalization, in which the functional group is separately added after initial synthesis. [23–29].
One of the more effective pre-synthetic functionalization techniques used for CO₂ capture is the synthesis of pillared-layer MOFs. Pillared-layer MOFs provide enhanced surface area and if an amino functionalized group is used as a pillar, they can also enhance CO₂ affinity. These MOFs contain two organic linkers instead of one that links the 2D layers formed by the metal ions and turn it into a 3D structure. This change in structure makes these kind of MOFs very effective and result in increased porosity, stability and enhanced the surface area available for adsorption [30–32]. Recently promising results have been obtained for the application of pillared-layer MOFs in the adsorption and storage of gases such as CO₂ and CH₄ [33–37]. Several researchers have reported that Zn₂(BDC)₂(DABCO) has a high CH₄ storage capacity as the DABCO connects different layers of the initial 2D lattice that increases surface area [33, 35]. However, there is very limited literature available about its CO₂ adsorption capacity. The adsorption capacity of the DABCO acts as a pillar and facilitates enhanced uptake of CO₂ because it forms a covalent bond with the metals in the structure that converts the 2D lattices into a high-surface-area 3D structure. CO₂ affinity for any MOF can be enhanced by adding an amino functional group. Since DABCO contains an amino group in its structure, it enhances the adsorption not only by increasing the surface area but also by introducing the amino group to the MOF. Similar DABCO based MOFs, Cu-DABCO and Ni-DABCO showed CO₂ adsorption capacity of 1.4 mmol g⁻¹ and 2.2 mmol g⁻¹ respectively [38].

In this study, two pillared-layer MOFs, Zn₂(BDC)₂(DABCO) and (Co₂(BDC)₂(DABCO), were synthesized, characterized, and tested for their performance in carbon dioxide adsorption. Zn₂(BDC)₂(DABCO) had previously shown promising results in CH₄ adsorption. This provided a motivation to study this MOF for CO₂ adsorption, specially because the DABCO in this MOF could act as an amino functionalized group and result in increased affinity for CO₂ molecules.

2. Experimental

2.1. Chemicals
Zinc Nitrate (Zn(NO₃)₂.6H₂O), Cobalt Nitrate (Co(NO₃)₂.6H₂O), Terephthalic acid (H₂BDC) were obtained from Sigma-Aldrich, and Dimethylformamide (DMF) was purchased from Merck. All chemicals were used without further purification. The CO₂ cylinder used in this research had a purity of 99.95%. The autoclave used was locally manufactured.

2.2. Synthesis of DABCO based Pillared Zn-BDC and Co-BDC MOFs
Both the MOFs were produced using the procedures mentioned in the literature [30]. For the synthesis process, Zn(NO₃)₂.6H₂O, H₂BDC, and DABCO in the ratio 1:0.5 respectively were mixed in DMF (40 ml) and then stirred to form a solution. The solution was heated at 120 °C for 48 h in a Teflon-lined stainless-steel autoclave. White crystals were formed which were first filtered, then washed with DMF three times, and then dried in a vacuum oven at 40 °C for 48 more hours. The same process was repeated for the preparation of (Co₂(NO₃)₂(DABCO) except that Co(NO₃)₂.6H₂O was used instead of Zn(NO₃)₂.6H₂O. Co-BDC and Zn-DABCO MOFs without DABCO were also synthesized for comparison purposes.

2.3. Characterization
Powder x-Ray Diffraction (PXRD) analysis of the samples was conducted using the D8 Advanced X-Ray diffraction system (Bruker, Germany). A 3KVA XRD Generator was used to produce a 1200 W intensity of the x-Ray beam. A timestep of 0.2 s was used with an increment of 0.01. The 2θ range of 5°-45° was used to record the diffraction pattern. The TESCAN SEM VEGA3 (TESCAN, Czech Republic) microscope was used for obtaining Scanning Electron Microscope (SEM) images of the synthesized samples. The thermal stability of the samples was tested using DTG-60H Thermo Gravimetric Analyzer (Shimadzo Japan). The temperature was increased from 25 °C–600 °C at a rate of 5 °C per minute. To identify the functional groups, present in the structure, the Fourier transform infrared spectra (FTIR) was carried out using Agilent Cary 630 (Agilent USA). N₂ adsorption studies of prepared samples were conducted to analyze the surface area and pore volume using a Nova 2200e (Quantachrome, USA) at 77 K at a relative pressure of P/P₀ = 0.05–1.0.

2.4. CO₂ Capture studies
High-pressure volumetric gas sorption analyzer (Quantachrome Isorb-HP100) was used to perform CO₂ adsorption testing. The samples were heated in a vacuum oven at 100 °C overnight before use to remove the presence of moisture content and guest molecules. Before CO₂ adsorption studies, samples were degassed at 150 °C under vacuum for 10 h. Sorption studies were performed at 298 K, over a pressure range of 0–25 bar. The produced Isotherms were studied and exported using Quantachrome software and then imported into Origin to draw the comparison graphs.
3. Result and discussion

In the XRD results, the major peaks of Zn-BDC DABCO MOF match well with the peaks of the reported pattern as can be seen in figure 1 [30]. The XRD results show that both the Co and Zn-based DABCO MOFs have similar XRD patterns and structure. MOF consists of paddle wheel structured Zn atoms which are linked together by anions of benzene-dicarboxylic acid to form a 2D square lattice. DABCO takes up the axial sites of the Zn atom to turn this 2-dimensional lattice into a 3-dimensional structure. This structure provides large interconnected 3D spaces for gas adsorption. The proposed structure of DABCO MOFs can be seen in figure 2. The red hexagonal structure shows benzene connected to one carboxylic acid molecule on each end which is connected to two Zn atoms forming a chain. This chain is connected by the DABCO molecule to form a 3D structure. This MOF structure was obtained by analyzing the crystallographic information file (.cif) [39] of Zn-BDC DABCO by using VESTA software. After importing the file, the 3D structure was seen as in figure 2, and the already present XRD simulation was rerun to produce a pattern. The XRD simulation of the cif file also confirmed the structure of our material as it was identical to our experimentally obtained XRD results.

Scanning Electron Microscope (SEM) analysis was used to study the morphology and surface of synthesized MOFs. For this process, the sample powder was first dried and then sprayed with gold to create a coating to avoid charging the material. The SEM (figure 3) shows a large number of three-dimensional crystals. These crystals when zoomed in to 1 μm show a range of random geometry including flat tetragonal flakes stacked over each other [40]. This is because the selected metal-organic framework crystals formed have a tetragon structure. In this system, the dicarboxylic layer of the terephthalic acid works as the ligand and links with the Zinc molecules to form 2D square lattices. These lattices are then connected using the pillar ligand (DABCO) [41].

The EDS of Co BDC DABCO is shown in figure 4. The weight percentage of carbon, oxygen, and cobalt present is very close to the expected percentages based on their molar mass contribution to the compound. Traces of gold are present due to the gold coating mechanism mentioned earlier.

Thermogravimetric analysis was used to evaluate the thermal stability of both samples (figure 5). There are two major steps in both the curves, that show the degradation of the material. The first one below ~200 °C
Figure 3. SEM images at 1 and 10 μm. Left: Co-BDC-DABCO, Right: Zn-BDC-DABCO.

| Elements | Weight% | Atomic% |
|----------|---------|---------|
| carbon   | 50.27   | 61.19   |
| oxygen   | 39.77   | 36.34   |
| cobalt   | 9.96    | 2.47    |

Totals: 100.00

Figure 4. EDS analysis of Co-BDC-DABCO MOF.

Figure 5. Thermal gravimetric analysis of Co-BDC-DABCO and Zn-BDC-DABCO MOFs.
corresponds to the removal of moisture content, guest molecules and DMF, it is represented in the graph as ‘DMF degradation’. The second one shows the decomposition of the framework which is mainly due to the degradation of the linker in the framework represented in the figure as ‘Linker degradation’. Since there are two linkers present in this MOF (BDC and DABCO) this step is divided into two parts [42]. The first step that starts at above ~300 °C shows the decomposition of BDC while the second part which starts above ~450 °C shows the decomposition of the DABCO in the framework. The difference in the results indicates that the Zn-BDC-DABCO showed less thermal stability as it started to decompose at around 450 °C while Co-BDC-DABCO holds up for a little longer and decomposes completely at around 480 °C. Detectable decomposition of the nanoparticles of Zn-BDC-DABCO thus starts about 30 degrees earlier than that of its bulk counterparts, possibly due to the much higher surface-to-volume ratio of the nano-particles, as more heat is needed to annihilate the lattices of the material.

The BET surface area of Zn-BDC-DABCO and Co-BDC-DABCO was calculated to be 511.7 and 98.2 m²g⁻¹ respectively. The isotherm curves from the BET testing are shown in figure 7. This is significant as the same MOFs without DABCO i.e. Zn BDC and Co BDC showed a surface area of 37.8 m²g⁻¹ and 17.9 m²g⁻¹ respectively [44]. Zn-BDC-DABCO shows high surface area compared to a number of other pillared-layer MOFs found in the literature. The detailed surface area comparison is provided in table 1.

To put the importance of the pillared layer (DABCO in this case) in perspective, the results of adsorption testing were compared to two samples of the same MOFs without DABCO. The CO₂ isotherms were measured at 25 °C and a pressure range of 0–25 bar. The desorption isotherms of all the samples were the same as the adsorption isotherms.

The graph (figure 8) shows that the adsorption capacity of these MOFs increases with increasing pressure which indicates typical behavior of physisorption. This also indicates that these MOFs can be used in Pressure Swing Adsorption (PSA) applications [48]. The curves in this figure show raw experimental data. The CO₂ adsorption capacity increases rapidly at low pressures and as we reach higher pressure values this increase is much slower. Zn BDC DABCO and Co BDC DABCO took up to 6.3 and 4.4 mmol g⁻¹ CO₂ respectively at 25 °C and 25 bar. The isotherm suggests that even at pressures as high as 25 bar, neither of our main samples reached saturation. Compared to samples without DABCO, both Zn-BDC-DABCO and Co-BDC-DABCO show a significant increase which can be credited to the change in structure from 2D to 3D.

Table 1 shows a list of similar MOFs with their surface area and CO₂ adsorption capacities at specific temperatures and pressures. It can be seen that other similar pillared MOFs show lower CO₂ adsorption in
Some MOFs like the Co(Imda)(4,4′-bpy)\textsuperscript{[41]}, SNU-M11\textsuperscript{[45]}, and MOOFOUR-1-Ni\textsuperscript{[46]} show lower CO\textsubscript{2} adsorption (3.06 mmol g\textsuperscript{-1}, 2.09 mmol g\textsuperscript{-1} and 2.45 mmol g\textsuperscript{-1} at 298 K and 1 bar respectively) despite surface area values similar to that of Zn BDC DABCO. Similarly, NDC\textsuperscript{[37]} has a much higher surface area (365 m\textsuperscript{2} g\textsuperscript{-1}) than that of Co BDC DABCO (100 m\textsuperscript{2} g\textsuperscript{-1}) but still shows low adsorption capacity in comparison (1.5 mmol g\textsuperscript{-1} at 298 K and 1 bar). The high adsorption capacity of Zn BDC DABCO and Co BDC DABCO can be credited to the presence of the amino group in the structure that results in an increased CO\textsubscript{2} affinity. The adsorption values are much greater than Zeolite 13X which shows maximum adsorption of 2.2 mmol g\textsuperscript{-1} at temperature of 298 K and 1 bar\textsuperscript{[37]}.

| Serial number | Name of MOF                      | BET surface area (m\textsuperscript{2} g\textsuperscript{-1}) | Adsorption capacity (mmol g\textsuperscript{-1}) | References     |
|---------------|---------------------------------|-------------------------------------------------------------|-------------------------------------------------|---------------|
| 1             | Zn BDC DABCO                    | 500                                                         | 6.3                                             | This work     |
| 2             | Co BDC DABCO                    | 100                                                         | 4.4                                             |               |
| 3             | Zn BDC                          | 37.8                                                        | 0.95                                            |               |
| 4             | Co BDC                          | 17.9                                                        | 0.67                                            |               |
| 5             | NDC                             | 365.1                                                       | 1.5                                             | [37]          |
| 6             | Co(Imda)(4,4′-bpy)              | 572                                                         | 3.06                                            | [41]          |
| 7             | SNU-M11                         | 505 (Langmuir)                                              | 2.09                                            | [45]          |
| 8             | [Zn\textsubscript{4}(TRZ\textsubscript{3})(TTBDC\textsubscript{2})\textsubscript{n}] | 255.5 (Langmuir)                                           | 1.39                                            | [46]          |
| 9             | MOOFOUR-1-Ni                    | 456 (Langmuir)                                              | 2.45                                            | [47]          |

Figure 7. BET analysis of Co-BDC-DABCO and Zn-BDC-DABCO MOFs.
4. Conclusion

In this study pillared layer, 3D metal-organic frameworks (MOFs) M-BDC-DABCO (M = Zn, Co) were synthesized. These MOFs were characterized and tested for their CO₂ adsorption capabilities using a series of pressure swing adsorption at room temperature for a pressure range of 0–25 bar. These MOFs show a tetragonal structure in which the DABCO acts as a pillar to connect multiple layers of Zn-BDC that results in a 3D structure with a high surface area. Thermogravimetric Analysis of these MOFs suggested thermal stability at temperatures below 300 °C. Zn-BDC-DABCO and Co-BDC-DABCO showed an adsorption capacity of 6.3 mmol g⁻¹ and 4.4 mmol g⁻¹ CO₂ respectively at room temperature when the pressure was increased to a maximum of 25 bar which is a significant increase when compared to the 0.95 mmol g⁻¹ and 0.67 mmol g⁻¹ of the Zn-BDC and the Co-BDC respectively. These results confirm that the addition of DABCO to MOFs as a pillar enhances CO₂ adsorption. This is due to two basic parameters; i) The addition of the pillar turns our 2D structure into a 3D structure which results in an increased surface area that in-turn enhances the adsorption capacity, and ii) Since DABCO is an amino functionalized group, it enhances the CO₂ affinity of the material which also results in increased adsorption capacity.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interests

There are no conflicts to declare.

Authors’ Contributions

N I and T N conceptualized this project, I A carried out MOF synthesis and characterization. N I and T N analysed results. I A and A A prepared the manuscript, T N and N I supervised the overall design, synthesis and development of the project.
References

[1] Kenarsari S D, Yang D, Jiang G, Zhang S, Wang J, Russell A G, Weil Q and Fan M 2013 Review of recent advances in carbon dioxide separation and capture RSC Adv. 3 22739–73
[2] DOE 2010 Report of the Interagency Task Force on Carbon Capture and Storage The U. S. Department of Energy and the Environmental Protection Agency 2010 https://www.osti.gov/secrets/purl/985209
[3] Haszeldine R S 2009 Carbon capture and storage: how green can black be? Science 325 1647–52
[4] Markewitz P, Kuckshinrichs W, Leitner W, Linsens J, Zapp P, Bongartz R, Schreiber A and Muller T E 2012 Worldwide innovations in the development of carbon capture technologies and the utilization of CO2 Energy Environ. Sci. 5 7281–305
[5] D’Alessandro D M, Smit B and Long J R 2010 Carbon dioxide capture: prospects for new materials Angew. Chem. Int. Ed. 49 6058–82
[6] Lee S Y and Park S J 2015 A review on solid adsorbents for carbon dioxide capture J. Ind. Eng. Chem. 23 1–11
[7] Shafeyan M S, Daud W M A W, Houshmard A and Shamiri A 2010 A review on surface modification of activated carbon for carbon dioxide adsorption J. Anal. Appl. Pyrolysis 89 143–51
[8] Skoulidas A I, Sholl D S and Johnson K J 2006 Adsorption and diffusion of carbon dioxide and nitrogen through single-walled carbon nanotube membranes J. Chem. Phys. 124 054708
[9] Zhao Y, Zhao L, Yao K X, Yang Y, Zhang Q and Han Y 2012 Novel porous carbon materials with ultrahigh nitrogen contents for selective CO2 capture J. Mater. Chem. 22 19726–31
[10] Sevilla M, Macia-Agulló I A and Fuertes A B 2011 Hydrothermal carbonization of biomass as a route for the sequestration of CO2: chemical and structural properties of the carbonized products Biomass Bioenergy 35 3152–9
[11] Xia Y, Mokaya R, Walker G S and Zha Y 2011 Superior CO2 adsorption capacity on N-doped, high-surface-area, microporous carbons templated from zeolite Adv. Energy Mater. 1 678–83
[12] Supriya S, Sriram G, Ngaini Z, Kavitha C, De Padova I P and Hegde G 2020 The role of temperature on physical–chemical properties of green synthesized porous carbon nanoparticles Waste Biomass Valori. 11 3821–31
[13] Choi S, Drees J H and Jones C W 2009 Adsorbent materials for carbon dioxide capture from large anthropogenic point sources Chem. Sus. Chem. 2 796–854
[14] Li J-R, Ma Y, McCarthy M C, Sculley J, Yu J, Jeong H-K, Balbuena P B and Zhou H C 2011 Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks Coord. Chem. Rev. 255 1791–823
[15] Aisha, Naseem I, Tayyaba N, Majid A and Tim E 2019 Efficient one-pot synthesis of a Hexamethylenetetramine-Doped Cu-BDC Metal-organic framework with enhanced CO2 adsorption Materials 9 1063
[16] Leena A, Naseem I, Aisha A and Tayyaba N 2020 Synthesis, characterization and gas adsorption analysis of solvent dependent Zn-BTC metal organic frameworks Sep. Sci. Technol. 56 2159–69
[17] Junaid K, Naseem I, Aisha A and Tayyaba N 2019 Mater. Res. Express 6 105539
[18] Jiang H L and Xu Q 2011 Porous metal-organic frameworks as platforms for functional applications Chem. Commun. 47 3351–70
[19] Dhakhshinamoorthy A and Garcia H 2012 Catalysis by metal nanoparticles embedded on metal–organic frameworks Chem. Soc. Rev. 41 2562–84
[20] Yoon M, Sridharbala R and Kim K 2012 Homochiral metal-organic frameworks for asymmetric heterogeneous catalysis Chem. Rev. 112 1196–231
[21] Gui Z-Y, Park J, Raiff A, Wei Z W and Zhou H-C 2008 Metal-organic frameworks as biomi- metic catalysts Chem. Cat. Chem. 6 67–75
[22] Zhao M, Ou S and Wu C-D 2010 The role of temperature on physical–chemical properties of green synthesized porous carbon nanoparticles Waste Biomass Valor. 11 3821–31
[23] Jiang H L and Xu Q 2011 Porous metal-organic frameworks as platforms for functional applications Chem. Commun. 47 3351–70
[24] López-Cabrelles J et al 2018 Isoreticular two-dimensional magnetic coordination polymers prepared through pre-synthetic ligand functionalization Nature Chem. 10 1001–7
[25] Yang B, Shen M, Liu J and Ren F 2017 Post-synthetic modification Nanoscale metal-organic frameworks for targeted drug delivery in cancer cells Pharm. Res. 34 2440–50
[26] Kandiah M, Nielsen H M, Usseglio S, Jakobsen S, Olsbye U, Tilsen M, Larabi C, Quadrelli E A, Bonino F and Lillerud K P 2010 Synthesis and stability of tagged UiO-66 Zr MOFs Chem. Mater. 22 6632–40
[27] Silva C, Gorma A and Garcia H 2010 Metal–organic frameworks as semiconductors J. Mater. Chem. 20 3141–56
[28] Öien S et al 2015 Probing reactive platinum sites in Uio-67 zirconium metal–organic frameworks Chem. Mater. 27 1042–56
[29] Arstad B et al 2008 Amine functionalised metal organic frameworks (MOFs) as adsorbents for carbon dioxide Adsorption 14 755–62
[30] Seki K and Mori W 2002 J. Phys. Chem. B 106 13830–5
[31] Dybbsk D N, Chun H and Kim K 2004 Angew. Chem. Int. Ed. 43 5033
[32] Chun H, Dybbsk D N, Kim H and Kim K 2005 Synthesis, x-ray crystal structures, and Gas sorption properties of pillared square grid nets based on paddle-wheel motifs: implications for hydrogen storage in porous materials Chemistry—A European Journal 11 3521–9

Senkovska I and Kaskel S 2008 Micro. Meso. Mater. 112 108

[33] Wang H, GETZSCHMANN J, SENKOVSKA I and KASKEL S 2008 Structural transformation and high pressure methane adsorption of CO2(BDC)2(dabco) Microporous Mesoporous Mater. 116 653–7
[34] Kim H et al 2009 Methane sorption and structural characterization of the sorption sites in Zn2BDC3(dabco) by single crystal x-ray crystallography Chem. Asian J. 4 886–91
[35] Rivas P S, Zapata E, Silva J A C, Rodrigues A E and Chen B 2007 J. Phys. Chem. B 111 6101–3
[36] Lee J, Olson D, Pan L, Emge T and Li J 2007 Microporous metal–organic frameworks with high gas sorption and separation capacity Adv. Funct. Mater. 17 1255–62
[37] Chen Z, Xiang S, Zhao D and Chen B 2009 Crystal Growth & Design 9 5293–6

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[37] Zhai Q G, Bai N, Li S, Bu X and Feng P 2015 Design of Pore Size and Functionality in Pillar-Layered Zn-Triazolate-Dicarboxylate Frameworks and Their High CO$_2$/CH$_4$ and C$_2$ Hydrocarbons/CH$_4$ Selectivity Inorg. Chem. 54 9862–8
[38] Mishra P, Edubilli S, Mandal B and Gunma S 2013 Adsorption of CO$_2$, CO, CH$_4$ and N$_2$ on DABCO based metal organic frameworks Microporous Mesoporous Mater. 169 75–80
[39] Kim Y, Haldar R, Kim H, Koo J and Kim K 2016 The guest-dependent thermal response of the flexible MOF Zn$_2$(BDC)$_2$(DABCO) Dalton Trans. 45 4187–92
[40] Asghar A, Iqbal N, Noor T, Kariuki B, Kidwell L and Easun T 2021 Efficient electrochemical synthesis of a manganese-based metal–organic framework for H$_2$ and CO$_2$ uptake Green Chemistry 23 1220–7
[41] Chen C, Jia M, Wang G, Li X and Li S 2015 High and selective CO$_2$ uptake in a nitrogen-rich pillar-layered metal organic framework’ RSC Adv. 5 104932–5
[42] Motakef-Kazemi N, Shojaosadati S and Morsali A 2016 Evaluation of the effect of nanoporous nanorods Zn$_2$(bdc)$_2$(dabco) dimension on ibuprofen loading and release J. Iran. Chem. Soc. 13 1205–12
[43] Carson C G, Hardcastle K, Schwartz J, Liu X, Hoffmann C, Gerhardt R A and Tannenbaum R 2009 Synthesis and structure characterization of copper terephthalate metal–organic frameworks Eur. J. Inorg. Chem. 16 2338–43
[44] Zha Q, Yuan F, Qin G and Ni Y 2020 Cobalt-Based MOF–on-MOF Two-Dimensional heterojunction Nanostructures for enhanced oxygen evolution reaction electrocatalytic activity Inorg. Chem. 59 1295–305
[45] Choi H S and Suh M P 2009 Angew. highly selective CO$_2$ capture in flexible 3D coordination polymer networks Angewandte Chemie International Edition 48 6865–9
[46] Yan X, Li S, Jiang Y, Hu M and Zhai Q 2015 Synthesis, crystal structures and gas adsorption of two porous pillar-layered MOFs decorated with different functional groups Inorg. Chem. Commun. 62 107–10
[47] Mohamed M H, Elsaid S K, Wojtas L, Pham T, Forrest K A, Tudor B, Space B and Zaworotko M J 2012 J. Am. Chem. Soc. 134 19556
[48] Pirngruber G et al 2012 A method for screening the potential of MOFs as CO$_2$ Adsorbents in pressure swing adsorption processes Chem. Sus. Chem 5 762–76