



Mixed-Metal Approach towards Assembling Highly Stable Metal-Organic Framework based Adsorbent for Simultaneous Capture of CO₂ and H₂S

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ABSTRACT

The common method employed to capture CO₂/H₂S, liquid amine scrubbing, is associated with high energy penalty and some other drawbacks. Adsorption based technology, using physisorbent solids, is considered economically viable option. This work presented the assembly of H₂S stable metal-organic framework (MOF) sorbent, Tb-Cu-bqdc MOF, with underlying fluorite net that showed huge potential to be deployed for simultaneous capture of CO₂ and H₂S. The 8-coordinated rectangular cuboid and the 4-coordinated tetrahedral molecular building units required to assemble the targeted MOF were generated *in situ* from terbium nitrate, copper nitrate and 2,2'-biquinoline-4,4'-dicarboxylic acid under suitable solvothermal reactions. The structure, porosity, H₂S stability and other properties of the synthesized MOF were confirmed by XRD, ICP-OES, TGA, gas sorption, etc. The MOF's high H₂S stability was evidenced in PXRD and cyclic CO₂ sorption studies with no loss of crystallinity, no phase change and no alteration in CO₂ uptake being observed upon exposure to H₂S. To realize the potential of the MOF for CO₂/H₂S removal, single gas and mixed gas sorption tests were performed. Appreciable breakthrough uptakes for H₂S and CO₂ (≈ 1.42 and ≈ 0.24 mmol g⁻¹, respectively, at room temperature and 1 bar) with negligible sorption of the common gases (CH₄ and N₂) by the MOF, showed potential of the material for the purification of variety of gas streams containing CO₂ and H₂S. The preferential sorption of H₂S over CO₂ (selectivity ≈ 6.0) is also a merit in further processing of the captured acid gas to produce pure H₂S, raw material in Claus process.

Keywords: MOF, Mixed-metal MOF, CO₂/H₂S capture, Single-gas sorption, Mixed-gas sorption.

INTRODUCTION

As a result of industrial and other human activities, carbon dioxide (CO₂) emission in the atmosphere is increasing at an alarming rate. CO₂ capture is then one of the issues which received extensive attention for reducing global warming and its adverse environmental effects. Most of the sources that contribute to CO₂ emission also contain significant amount of hydrogen sulfide (H₂S) impurity (Hao et al., 2002; Noyola et al., 2006). For example, natural gas, an important fuel for production of energy with methane (CH₄) being the major component, contains H₂S at various compositions ranging from ppm to more than 20% levels (mainly as mixture with CO₂ forming acid gas) (Hao et al., 2002). Biogas, the other energy source for stationary power generation and the transportation sector, also contains significant amounts of CO₂ and H₂S impurities mixed with its major component, i.e., CH₄ (Noyola et al., 2006). CO₂ and H₂S are also impurities in some refinery gases as well as in synthesis gas for hydrogen

production. As a result, capturing of these undesirable impurities is very crucial for upgrading of fuels, for reducing their emissions into the atmosphere, to minimize the economic loss due to poisoning of both the adsorbents used in different natural gas treatment, biogas upgrading steps, and catalysts involved in the subsequent utilization of CH₄. Due to these concerns, the issue on capture of CO₂ and H₂S has recently been on the rise. Various acid gas removal techniques have been proposed to alleviate the problem.

Among the various processes deployed to remove CO₂ and H₂S, the most common one is liquid amine scrubbing. However, this technology has several disadvantages such as high regeneration cost, oxidative degradation of amine resulting in corrosion, undesirable degradation products, and environment-related issues (Veawab et al., 2006). This then necessitates the development of alternative cost and energy-efficient processes and materials that could offer great prospects to address this challenge. Adsorption based technology, using physisorbent solids, is considered to be more economical option for such application (Barea, et

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al., 2014; Belmabkhout et al., 2017). The key in this regard is the choice of appropriate adsorbent with high stability towards humidity and H₂S, good acid gas adsorption capacity, selectivity, and easy regeneration. Among the traditional adsorbents, activated carbons have been largely explored (Adib et al., 2000; Bandosz, 2002; Yan et al., 2004; Bagreev et al., 2005; Xiao et al., 2008). According to the reported results, activated carbons are generally regarded to have good H₂S/CO₂ selectivity but suffer from low affinity for CO₂.

Metal-organic frameworks (MOFs) are relatively new classes of solid materials that have shown to be materials of enormous surface areas, adjustable pore geometries, and customizable surface properties (Farha et al., 2012; Zhou et al., 2012). They are classes of extended framework crystalline solid materials built up by linking organic and inorganic building units by strong coordinate covalent bonds in a rigid periodic networked structure. MOF-based materials, due to their unique structural features such as their amenability to be tuned and their ease of modification either by pre-targeted design prior to synthesis or by post synthetic modification, have attracted a lot of attention and are being extensively studied for various applications (Lee et al., 2009; Zacher et al., 2009; Kreno et al., 2012; Qiu et al., 2014). The possibility to understand MOF's structure and acid gas capture property relationships, due to their well-defined chemical structures, boost the interest of researchers to investigate the role of these classes of materials in acid gas capture application (Belmabkhout et al., 2017; Bhatt et al., 2017). However, only few examples of MOFs are reported to have potential for this application since a large number of MOFs were found unstable to H₂S and moisture.

Among the various types of MOFs, those based on tetrahedral organic ligands are less explored. This is mainly due to the synthetic challenges to prepare tetrahedrally oriented organic building units with functional groups suitable for MOF's of a particular topology and pore structure (Wen, et al., 2012a; Zhang et al., 2014). However, the inorganic CaF₂ structure was used as blueprint net to guide the assembly of some of the very few examples of MOFs from tetrahedral shaped linkers (Furukawa et al., 2014; Zhang et al., 2014). A MOF that mimics the fluorite structure is particular interest for us. This is because the previously reported MOFs with underlying fluorite net showed interesting chemical stability and water sorption properties (Furukawa et al., 2014).

In this work, the synthesis, characterization, and simultaneous CO₂ and H₂S removal test of a chemically stable mixed-metal (Tb-Cu) MOF assembled from *in-situ* generated Cu-based

tetrahedrally oriented metallo-linker and Tb hexanuclear cluster building units are presented. To avoid lengthy and complicated steps required to synthesize tetrahedral shaped organic ligands, *in-situ* linker formation was considered as an alternative strategy to assemble the tetrahedral building unit with appropriate substituent groups. Moreover, copper is well known in forming tetrahedral coordination complexes up on coordination to properly positioned N-donors (Patil, et al., 2017). The use of single metal sources (Tb or Cu) for synthesis doesn't lead to the targeted MOF topology for coordination chemistry reasons. The synthesized fluorite net based MOF was then explored for its potential deployment in simultaneous capture of CO₂ and H₂S, which is a very important step in the upgrading of natural gas and biogas. Besides the sorption of the acid gases, the material to be employed for such application should also be stable towards humidity, SO₂, etc. since these are also contaminants which are commonly found in many natural gas and biogas streams (Hao et al., 2002; Noyola et al., 2006). Hence, the synthesized MOF was tested for stability towards such impurities prior to the targeted acid gas capture test.

MATERIALS AND METHODS

Materials:

All the starting materials used were purchased from commercial sources and used without further purification. The water used in all the synthetic conditions is deionized water unless and otherwise stated. Terbium nitrate pentahydrate (Tb(NO₃)₃·5H₂O) (99.9%, Alfa Aesar), copper nitrate hemi-pentahydrate (Cu(NO₃)₂·2.5H₂O) (98%, Alfa Aesar), N,N-dimethylformamide (DMF) (98%, Merck), 2,2'-biquinoline-4,4'-dicarboxylic acid (H₂bqdc) (90%, Sigma Aldrich), nitric acid (HNO₃) (69%, Fluka), 2-fluorobenzoic acid (2-FBA) (98%, ACROs Organics) and acetone (98%, Merck) were the main chemical reagents used in this work.

MOF synthesis

The Tb-Cu-bqdc MOF with underlying fluorite topology was prepared under solvothermal conditions by heating solutions containing metal salts, organic ligand, and 2-FBA modulating agent. Hence, 2,2'-biquinoline-4,4'-dicarboxylic acid (3.2 mg, 0.009 mmol), Tb(NO₃)₃·5H₂O (8.3 mg, 0.022 mmol), Cu(NO₃)₂·2.5H₂O (2.0 mg, 0.009 mmol), 2-FBA (56.4 mg, 0.4 mmol), DMF (1.7 mL), water (0.5 mL) and 0.1 mL HNO₃ (4.0 M in DMF) were combined in 20 mL scintillation vial and properly sealed. The mixture was then sonicated for about 30 min and then placed in a pre-heated oven set at 115 °C for 48 h. Once product formation was confirmed, the vial was taken out from the oven and slowly cooled to room temperature. Brown

block shaped crystals were then collected. The as-synthesized sample was washed with DMF and immersed in about 10 mL of acetone for 3 days, during which time the acetone was replaced three times per day. The solid was then dried at 200 °C under vacuum for 12 h to yield activated/evacuated sample.

MOF characterization

The MOF prepared in this study was characterized by single crystal X-ray diffraction (SCXRD), Powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), Elemental microanalysis (EA), Inductively coupled plasma optical emission spectroscopy (ICP-OES) and low-pressure gas/vapor sorption measurements.

PXRD measurements were carried out at room temperature on a PANalytical X'Pert PRO diffractometer 45 kV, 40 mA for CuK α ($\lambda = 1.5418 \text{ \AA}$), with a scan speed of $1.0^\circ \text{ min}^{-1}$ and a step size of 0.02° in 2θ .

SCXRD data were collected using a Bruker X8 PROSPECTOR APEX2 CCD diffractometer (Cu K α , $\lambda = 1.54178 \text{ \AA}$) at 296 K. Structure was solved using Direct Method (SHELXS-97) and refined using SHELXL-97.

TGA was performed under a continuous O₂ flow and recorded on a TA Instruments hi-res TGA Q500 thermogravimetric analyzer with a heating rate of $1^\circ \text{ C per minute}$.

Elemental (CHN) microanalyses (EA) were performed using a Perkin Elmer 2400 Series II CHNS elemental analyzer. A PerkinElmer 2000DV ICP-OES instrument was used for metal analysis.

Sorption study

Low pressure gas sorption measurements were performed on 3-Flex Surface Characterization Analyzer (Micromeritics) at relative pressures up to 1 atm. The cryogenic temperature for N₂ was controlled using liquid nitrogen bath at 77 K. The surface area was determined from the N₂ sorption isotherm collected at 77 K by applying the Brunauer-Emmett-Teller (BET) model. The bath temperature for room temperature H₂S, CH₄ and CO₂ sorption measurements were controlled using a recirculating bath containing an ethylene glycol/H₂O mixture.

Commercially available breakthrough system (purchased from L&C Science and Technology) was used for the breakthrough experiment. The whole set up was kept in a highly ventilated closed glass cabinet to avoid exposure to H₂S. For breakthrough experiment, 1.0 g of the MOF

sorbent was packed in the column and was activated at 180 °C for 12 hours under He flow. Before starting each experiment, helium reference gas is flushed through the column and then the gas flow is switched to the desired gas mixture at the same flow rate of $10 \text{ cm}^3 \text{ min}^{-1}$. The gas mixture downstream the column was monitored using mass-spectrometer.

RESULTS

Tb-Cu based hetero-metallic MOF is designed and constructed using judiciously selected in-situ formed metallo-linker and Tb₆ hexanuclear cluster building units (Fig. 1). To be specific, Tb + Cu based mixed metal strategy was used to assemble a MOF that mimics CaF₂ structure using judiciously selected 2,2'-biquinoline-4,4'-dicarboxylic acid (H₂bqdc) linker keeping in mind the chelating of softer copper ions to two N atoms of the linker and the availability of carboxylate-based oxygen donors to coordinate to the harder terbium cations.

The use of the solvothermal synthetic condition described in the experimental part resulted in brown block shaped crystals (quadrangular prism type) of size about $0.20 \times 0.20 \times 0.40 \text{ mm}$.

A suitable crystal was selected from the bulk sample and then mounted on single crystal diffractometer for data collection. After data collection using single crystal diffractometer,

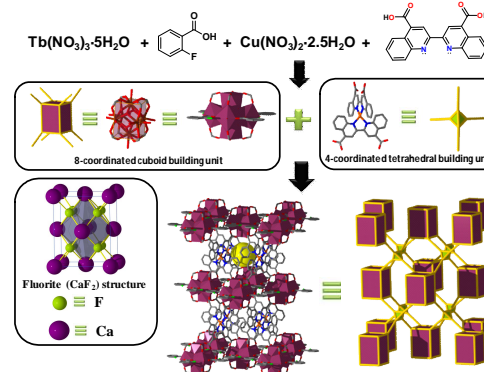


Fig.1: Schematic showing the assembly of Tb-Cu-bqdc-MOF that mimic fluorite (CaF₂) structure from in-situ generated rectangular cuboid and tetrahedral building units. The yellow ball indicates the pore space after guest solvent removal.

indexing and space group determination, the structure was refined and solved. The obtained crystallographic data is summarized in Table 1. From the collected SCXRD data, the as-synthesized sample was then formulated as $\text{Tb}_6\text{Cu}_2(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_4)_4(\text{H}_2\text{O})_4(2\text{-FBA})_4(\text{bqdc})_4 \cdot x(\text{solv})$ (2-FBA = $\text{C}_7\text{H}_4\text{FO}_2$, bqdc = $\text{C}_{20}\text{H}_{10}\text{N}_2\text{O}_4$).

Table 1: Crystal and refinement data for Tb-Cu-bqdc MOF.

Empirical formula	$C_{80}H_{40}Cu_2F_{0.5}N_8O_{52}Tb_6$
Crystal system	Tetragonal
Space group	$I4/m$
Unit cell dimensions	$a = b = 13.8285(4) \text{ \AA}$, $c = 33.7264(11) \text{ \AA}$
	$\alpha = \beta = \gamma = 90^\circ$
Volume	$6449.4(3) \text{ \AA}^3$
Z, calculated density	2, 1.563 mg m^{-3}
θ range for data collection	$2.6\text{--}67.3^\circ$
Completeness to $\theta_{\max} = 64.8^\circ$	98%
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0508$, $wR_2 = 0.1571$
Final R indices (all data)	$R_1 = 0.0509$, $wR_2 = 0.1572$
Goodness-of-fit	1.079

Table 2: Elemental analyses result for Y-Cu-bqdc MOF.

% C		% H		% N	
Measured	Calculated	Measured	Calculated	Measured	Calculated
39.94	40.35	2.41	2.26	3.38	3.49

Prior to further characterization and sorption study, the bulk phase purity of the prepared compound was checked by collecting powder X-ray diffraction patterns (Fig. 2).

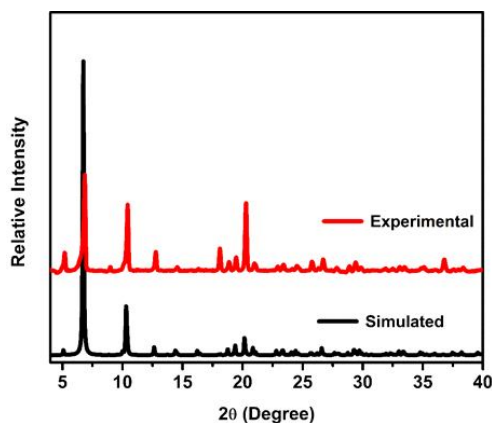


Fig. 2: Comparison of experimental and calculated PXRD diagrams for the synthesized MOF showing bulk phase purity of the as synthesized sample.

Percentage compositions of the elements found in the synthesized compound, after evacuating it to make it guest-free, were checked by CHN analyzer and ICP-OES. The CHN elemental analyses results are summarized in Table 2. The percentage compositions of the elements deduced from the formulated crystal structure are also tabulated together for comparison. To have insights on the metallic element constituents of the synthesized product, ICP-OES experiment was conducted resulting in terbium to copper ratio of 3.1.

Thermal characterization of the prepared MOF was done by conducting thermogravimetric measurement for the acetone exchanged and air

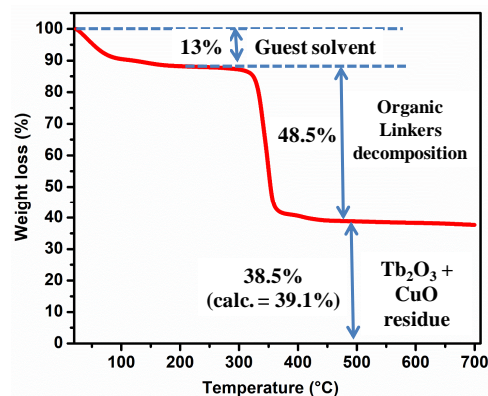


Fig. 3: TGA traces of the synthesized Tb-Cu-bqdc MOF after acetone exchange and drying at room temperature.

dried sample with the result displayed in Fig. 3. The result shows weight losses in two steps.

In order to check the porosity and deduce the surface area and pore volume of the MOF, N_2 sorption isotherm was collected at 77 K. The obtained steep sorption isotherm is shown in Fig. 4.

Prior to the targeted CO_2/H_2S sorption experiments, the stability of the MOF up on long time exposure to H_2O , H_2S and SO_2 was characterized by powder X-ray diffraction and CO_2 sorption measurements before and after exposure of the sample to the chemicals. The characterization results are shown in Fig. 5.

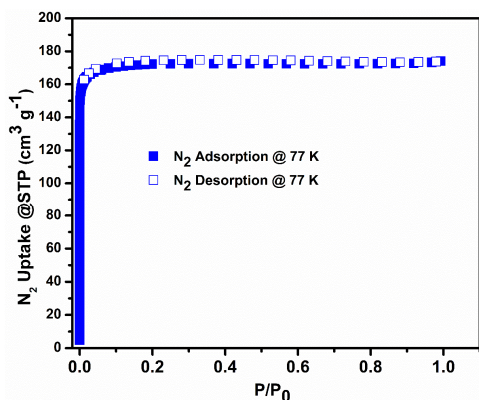


Fig. 4: N₂ sorption isotherm for Tb-Cu-bqdc-MOF collected at 77 K.

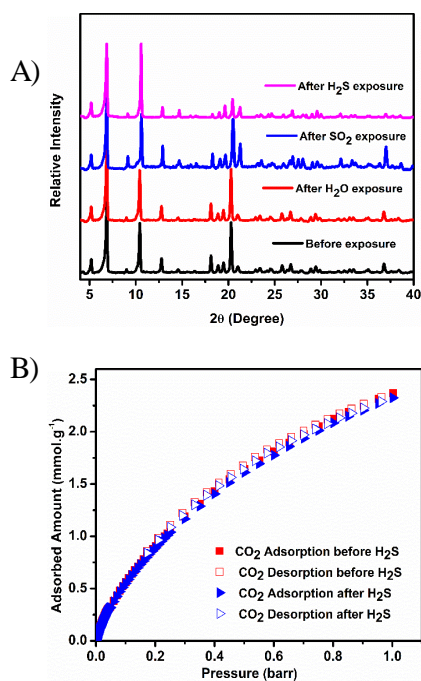


Fig. 5: PXRD patterns for Tb-Cu-bqdc-MOF before and after exposure to H₂O, H₂S and SO₂ (A); CO₂ sorption isotherms collected at 298K before and after exposure of the MOF crystals to H₂S (B), indicating the phase integrity of the material after exposure to these gases.

Following detailed characterizations, the prepared MOF was tested for its CO₂ and H₂S adsorptive separation properties. The sorption isotherms collected at room temperature for pure CH₄, pure CO₂ and pure H₂S is shown in Fig. 6. The results show sorption of CO₂ and H₂S by the MOF with negligible sorption of CH₄.

Adsorption breakthrough column set-up was employed for the mixed-gas sorption test. A gas mixture composition of 5% H₂S/5% CO₂/90% CH₄ was then used at flow rate of 10 cm³/min. The

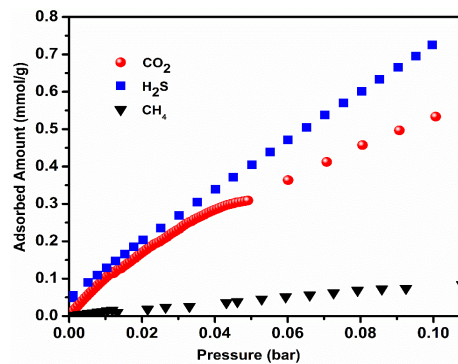


Fig. 6: Single component sorption isotherms of CO₂, H₂S and CH₄ for Tb-Cu-bqdc-MOF collected at room temperature.

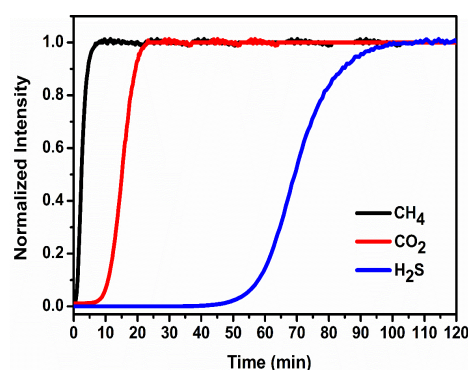


Fig. 7: Column breakthrough sorption measurement for the prepared MOF with H₂S/CO₂/CH₄ (5%/5%/90%) gas mixture at 25 °C at 1 bar total pressure (10 cm³/min flow rate).

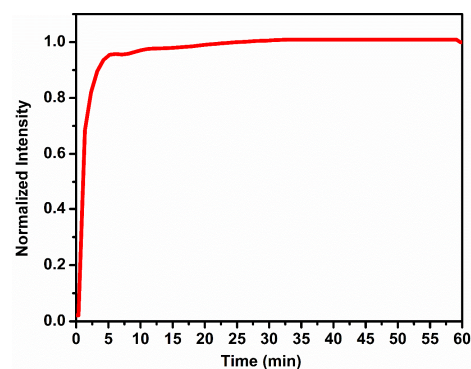


Fig. 8: Column breakthrough test for Tb-Cu-bqdc-MOF with 100% N₂ with flow rate of 10 cm³/min. It can be seen that N₂ breakthroughs almost immediately without any sorption.

experiment, conducted at 25 °C and 1 bar using 1.0 g sample, gave the result shown in Fig. 7. As can be seen in the Figure, both H₂S and CO₂ are

Table 3: Comparison of the retention times of CO₂ and H₂S in the column packed with Tb-Cu-bqdc MOF for the five cycle column breakthrough tests at 25 °C.

Gas	Retention time (min)				
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
H ₂ S	64	62	64	63	62
CO ₂	11	12	10	11	10

adsorbed by the MOF packed in the column with retention times of about 64 min for H₂S and of about 11 min for CO₂. The retention times correspond to ≈ 1.42 and ≈ 0.24 mmol g⁻¹ uptakes of H₂S and CO₂, respectively. However, CH₄ is not retained in the column (i.e., negligible uptake of methane by the MOF). The results also show H₂S/CO₂ selectivity of about 6.0. The MOF can be completely regenerated either by evacuating or flushing with inert gas like helium at 25 °C leading to recyclable sorption profiles for the component gases as evidenced by the reproducible H₂S and CO₂ sorption uptakes for five cycles measured under similar conditions (i.e., Gas mixture CO₂/H₂S/CH₄ (5/5/90) with 10 cm³/min flow rate was used for each experiment but by evacuating the MOF at room temperature in between each cycle). The H₂S and CO₂ retention times for the five cycles are shown in Table 3.

Column breakthrough experiment was also conducted using 100% N₂ gas to check the room temperature N₂ sorption property of the prepared MOF and the obtained result is displayed in Fig. 8. As can be visualized from the Figure, N₂ was not retained in the column since it breakthroughs almost instantaneously confirming that it is not adsorbed by the MOF crystals packed in the column.

DISCUSSION

To assemble a MOF that mimics fluorite net, 8-coordinated rectangular cuboid metal cluster that takes the position of Ca and tetrahedral linker that takes the position of F is needed (Fig. 1). 8-coordinated rectangular cuboid molecular building units can be targeted either from Zr₆ or RE₆ in situ generated metal clusters. In our case, we chose Tb as representative example of rare-earths and targeted in-situ formation of Tb₆ cluster that resembles rectangular cuboid geometrical building unit up on using the carboxylate carbons of ligands to be coordinated to the cluster as points of extension. The choice of Cu is to avoid the lengthy steps required to synthesize tetrahedrally oriented tetracarboxylate organic ligands. It has already been proved that the use of 2-fluorbenzoic acid (2-FBA) modulator enables *in-situ* generation of well-defined rare-earth hexanuclear cluster molecular building blocks (Xue et al., 2013) and so we chose this strategy to form 8-coordinated Tb₆ oxo-cluster that can take the place of Ca in the targeted fluorite

structure. The tetrahedral metallo-linker was hypothesized to be generated *in-situ* by using H₂bqdc linker and copper salt since it is difficult to synthesize such functionalized ligand by employing organic synthesis. The targeted MOF-based material was then expected to be assembled by applying solvothermal synthesis approach using appropriate reagents that enable the simultaneous *in-situ* control and generation of the tetrahedral metallo-linker and terbium based hexanuclear cluster building units that can be linked to each other leading to the 3D MOF structure. Inspection of the obtained crystal structure confirmed the hypothesis since it revealed that the MOF is an extended framework constructed from 4-c tetrahedral building unit, formed *in-situ* from N-donors of bqdc linker and copper, which is further coordinated to terbium hexanuclear cluster *via* eight carboxylate groups of the bqdc linker (Fig. 1).

Before undertaking any further characterization and sorption study, the purity of the synthesized MOF was established by comparing the simulated PXRD pattern from the crystal structure with the experimental PXRD patterns (Fig. 2). The similarity between the measured and calculated PXRD patterns clearly demonstrated the bulk phase purity of the synthesized compound.

Further analytical techniques were also performed on the fluorite MOF to validate the structure obtained by solving the SCXRD data. Elemental (CHN) analysis of the MOF after activation to remove guests from the pores supports the chemical formula as Tb₆Cu₂(OH)₈(H₂O)₄(2-FBA)₄(bqdc)₄ with the calculated and experimental C, H and N compositions being in very good agreement to each other (Table 2). The metal compositions of the compounds were further characterized and confirmed by ICP-OES analysis which gave Tb to Cu ratio of 3.1 and is in good agreement with the anticipated value (3.0) deduced from the SCXRD data (Tb₆Cu₂).

Thermogravimetric analysis (TGA) of the synthesized MOF shows weight losses in two steps (Fig. 3). The first step occurs till about 200 °C and corresponds to the loss of guest solvent molecules trapped inside the pores; including the coordinating water molecules. The second step which occurs around 350 °C can be attributed to

the thermal decomposition of the organic ligand leading to the final metal oxides. The residual combined weight % of Tb_2O_3 and CuO (38.5%) in the TGA of the solvent exchanged and dried samples measured in oxygen substantiates that the experimental weight losses are in good agreement to the calculated ones from the formulated crystal structures (39.1% combined Tb_2O_3 and CuO residue). Calculation was done based on the framework formula, $Tb_6Cu_2(OH)_8(C_7H_4FO_2)_4(H_2O)_4(C_{20}H_{10}N_2O_4)_4$, deduced from the SCXRD analysis.

Porosity analysis after collecting nitrogen sorption isotherm at 77 K (Fig. 4) indicated typical microporosity of the MOF with type I adsorption isotherm (according to the International Union of Pure and Applied Chemistry or IUPAC classification of isotherms) giving specific BET surface area of $688 \text{ m}^2\text{g}^{-1}$ and pore volume of $0.27 \text{ cm}^3\text{g}^{-1}$.

In addition to thermal stability, chemical and hydrolytic stabilities of materials are very important for deployment in industrial applications. Interestingly, the MOF showed excellent stability upon exposure to H_2O , H_2S and SO_2 as evidenced by the maintenance of crystallinity observed after months of exposure of the MOF crystals to these chemicals (Fig. 5A), which in turn makes the material very promising for sorption related applications involving these chemicals. These chemicals are chosen since they are common contaminants in natural gas and biogas streams. The MOF's H_2S stability was further supported by the retention of the material's CO_2 sorption uptake after long time exposure to H_2S . The performance of the material was not altered as the maximum CO_2 uptake was reached for H_2S exposed sample (Fig. 5B).

The excellent hydrolytic, chemical and thermal stability of the material in general and its high H_2S tolerance and stability in particular then became an impetus to further explore the potential of the prepared MOF-based adsorbent for the intended simultaneous removal of CO_2 and H_2S from different gas streams such as biogas and natural gas (which contains about 90% methane). To assess the potential of the MOF for simultaneous CO_2 and H_2S sorption and to assess the selectivity and stability, single gas and mixed gas sorption tests were performed. The single component sorption isotherms (Fig. 6) clearly evidenced the sorption of CO_2 and H_2S by the synthesized MOF with negligible uptake for methane at room temperature. In order to simulate real conditions that can exist in natural gas or biogas streams, the sorption experiment was then conducted using gas mixture composition of 5% H_2S /5% CO_2 /90% CH_4 . As shown in the Fig. 7, both H_2S and CO_2 are adsorbed by the MOF with favorable preferential

sorption for H_2S as evidenced by the higher retention time for H_2S than for CO_2 . As expected, CH_4 is not retained in the column reflecting the simultaneous capture and selective removal of CO_2 and H_2S from CH_4 (as in natural gas and biogas).

The H_2S/CO_2 selectivity of about 6.0 for the MOF-based adsorbent also suggests the potential of the MOF material for the selective removal of H_2S in presence of CO_2 . The captured H_2S is generally used in Claus process to produce elemental sulfur; however, this H_2S should have none or very low amounts of CO_2 and other impurities in order to achieve high efficiency conversion (Chardonneau et al., 2015). Materials like the Tb-Cu-bqdc-MOF reported herein that can remove H_2S preferentially over CO_2 and other impurities can therefore be useful for obtaining H_2S with acceptable quality for Claus process.

The reproducibility of the sorption profiles (Table 3) in turn promotes the MOF-based adsorbent as a strong candidate for industrially important and economically viable processes, vacuum swing regeneration (VSR) or pressure swing regeneration (PSR). The negligible N_2 uptake by the MOF was also proved experimentally by undertaking column breakthrough test using 100% nitrogen gas. The simultaneous sorption of H_2S and CO_2 together with negligible uptake of CH_4 and N_2 suggests that the MOF-based adsorbent can be suitable candidate for purification and upgrading of gas streams containing acid-gases.

Comparison of the performance of the MOF with an activated charcoal and other MOFs (Belmabkhout et al., 2017; Bhatt et al., 2017), previously explored for CO_2 and H_2S removal from natural gas under similar conditions used for this experiment, showed that the Tb-Cu-bqdc-MOF adsorbent offers a higher H_2S uptake and H_2S/CO_2 selectivity than the activated charcoal. The MOF adsorbent also showed comparable and in some cases better performance when compared with the previously reported MOF-based adsorbents investigated for similar acid gas removal application under similar experimental conditions (Belmabkhout et al., 2017; Bhatt et al., 2017). It is, however, worth mentioning that the breakthrough sorption uptakes shouldn't be considered as the maximum sorption capacities of the MOF sorbent at the temperature and pressure conditions used for the experiments. During breakthrough experiments, the full sorption capacity is not reached because it is a fast experiment not allowing thermodynamic equilibrium to be attained (MASD Barros, 2013). Breakthrough experiments mainly show the dynamics of the sorption process. The values can only be used to show the relative uptakes of the MOF for H_2S and CO_2 under the specified flow

rate and to compare results obtained under similar experimental conditions.

In conclusion, judicious choice of Tb and Cu based inorganic salts and H₂bqdc organic linker precursors under appropriate solvothermal reaction route led to *in-situ* generation of organic and inorganic molecular building blocks that are otherwise difficult to be obtained. The *in-situ* formed building units then enabled the assembly of mixed-metal MOF, Tb-Cu-bqdc-MOF, with underlying fluorite (CaF₂) topology. The synthesized compound displayed excellent stability towards H₂S, H₂O and SO₂ as evidenced by PXRD characterizations. The prepared porous MOF-based adsorbent material (BET surface area of 688 m²g⁻¹ and pore volume of 0.27 cm³g⁻¹) has also shown very promising potential to address simultaneous capture of CO₂ and H₂S from gas streams containing these acid gas impurities such as natural gas and biogas. The result was evidenced by both single gas and mixed-gas sorption tests performed at room temperature. Its high H₂S uptake (≈1.42 mmol g⁻¹ at room temperature and 1 bar up on using 10 cm³ min⁻¹ flow rate), favorable H₂S vs CO₂ selectivity (≈6.0), which outperform some common porous materials like activated charcoal, and negligible uptake of N₂ and CH₄ also offer great prospective to produce high-quality H₂S that can be used in Claus process. Prominently, the mixed metal approach to assemble MOF based adsorbent offers feasible alternative strategy to synthesize MOFs with properly adjusted pore system size and functionality when pre-synthesis of the organic ligand is difficult or impossible. Moreover, the fluorite MOF platform can still have huge potential for further adjustment of the pore system in order to achieve efficient separation of other gases/vapors.

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