

Fluorescence Sensing and Gas Sorption Properties of Water-Stable, Functionalized Metal- Organic Frameworks with Tetravalent Metal Ions and Carboxylate-Based Ligands

*A Dissertation
Submitted in Partial Fulfilment of the
Requirements for the Degree of
Doctor of Philosophy
by
Mostakim SK*



**Department of Chemistry
Indian Institute of Technology Guwahati
Guwahati-781039
INDIA
April 2019**

CERTIFICATE

This is to certify that the work presented in this thesis titled as, “**Fluorescence Sensing and Gas Sorption Properties of Water-Stable, Functionalized Metal-Organic Frameworks with Tetravalent Metal Ions and Carboxylate-Based Ligands**” submitted to the Indian Institute of Technology Guwahati by Mostakim SK, was worked out by the candidate at the Indian Institute of Technology Guwahati, under my supervision.

Dr. Shyam Prosad Biswas

Date:

(Researcher Supervisor),

Department of Chemistry,

Indian Institute of Technology Guwahati,

Guwahati, Assam, India, 781039

CANDIDATE'S DECLARATION

I hereby declared that my work on this thesis titled as, “**Fluorescence Sensing and Gas Sorption Properties of Water-Stable, Functionalized Metal-Organic Frameworks with Tetravalent Metal Ions and Carboxylate-Based Ligands**” submitted for the award of degree of *Doctor of Philosophy* in chemistry to the Indian Institute of Technology Guwahati.

Mostakim SK

Date:

Indian Institute of Technology Guwahati,

Guwahati, Assam, 781039, India



Dedicated to My

Beloved Family

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Thesis Title: Fluorescence Sensing and Gas Sorption Properties of Water-Stable, Functionalized Metal-Organic Frameworks with Tetravalent Metal Ions and Carboxylate-Based Ligands

Name of the Candidate: Mr. Mostakim SK

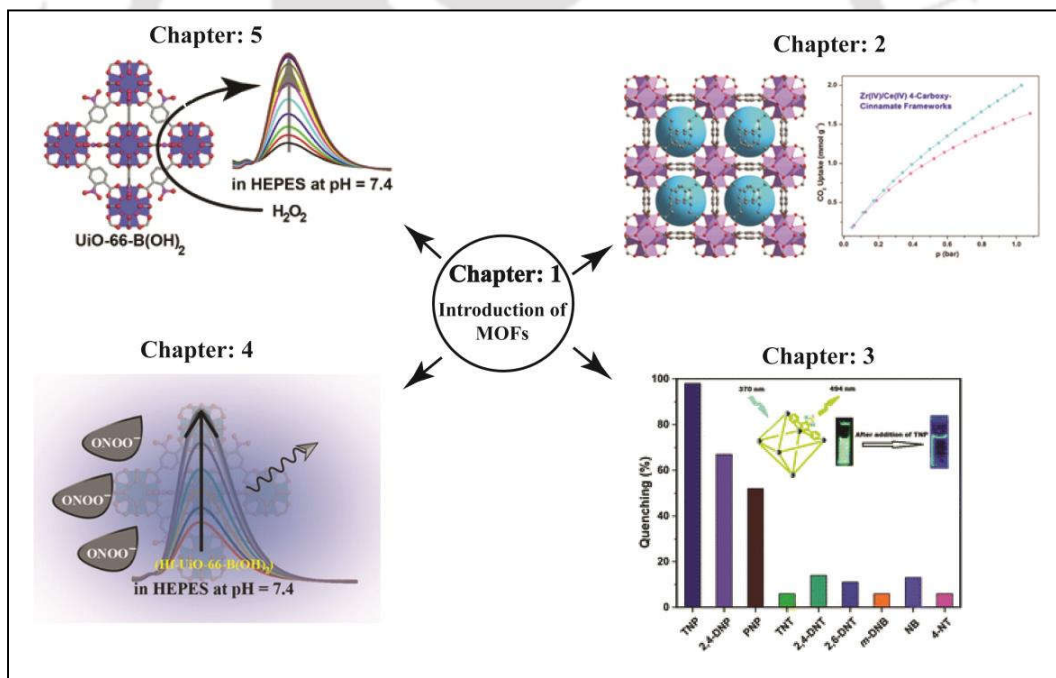
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Thesis Supervisor: Dr. Shyam Prosad Biswas

Department: Chemistry

Institute: Indian Institute of Technology Guwahati, Guwahati, Assam, 781039, India.

Thesis Overview:



Chapter 1: Metal-organic frameworks (MOFs) are a new class of highly porous coordination polymers. They are interconnected by the inorganic building units and organic linkers in a 2D or 3D fashion. MOFs have emerged as a new class of highly crystalline materials over other traditional porous materials such as zeolites, silicas, activated carbons, etc. MOFs have large surface areas and permanent porosity. Extending

the length of organic linkers leads to increase in pore sizes for the resulting MOFs. Attaching hydrophobic functional groups with the organic linkers enhances hydrophobicity of the MOFs. The tuneable functionality and precise arrangement of the organic linkers make them potential candidates for selective gas adsorption, separation, chemical sensing, proton conductivity, electrical conductivity, heterogeneous catalysis, photo-catalysis, drug delivery, etc. The MOF-based fluorescence sensing results from the incorporation fluorescent linkers or incorporation of f-block metal ions. Post-synthetic modification of MOFs also enhances some additional properties in chemical sensing, drug delivery, gas sensing, chemical stability, etc. Due to the formation of strong bonds between metal ions (specially in high oxidation states) and carboxylate groups of organic linkers, the resulting MOF materials show high thermal and chemical stability, which are desirable for practical applications such as gas adsorption and chemical sensing. Inspired by the above-mentioned advantages, a broad variety of MOF materials have been investigated for gas storage as well sensing of a wide range of analytes including cations, anions, biomolecules, small molecules, volatile organic compounds and nitro explosive materials.

Chapter 2 presents two different types of Zr(IV) and Ce(IV)-based MOFs having the same crystal structure. The compounds were synthesized under solvothermal conditions by using 4-carboxycinnamic acid (H_2CCA). Zr-MOF (**1**) was synthesized from a mixture of ZrCl_4 , H_2CCA ligand and acetic acid with a molar ratio of 1:1:10 in DMF at 150 °C for 24 h. Ce-MOF (**2**) was synthesized by solvothermal reaction of a mixture of ammonium cerium(IV) nitrate and H_2CCA ligand in a DMF/ H_2O mixture at 100 °C for 20 min. The as-synthesized and activated forms (**1'** and **2'**) of the compounds were characterized by XRPD (Figures 1 and 2), FT-IR, TG and elemental analysis. The TG analysis revealed that **1** and **2** show high thermal stability up to 390 and 300 °C in air atmosphere, respectively. The chemical stability of both compounds were characterized by XRPD measurements. Both compounds showed moderate stability in water, but they lost their crystallinity in 1 M HCl. N_2 sorption experiments revealed that **1'** and **2'** possess BET surface areas of 870 and 1210 $\text{m}^2 \text{g}^{-1}$, respectively (Figure 3). The CO_2 uptake values of **1'** and **2'** at 0 °C and 1 bar were 2.0 and 1.6 mmol g^{-1} , respectively.

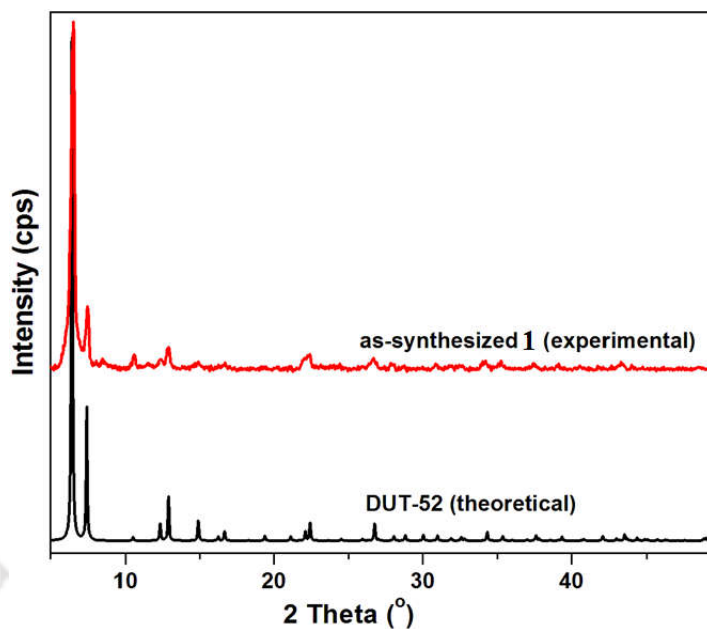


Figure 1. Theoretical (black) XRPD pattern of DUT-52 and experimental (red) XRPD pattern of as-synthesized compound **1**. (*Microporous Mesoporous Mater.*, 2017, **237**, 275-281)

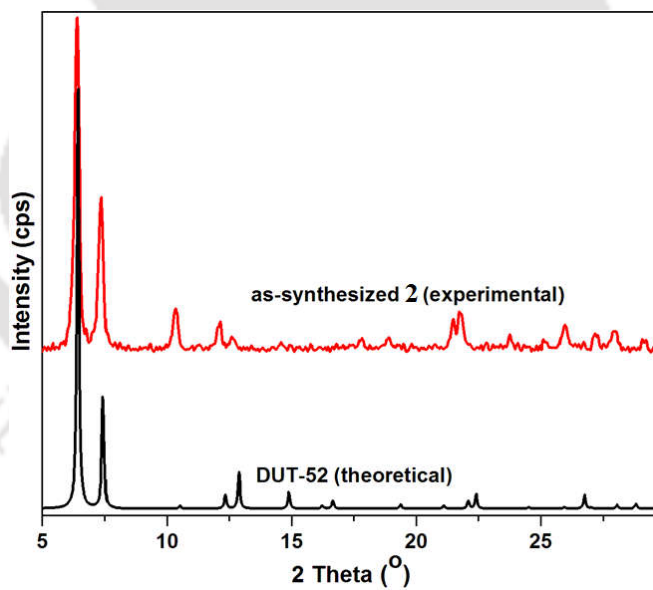


Figure 2. Theoretical (black) XRPD pattern of DUT-52 and experimental (red) XRPD pattern of as-synthesized compound **2**. (*Microporous Mesoporous Mater.*, 2017, **237**, 275-281)

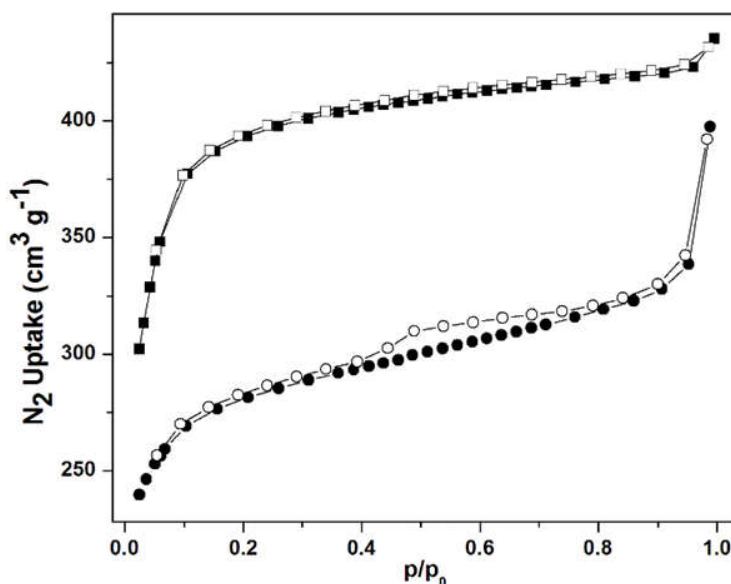


Figure 3. N₂ adsorption (filled symbols) and desorption (empty symbols) isotherms of **1'** (circles) and **2'** (squares) measured at $-196\text{ }^{\circ}\text{C}$. (*Microporous Mesoporous Mater.*, 2017, **237**, 275-281)

Chapter 3 presents a new fluorescent MOF called Zr-BTDB which was synthesized by using H₂BTDB {H₂BTDB = 4,4'-(benzo[*c*][1,2,5]thiadiazole-4,7-diyl)dibenzoic acid} ligand. Zr-BTDB was prepared under solvothermal conditions from a mixture of ZrCl₄, H₂BTDB and trifluoroacetic acid (used as a modulator) in DMF at $150\text{ }^{\circ}\text{C}$ for 24 h. The as-synthesized material (**3**) was characterized by XRPD analysis, FT-IR spectroscopy and elemental analysis. The thermal stability of **3** was envisaged by using TG analysis which revealed that **3** is stable up to $400\text{ }^{\circ}\text{C}$. The activated form (called **3'**) of **3** was obtained by solvent exchange with methanol, followed by heating under high vacuum. XRPD experiments verified that the activated **3'** retained its crystallinity when exposed to water, acetic acid and 1 M HCl solutions. From the steady-state fluorescence titration experiments of the activated compound **3'**, showed a selective sensing behavior towards 2,4,6-trinitrophenol (TNP, commonly known as picric acid) (Figure 4), even in the presence of other potentially competing explosive nitroaromatic compounds (Figure 5). The detection limit of **3'** was $1.63 \times 10^{-6}\text{ M}$. The fluorescence quenching ability of TNP can be ascribed to both energy and electron transfer processes as well as electrostatic interactions between the hydroxyl group of TNP and the Lewis basic N-donor sites of the BTDB ligand in the structural framework.

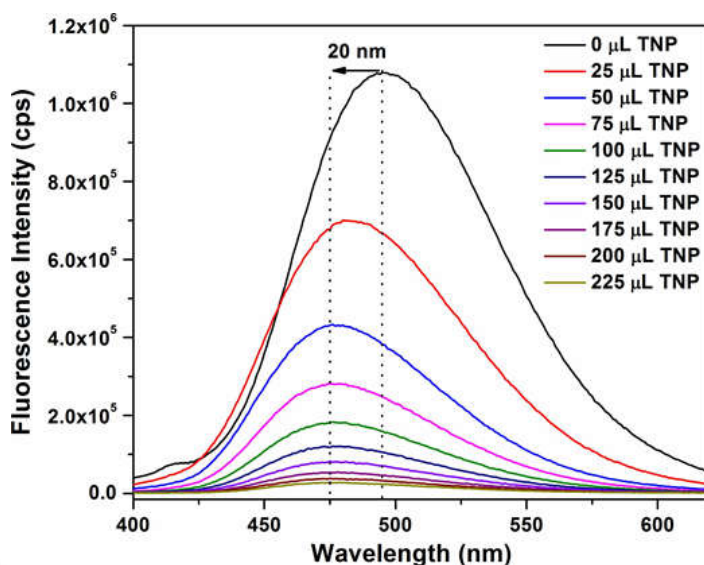


Figure 4. Quenching of the fluorescence intensity of **3'** by gradual addition of 3 mM TNP solution to a 3 mL well-dispersed methanol suspension of **3'** ($\lambda_{\text{ex}} = 370$ nm and $\lambda_{\text{max}} = 494$ nm). (*CrystEngComm*, 2016, **18**, 3104-3113)

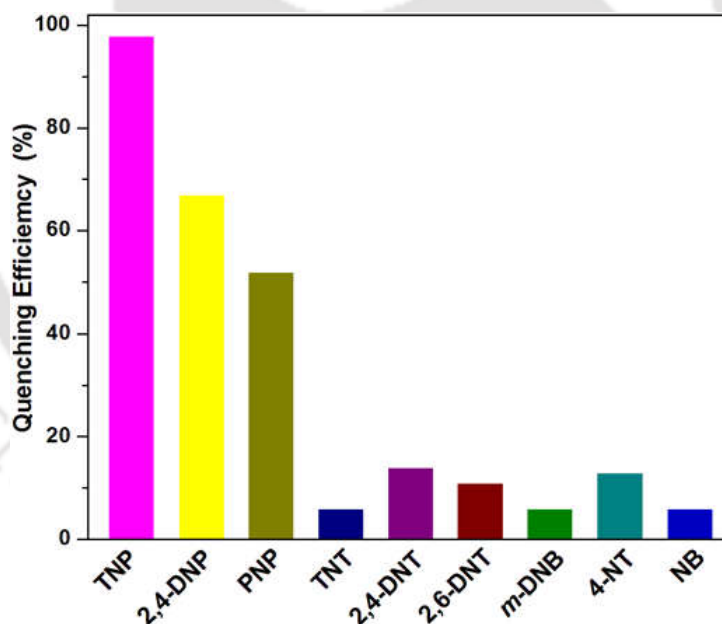


Figure 5. Fluorescence quenching efficiencies of various nitroaromatic explosives towards **3'** at 3 mM concentration ($\lambda_{\text{ex}} = 370$ nm and $\lambda_{\text{max}} = 494$ nm). (*CrystEngComm*, 2016, **18**, 3104-3113)

Chapter 4 presents a boronic acid functionalized Hf-based MOF called UiO-66-B(OH)₂ which has capability of selectively sensing of ONOO⁻ in live cells. Hf-UiO-66-B(OH)₂ MOF was synthesized from a mixture of HfCl₄ and 2-borono-1,4-benzenedicarboxylic

acid [$\text{H}_2\text{BDC-B(OH)}_2$] ligand in DMF in the presence of formic acid at 130 °C for 48 h. The phase purity of the as-synthesized material (**4**) was confirmed by comparison of XRPD pattern of **4** with the XRPD pattern of Hf-based UiO-66 framework (Figure 6). The as-synthesized material (**4**) was activated by exchange with methanol, followed by heating under high vacuum. The activated material (**4'**) was utilized as a fluorescent turn-on probe for the rapid sensing of extracellular peroxynitrite (ONOO^-) under conditions mimicking those of biological medium (10 mM HEPES buffer, pH 7.4) (Figure 7). Selective sensing of ONOO^- over other ROS/RNS was also achieved by **4'** (Figure 8). The selective turn-on sensing behavior towards ONOO^- can be ascribed to the oxidative cleavage of attached boronic acid groups forming corresponding hydroxy-functionalized ligands. The probe showed extraordinary sensitivity (detection limit = 9.0 nM) toward ONOO^- in 10 mM HEPES buffer at pH 7.4. The probe-loaded cells did not affect the cellular cytotoxicity and morphological deformities. It is remarkable that the probe inside the cells responded toward the ONOO^- solution to give an intense blue fluorescent signal. The fluorescence microscopy study with J774A.1 macrophage cells unambiguously demonstrated that probe **4'** is suitable to image peroxynitrite in living cells (Figure 9).

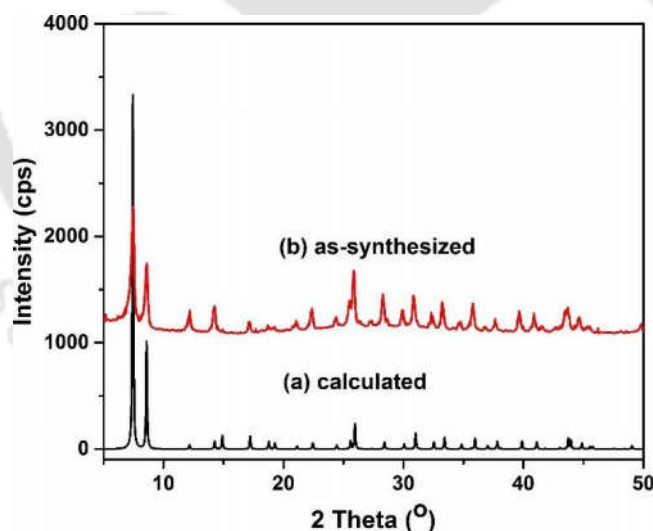


Figure 6. Comparison between (a) calculated XRPD pattern of Hf-UiO-66 and (b) experimental XRPD pattern of as-synthesized **4**. (*Inorg. Chem.*, 2018, **57**, 10128-10136)

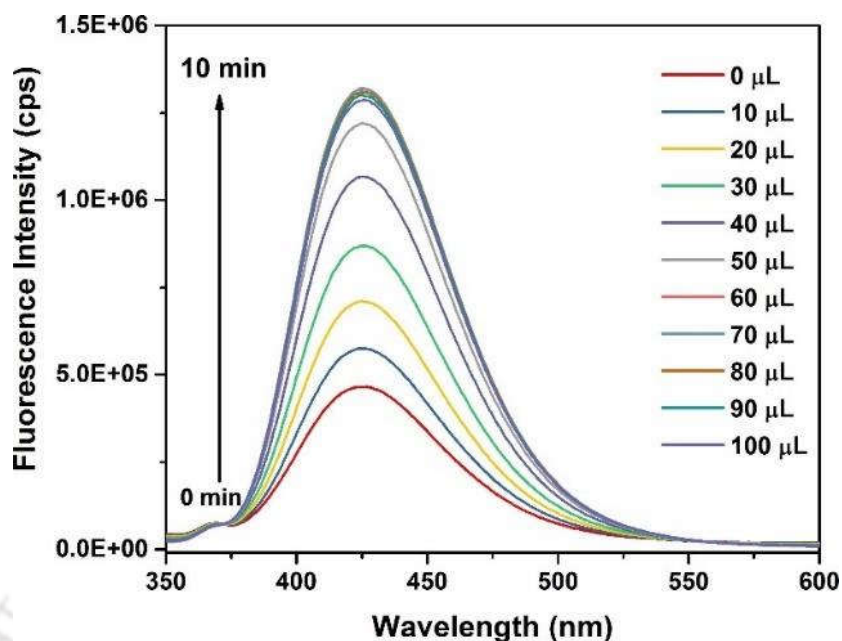


Figure 7. Selective turn-on response of 4' (in 10 mM HEPES buffer at pH = 7.4) upon incremental addition of 0.5 mM ONOO^- solution. (*Inorg. Chem.*, 2018, **57**, 10128-10136)

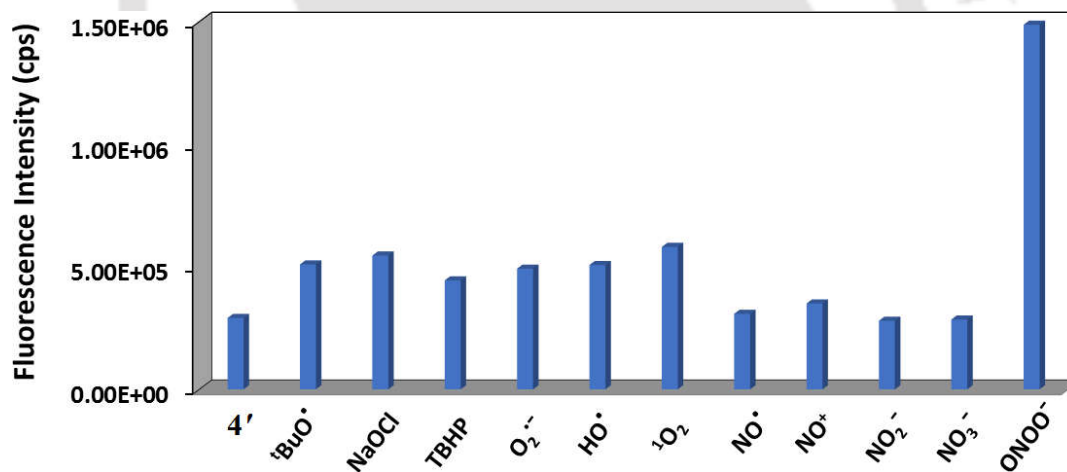


Figure 8. Comparative fluorescence enhancement behavior of 4' in HEPES buffer (10 mM, pH = 7.4) towards different ROS/RNS (4', 0.5 mM of $^t\text{BuO}^\bullet$, NaOCl, TBHP, $\text{O}_2^{\bullet-}$, $\text{HO}^\bullet$, $^1\text{O}_2$, $\text{NO}^\bullet$, NO^+ , NO_2^- , NO_3^- and ONOO^-) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 426$ nm). (*Inorg. Chem.*, 2018, **57**, 10128-10136)

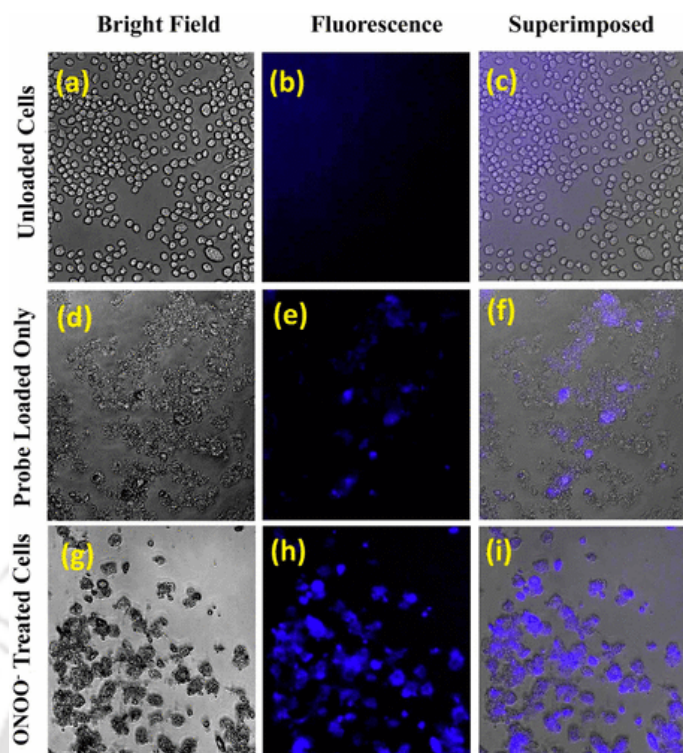


Figure 9. Sensing of ONOO^- in J774A.1 macrophage cells using **4'**. Bright-field (a, d, g) and fluorescence channel (b, e, h) images as well as their superposition (c, f, i) are shown for the unloaded cells, probe-loaded cells, and probe-loaded cells after treatment with ONOO^- . Remarkably, the cells loaded with probe **4'** ($5\ \mu\text{M}$) showed bright blue fluorescence after treatment with ONOO^- ($50\ \mu\text{M}$) solution (h, i). (*Inorg. Chem.*, 2018, **57**, 10128-10136)

Chapter 5 demonstrates a new boronic acid ($\text{H}_2\text{BDC-B(OH)}_2$) functionalized Zr(IV) metal-organic framework (Zr-UiO-66-B(OH)_2) having the capability of sensing H_2O_2 in live cells. XRPD analysis revealed that the structure of as-synthesized material (**5**) was similar as the UiO-66 framework (Figure 10). The activated material was denoted as **5'**. Compound **5'** was highly selective for fluorogenic detection of H_2O_2 in 10 mM HEPES buffer at $\text{pH} = 7.4$ (Figure 11), even in the presence of interfering ROS (ROS = reactive oxygen species) and other biologically relevant analytes (Figure 12). The fluorescent probe was found to display extraordinary sensitivity for H_2O_2 (detection limit = $0.015\ \mu\text{M}$) in HEPES buffer, which represents lower value than the MOF probes documented so far for sensing H_2O_2 using other analytical methods. For high selectivity and sensitivity of H_2O_2 in HEPES buffer, the probe was employed for the imaging of intracellular H_2O_2 . Imaging studies with MDAMB-231 cells revealed the emergence of bright blue fluorescence after loading with probe **5'** and subsequent treatment with H_2O_2 solution (Figure 13).

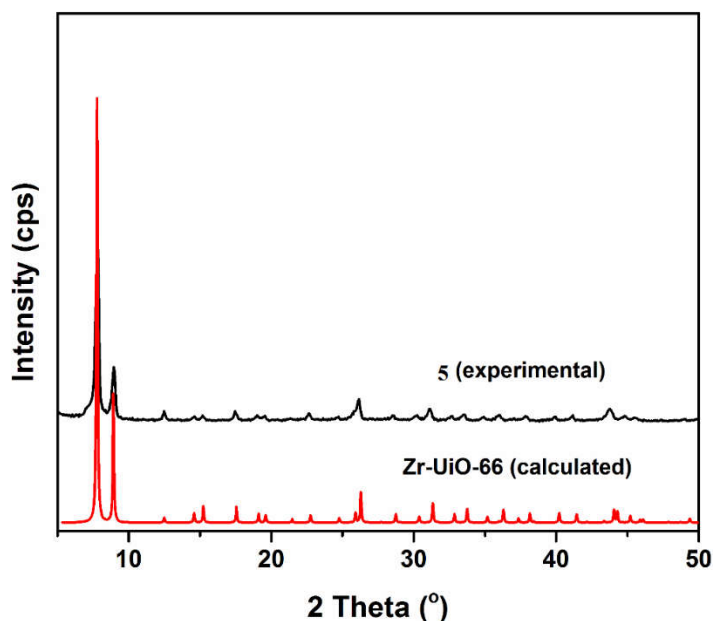


Figure 10. Comparison between the experimental XRPD pattern of **5** and calculated XRPD pattern of Zr-Uio-66. (*Inorg. Chem.*, 2018, **57**, 14574–14581)

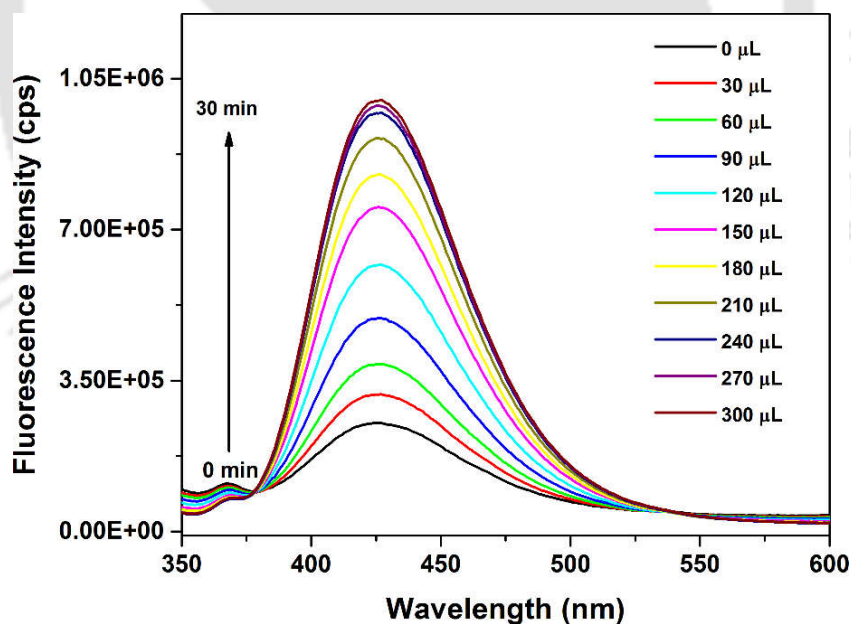


Figure 11. Fluorescence turn-on response of **5'** (suspended in 10 mM HEPES buffer, pH = 7.4) upon the stepwise addition of 10 mM H₂O₂ solution at room temperature. The spectra were collected after 3 min of each addition. (*Inorg. Chem.*, 2018, **57**, 14574–14581)

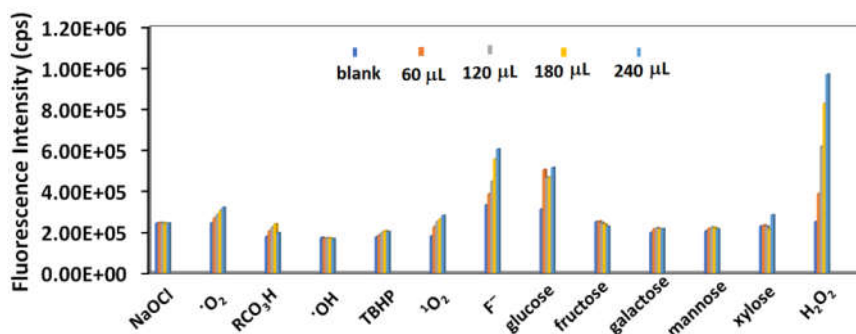


Figure 12. Fluorescence responses of **5'** (suspended in 10 mM HEPES buffer, pH = 7.4) upon the addition of solutions of various ROS (10 mM of ClO^- , $\text{O}_2^{\bullet-}$, $^t\text{BuO}^\bullet$, $\text{HO}^\bullet$, TBHP, $^1\text{O}_2$ and H_2O_2) and other biologically relevant species (10 mM of F^- , glucose, fructose, galactose, xylose and mannose) at room temperature. The bars denote fluorescence intensity after the addition of blank, 60, 120, 180 and 240 μL of each ROS. The spectra were collected after 6 min of each addition. (*Inorg. Chem.*, 2018, **57**, 14574–14581)

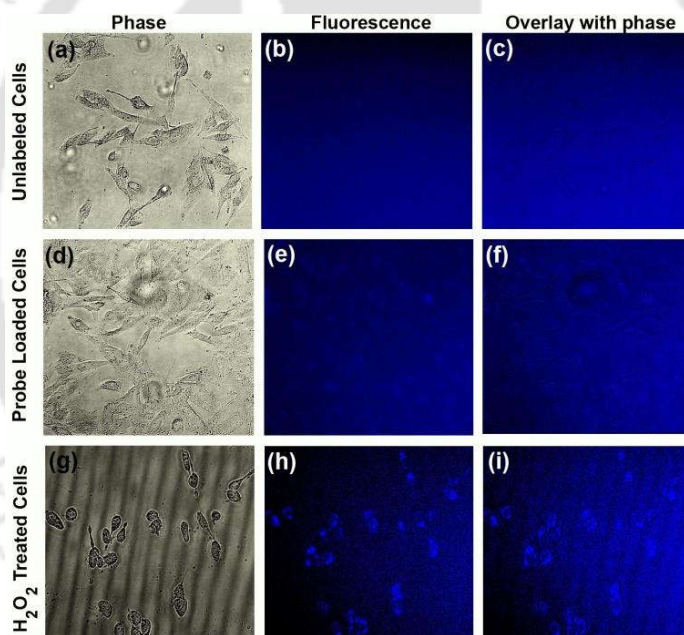


Figure 13. Detection of H_2O_2 inside the MDAMB-231 cells loaded with probe **5'**. The panel (a-c) is the unlabeled cells, (d-f) denotes probe-loaded cells and (g-i) represents probe-loaded cells treated with H_2O_2 . The cells either remained unloaded (a-c) or probe (5 μM) loaded cells either remained untreated (d-f) or treated (g-i) with H_2O_2 (1 μM) for 5 min at 37 $^\circ\text{C}$. The H_2O_2 -treated cells showed bright blue fluorescence as compared to the probe-loaded cells. An overlay of bright field and fluorescence images indicates that the fluorescence is arising from the cell. (*Inorg. Chem.*, 2018, **57**, 14574–14581)

1.1 Introduction

The storage and separation of gases in the modern era have important impacts on the ongoing research for the development of porous materials which are sustainable. The use of fossil fuels immensely affects the environmental balance due to the release of pollutants emitted during the burning of these fuels.¹ The by-product during the burning of fossil fuels is one of the world's most threatened pollutant to human health and future.² Globally, the majority of pollutant gases come from the burning of coal, diesel fuel, gasoline, oil, and natural gas for the generation of electricity, heating, transportation and industry.² Therefore, continuous emission of these gases increases global warming and hazardous gases have immense effects on human health. To solve the problems of gaseous pollution, porous materials can be used for the storage/separation of gaseous compounds.

Other than gaseous pollutants, toxic anions, metal ions, nitroaromatic explosive, volatile organic compounds, etc. may pollute the environment. One of the important routes to detect the metal ions, explosive compounds, biomolecules, organic vapors, moisture and contaminations of water is chemical sensing. Chemical sensing can be achieved due to quenching or enhancement of fluorescence of the probe. Nowadays, the luminescent porous materials are one of the best probes to confirm the real interactions between analytes and probes. These luminescent porous materials are reusable because of their high robustness and high thermal and chemical stability. Due to porosity and pore sizes of these materials, the target analytes can enter into the pores of these materials and interact with the probe.

Old porous materials (such as zeolites, activated carbons, metal hydrides, chalcogens, etc.) have low void space, pore size and less possibility of functionalization. In addition, less number of functionalized materials are employed for chemical sensing, biological and cell imaging applications.³ Owing to these drawbacks of these old porous materials, there is a urgent need of new porous materials which will overcome all difficulties of traditionally used porous materials.

In this regard, a new class of crystalline porous materials called metal-organic frameworks (MOFs) has been developed with high surface areas and pore volumes.⁴ They attract significant interest for their promising applications in fluorescence based chemical sensing as well as gas adsorption/separation,⁵ metal ions,⁶ chemical sensing,⁷ drug delivery,⁸ proton conduction⁹ and heterogenous catalysis.¹⁰ However, several MOFs

(example: MOF-5)¹¹ are very sensitive to water due to lability of the metal-ligand bonds and presence of open metal sites.¹² They are gradually decomposed when the water molecules interact with the frameworks. To overcome these difficulties, high valent metal ions have been used to increase the stability of metal-ligand bond.¹³ Organic ligands containing hydrophobic groups enhance the water stability of the MOF materials. In addition, O-donor ligands form strong bond with metal ions in comparison with N-donor organic ligands. The stability of the MOFs in water is required for applications in aqueous and humid conditions.

1.2 Basic Principles for Design of MOF Materials

Two different types of strategies have been employed for the synthesis of MOF materials. They are mainly:

- i. Node and Spacer.
- ii. Secondary Building Units (SBUs).

1.2.1 Node and Spacer

This strategy can be applied to construct extended MOF structures. The organic ligands are generally termed as ‘spacers’ and metal ions as ‘nodes’. The shape of spacers and nodes may have different types (e.g. square, tetrahedral, octahedral, etc) which are utilized during the synthesis of MOFs. Several combinations of organic ligands with the metal ions lead to the formation of metal-organic networks with diverse topology.¹⁴ Figure 1.1 represents the different organic ligands with linear, angular, trigonal and tetrahedral shapes.

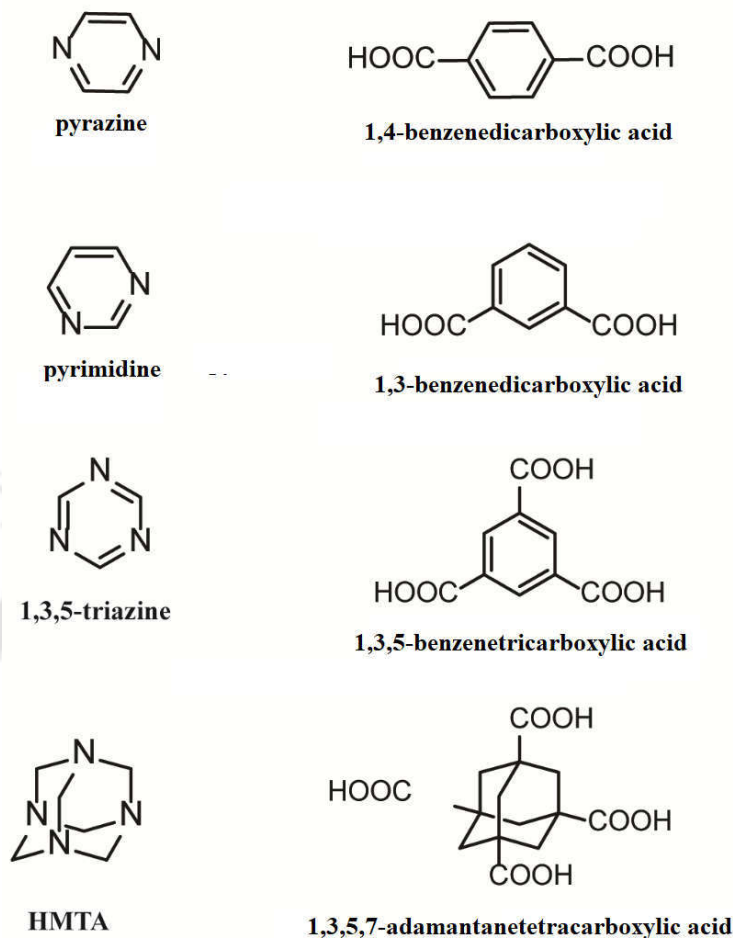


Figure 1.1 Examples of organic ligands for the construction of MOFs (HMTA = hexamethylenetetramine).

1.2.2 Secondary Building Units (SBUs)

The term ‘secondary building unit’ is generally used in the zeolite chemistry where the SBUs are denoted as main structural motif which occur in various tetrahedral frameworks.¹⁵ Yaghi and co-workers have introduced the ‘secondary building unit (SBU)’ strategy for the construction of rigid and porous frameworks. These SBUs are constructed from the metal clusters and organic ligands which form well-defined and systematic coordination structures. The SBUs in MOFs act as rigid vertices which are connected with the organic ligands to construct the 3D structures of MOFs with permanent porosity (Figure 1.2).¹⁶

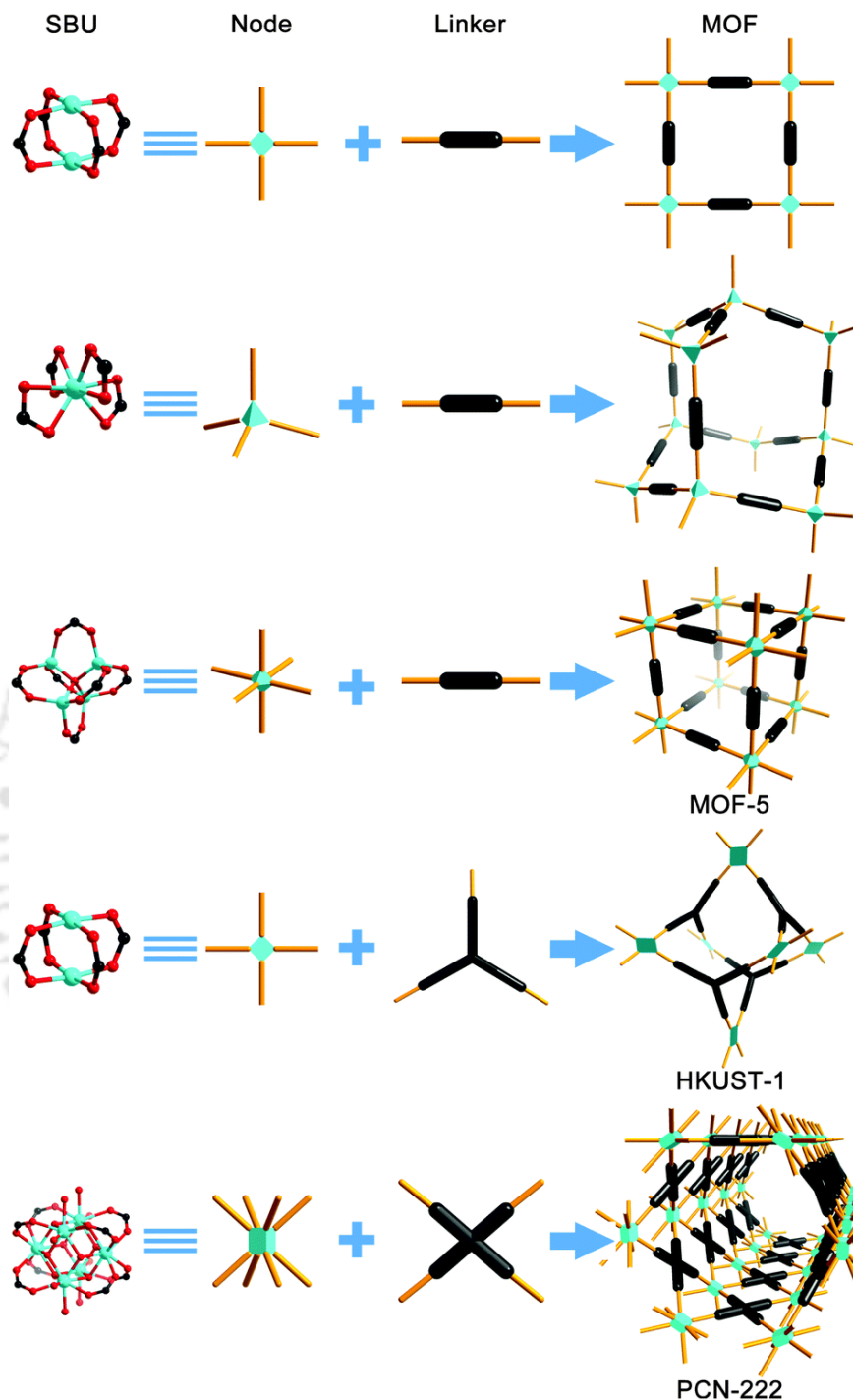


Figure 1.2 The formation of MOF materials via coordination of the organic ligands with SBUs. These constructions lead to the formation various MOFs (metal ion = sea green; carbon = black; oxygen = red and linker = black rod shape). Reproduced with permission from ref. 16. Copyright 2005 Royal Society of Chemistry.

1.3 Basic Strategies for Design of Water-Stable MOFs

The presence of water molecules results in decomposition of MOF materials due to lability of metal-ligand bonds and presence of open metal sites.¹² The stability of MOF materials in the presence of water is highly desirable when MOFs are utilized for adsorption/separation in humid conditions,¹⁷ and detection of toxic metals,¹⁸⁻²¹ pharmaceutical ingredients,^{22, 23} harmful pollutants²⁴⁻²⁶ in aqueous phase.^{27, 28} In order to design the water-stable MOF materials, the following strategies have been used:

- i. The strong metal-ligand bond contributes to the hydrolytic stability of MOF materials in water. Strong bond between metal and ligand prevents the attack from water molecules.²⁹ Valency of metal ions can govern the chemical stability of MOFs. The high valent metal ions (such as, Zr(IV), Hf(IV), Ce(IV), Ti(IV), etc.) form strong bonds with ligands which is crucial for high water stability of MOFs.³⁰⁻³⁵
- ii. Hydrophobicity of the organic ligands can play important role for improving the stability of MOFs in water. The hydrophobicity can be incorporated into MOFs by using hydrophobic fluorinated and alkyl-functionalized organic ligands during the synthesis of MOFs.³⁶⁻³⁸
- iii. Steric factors in MOFs can reduce the close interactions between water molecules and metal clusters of MOFs. The steric factors in MOFs can be introduced by increasing the coordination number of metal ions^{32, 33} and incorporating bulky side functional groups in the organic ligands, which create a crowding effect around metal ions.

1.4 Synthesis Procedures of MOF Materials

MOF compounds have two major units: metal ions and organic ligands. Usually, the organic ligands consist of aromatic³⁹ and aliphatic carboxylates,⁴⁰ imidazoles,^{41, 42} triazoles,⁴³ tetrazoles,⁴⁴ pyridyls⁴⁵ etc. The metal ions can be chosen from the periodic table depending on their oxidation states as well as coordination modes. Numerous possibilities of the binding modes of the metal ions can build up the MOF materials with different topologies. The coordination mode of the organic ligands can be also tuned to synthesize MOF materials with different structural geometries (Figure 1.3).

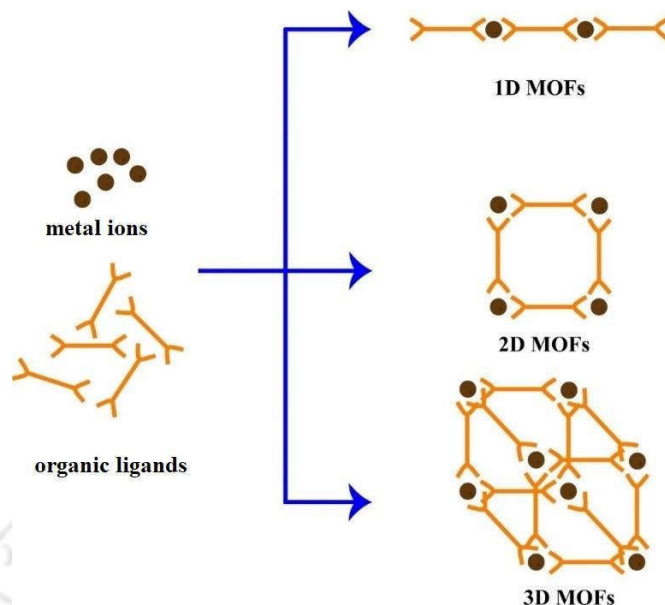


Figure 1.3 Schematic showing synthesis of MOFs from metal ions and organic ligands to form 1D, 2D or 3D MOFs depending on degree of extension.

All the MOF materials are crystalline in nature and their structures can be determined by single-crystal or powder X-ray diffraction method. For single-crystal X-ray diffraction analysis, single-crystals of MOFs with acceptable size are required. On the other hand, crystalline powder phase of MOFs is required for powder X-ray diffraction method. In the following section, the different methods which are used to get the single-crystals and powder forms of MOF materials are discussed.

1.4.1 Solvo/Hydro-thermal Synthesis Using Electric Heating

Solvothermal reaction occurs in a closed reaction vessel where reaction is carried out at a temperature higher than the boiling point of the used solvent under autogenous pressure.⁴⁶ Generally, Teflon-lined steel autoclave reactors (Figure 1.4) are used for solvothermal reaction. At higher temperature, viscosity and dielectric constant of the solvent are reduced. Reduction of viscosity and dielectric constant increases the diffusion process of the solvent molecules and consequently enhances the crystal growth process.

The method of hydrothermal synthesis is similar to the solvothermal synthesis, except that corresponding solvent is replaced by water during hydrothermal synthesis.



Figure 1.4 Image of the different parts of a Teflon-lined steel autoclave used in solvo/hydro-thermal reaction for the synthesis of MOF materials.

1.4.2 Solvothermal Synthesis Using Microwave Radiation

Microwave-assisted synthesis of MOFs is mainly based on the interactions of electromagnetic waves with mobile electric charges of metal ions and ligands.⁴⁷ By applying the acceptable frequency, the collision between the molecules/ions takes place, which leads to increase in kinetic energy and enhancement in rate of reaction.⁴⁷ The microwave-assisted MOF synthesis has several advantages such as acceleration of crystallization process, reduction of synthesis time and formation of products with high purity (Figure 1.5).⁴⁸

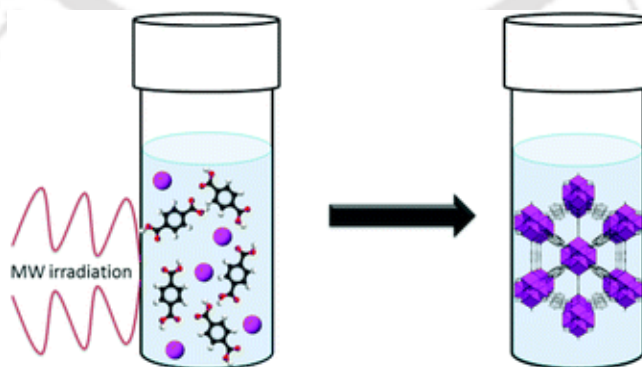


Figure 1.5 Microwave-assisted synthesis of highly crystalline UiO-66 MOF. Reproduced with permission from ref. 48. Copyright 2015 Royal Society of Chemistry.

1.4.3 Room Temperature Synthesis

Room temperature synthesis of MOF materials is the easiest method where high temperature or high pressure is not needed (Figure 1.6).⁴⁹ Synthesis is conducted in open vessels at ambient temperature and pressure by mixing the starting materials in a polar solvent.⁵⁰ Polar bases like triethylamine, ethylamine, 2,6-lutidine etc. are used as bases, which deprotonate the organic ligand to precipitate the MOF compound.

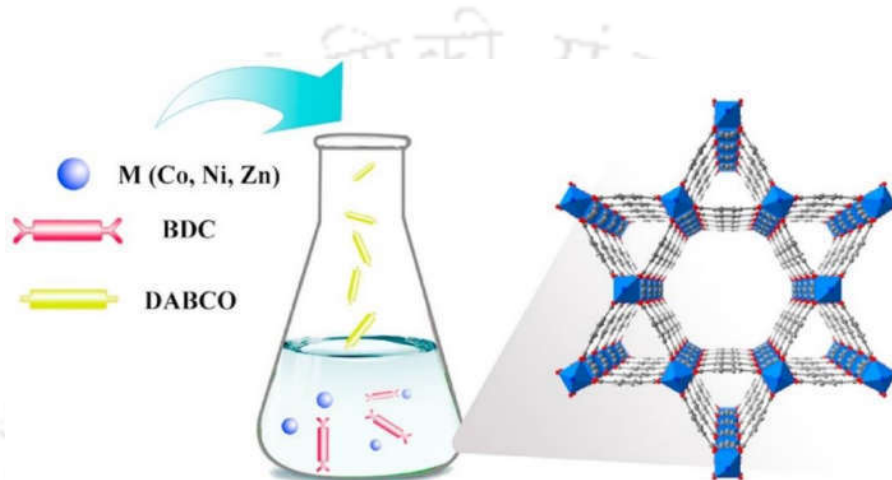


Figure 1.6 Room temperature synthesis of highly crystalline $M_2(bdc)_2(dabco)$ ($M = \text{Zn(II)}, \text{Ni(II)}, \text{Co(II)}$; $bdc = 1,4\text{-benzene dicarboxylate}$ and $dabco = 1,4\text{-diazabicyclo[2.2.2]octane}$) MOFs. Reproduced with permission from ref. 49. Copyright 2017 Elsevier.

1.4.4 Mechanochemical Synthesis

Mechanochemical method for the synthesis of MOF material is an environment friendly process. In mechanochemical synthesis, external forces are applied to synthesize MOF materials.⁵¹ In this method, the mechanical forces break the intramolecular bonds followed by a chemical transformation. Starting materials are mixed in a steel reactor containing a steel ball, or mortar and pestles are used to mix the reactants.

1.4.5 Electrochemical Synthesis

In electrochemical synthesis, electromotive force is applied to prepare the MOF materials. During synthesis of MOF by this method, metal ions are continuously

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introduced through anodic dissolution rather than the addition of metal salts, which react with the ligands present in the reaction medium (Figure 1.7).⁵²

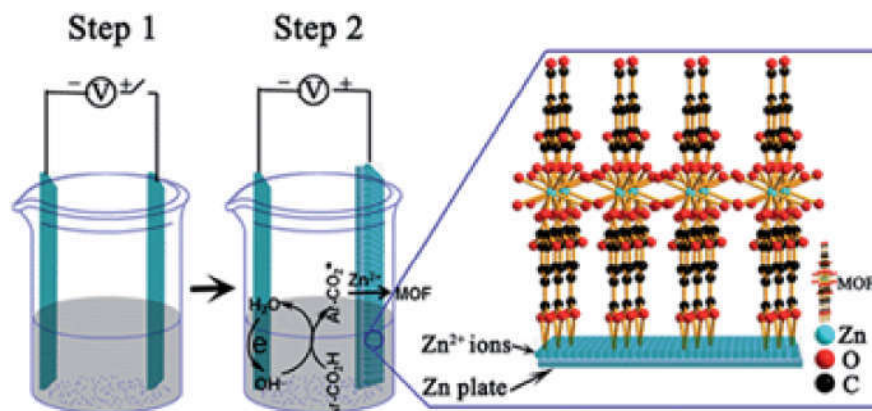


Figure 1.7 Electrochemical synthesis of highly crystalline $\text{Zn}_3(\text{BTC})_2$ (BTC = 1,3,5-benzenetricarboxylate) MOF. Reproduced with permission from ref. 52. Copyright 2014 Royal Society of Chemistry.

1.4.6 Post-Synthetic Modification

Direct synthesis of functionalized MOF materials is restricted because of the reactivity of labile functional groups during the solvothermal synthesis. Modification of the functional groups in the framework can be achieved by post-synthetic modification (PSM).⁵³ In PSM, the MOF materials are initially synthesized with the inert functional groups and subsequently those functional groups are transformed into reactive functional groups. As a result, newly functionalized MOFs are obtained.⁵³

1.5 Applications of MOFs

The old porous materials like zeolites, carbon nanotubes, activated carbons, metal hydrides, clathrates etc. are used for gas adsorption/separation,⁵⁴ separation of metal ions,⁵⁵ gas sensing,⁵⁶ catalysis, etc.⁵⁷ They have limited applications due to their low possibility of synthetic expansion.⁵⁸ Clathrates and metal hydrides mostly follow the chemisorption rather physisorption in gas separation applications.⁵⁹ The chemisorption is an irreversible process. Hence, these materials are not suitable for real field application in terms reusability. Separation of metal ions by zeolites has limited applications due to the

availability of a limited number of functional groups present in zeolites.⁶⁰ Zeolites, metal hydrides and activated carbons are used as heterogeneous catalysts. But, large substrates cannot enter into their smaller pores during catalysis.^{58, 61} Thus, applications of the traditional porous materials are restricted in several fields.

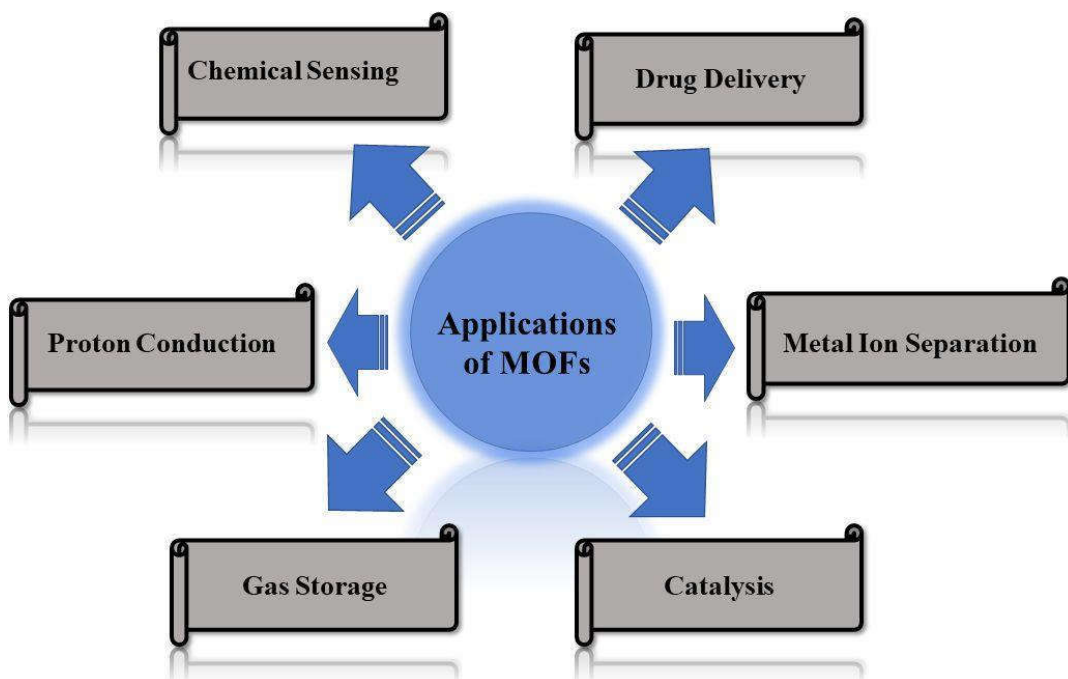


Figure 1.8 Various representative applications of MOFs.

MOFs are now more promising candidates over other old porous materials due to their tunable pore size, surface area and diverse functionality. By changing the lengths of the ligands, MOFs with various surface areas can be obtained. In addition, incorporation of different ligands can change the pore sizes of the MOFs and enhances the selectivity towards the target gas molecules. In addition, introduction of various functionality in the ligands present in the framework can enhance the selective sensing nature of the material. Moreover, this functional group incorporation process in the framework does not alter the structural integrity of the MOF material. The high crystallinity of MOF allows the accurate structure determination by X-ray diffraction method, which permits the exact knowledge of atomic positions and interactions that may be involved in the detection of an analyte or adsorption of a gas. Several MOFs with coordinatively unsaturated metal sites promote gas adsorption. Other than the pore size and active site, the microenvironment present in MOF material ensures close interactions between the MOF and analyte species during

sensing event. Additionally, the stability of MOF material in water medium including harsh conditions makes it a promising candidate for real field applications in gas storage and fluorescence sensing over other porous materials. Recently, MOFs are utilized in several fields like gas separation/storage,^{5, 62, 63} fluorescence sensing,⁶⁴⁻⁶⁷ photocatalysis,^{68, 69} proton conduction⁹ and drug delivery (Figure 1.8).⁷⁰ In this thesis work, we have mainly focused on gas adsorption and fluorescent based chemical sensing applications of MOF materials.

1.5.1 CO₂ Adsorption

The combustion of fossil fuels such as coal, petroleum and natural gas, etc. is the major sources of CO₂ emission, which contributes above 80% of greenhouse gas to the environment.⁷¹ The annual increment of global emission of CO₂ is approximately 80% between 1970 and 2004. It is predictable that continuous increase of CO₂ emission will happen due to economic growth and industrial development. To solve this global problem, urgent need of technologies/processes are required to reduce the atmospheric CO₂ levels. Several processes have been employed for the effective capture and separation of CO₂ such as chemical adsorption with solvents, membrane separation, adsorption with solid adsorbents, electrochemical separation, cryogenic separation and fuel cells.⁷² The most crucial parameter of any CO₂ capturing material is high selectivity toward CO₂ over other gaseous components for complete removal of CO₂ from a mixture of gases. The affinity of the material toward CO₂ is an important parameter which controls interaction of CO₂ toward the material. But, if the interaction is too strong, a high energy will be required in order to release the captured CO₂. Weak interaction lowers the regeneration cost but it may lower the selectivity towards CO₂. Hence, those materials which exhibit high stability under the conditions of capture and release of CO₂, is preferable to reduce the environmental CO₂.

The CO₂ adsorption and storage capacity of porous materials can be estimated by both volumetric and gravimetric methods. The volumetric adsorption of CO₂ refers to how densely CO₂ is present within the porous material whereas the gravimetric CO₂ adsorption corresponds to the quantity of CO₂ adsorbed within a unit mass of the porous material. The porous materials are preferred as potential candidates for CO₂ adsorption owing to their high porosity and surface area. The CO₂ storage and adsorption within the pores of the

porous materials depend on various factors including open metal sites⁷³, surface functionalization⁷⁴ and structural defect.⁷⁵ Along with porous materials, aqueous alkanolamine solutions (such as monoethanolamine, triethylamine, etc.) have great affinity towards CO₂. These alkaline solutions react with CO₂ and form carbamates or bicarbonates,^{76, 77} as shown in Figure 1.9.

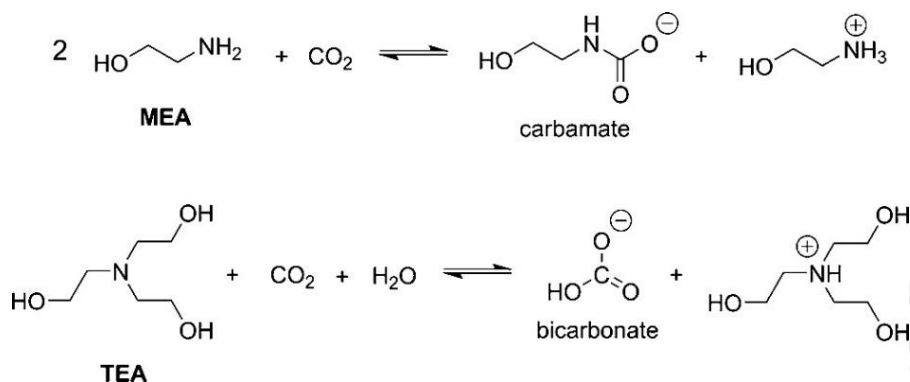


Figure 1.9 First row represents the reaction of CO₂ with basic monoethanolamine (MEA) to give carbamate product (upper), and second row represents the corresponding reaction with triethanolamine (TEA) resulting in a bicarbonate species (lower). Reproduced with permission from ref. 77. Copyright 2012 American Chemical Society.

The alkaline amine solutions are not useful for CO₂ storage in spite of high affinity of these solutions towards CO₂ because these carbamates or bicarbonates are relatively unstable towards heat. Moreover, due to instability of amine compounds, lifetime of the compounds decreases and performance of the compounds is reduced day by day. In addition, the corrosive nature of the amine solutions prevents their applications in practical purpose. Compared to absorption process, the removal of CO₂ via adsorption technologies has drawn more attention because solid adsorbents have shown energy-efficient CO₂ uptake with good regeneration. Solid adsorbents such as activated carbons, zeolites, basic oxides and hydrolytic materials have been employed for CO₂ uptake. Recently, zeolite LTA is utilized for CO₂ adsorption but it is not useful because of its high hydrophilic nature.⁷⁸ To overcome this problem, hydrophobic activated carbon is employed which shows effective adsorption of CO₂ compared to zeolite. Hence, development of robust porous materials having high affinity towards CO₂ is highly desirable. Recently, MOF materials are considered as potential candidates for CO₂ adsorption due to their unique

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structural properties including robustness, high internal surface areas, high chemical and thermal stabilities and functionalization with basic amine groups (example: IRMOF-74-III-(CH₂NH₂)₂).⁷⁹ In addition, the presence of coordinatively unsaturated metal centers (i.e. open metal sites) in the frameworks provides Lewis acidity to MOF materials. Along with large surface area and pore volume, the available open metal sites in some MOFs (example: M₂-dobdc or M-MOF-74; M = Mg, Mn, Fe, Co, Ni, Zn; dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate)⁸⁰ make them promising materials for CO₂ uptake. The MOF materials which are utilized for CO₂ adsorption are documented in Table 1.1.

Table 1.1 Representative examples of MOF materials used for CO₂ adsorption.

MOFs	Conditions	Adsorbed Amount (mmol/g)	Ref.
Mg-MOF-74	298 K, 1 bar	8.48	81
HKUST-1	298 K, 1 bar, 4% hydrated	8.18	80
Mg-MOF-74	296 K, 1 atm	8.00	82
Co-MOF-74	298 K, 1 bar	7.55	81
Ni-MOF-74	298 K, 1 bar	7.15	81
Co-MOF-74	296 K, 1 atm	6.95	82
Mg-MOF-74	298 K, 1 atm	6.98	83
Ni-MOF-74	298 K, 1 atm	6.98	83
bio-MOF-11	273 K, 1 bar	6.00	84
Ni-MOF-74	296 K, 1 atm	5.82	82
Zn-MOF-74	296 K, 1 atm	5.54	82
Ni-MOF-74	303 K, 1 atm	5.00	85
HKUST-1	295.25 K, 1 bar	4.20	86
bio-MOF-11	298 K, 1 bar	4.10	84
HKUST-1	298 K, 1 bar	4.07	87
CUK-1	298 K, 760 torr	3.48	88
YO-MOF	273 K, 1 atm	3.39	89
SNU-M10	273 K, 1 atm	3.3	90

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H ₃ [(Cu ₄ Cl) ₃ (BTtri) ₈]	298 K, 1 bar	3.25	91
USO-2-Ni-A	303 K, 1 atm	3.18	92
USO-1-Al-A	303 K, 1 atm	2.73	92
ZIF-69	273 K, 1 atm	2.26	93
HKUST-1	318.15 K, 1 bar	2.60	86
Ni-STA-12	298 K, 1 bar	2.60	94
[Pd(μ-F-pymo-N ¹ ,N ³) ₂ ·(H ₂ O) _m] _n	293 K, 650 torr	2.49	95
[Fe(PZ)Ni(CN) ₄]	298 K, 1 bar	2.48	96
MIL-53(Cr)	303 K, 0.1 Mpa	2.39	97
USO-1-Al	303 K, 1 atm	2.27	92
MOF-5	296 K, 1 bar	2.10	98
SNU-M10	298 K, 1 atm	2.10	90
USO-2-Ni	303 K, 1 atm	2.05	92
amino-MIL-53(Al)	288 K, 1 bar	2.00	99
MIL-53	304 K, 1 bar	2.00	100
UoC-1	273 K, 1 bar	2.00	101
MOF-5	298 K, 1 bar	1.92	98
[Cu ₂ (IMTA)(DMSO) ₂] ₂ ·2H ₂ O	298 K, 1 bar	1.80	102
ZIF-100	273 K, 1 atm	1.70	103
[Pd(2-PYMO) ₂] _n	298 K, 1 atm	1.68	104
SNU-9	273 K, 1 atm	1.25	105
Zn ₂ (L ₁)(bpy)	298 K, 1 bar	1.14	106
[Cu ₂ (HBTB) ₂ (H ₂ O)(EtOH)]·H ₂ O·EtOH	298 K, 1 bar	1.00	107
[Cu ₃ (m-TATB) ₂ Py(CH ₃ OH) ₂]	273 K, 1 atm	0.82	108
[Zn ₂ (L ₂)(py-CF ₃) ₂] _n	98 K, 1 bar	0.62	109
[Mg(HCOO) ₂ ·(H ₂ O) ₂]	298 K, 700 torr	0.30	110
ZIF-20	273 K, 760 torr	0.16	111

Ligand abbreviations: BTtri = 1,3,5-tris(1H-1,2,3-triazol-5-yl)benzene; pymo = 5-fluoropyrimidin-2-olate; PZ = pyrazine; IMTA = imidazolium tetracarboxylic acid; BTB = 1,3,5-tris(4-carboxyphenyl)benzene; L₁ = tetrakis[4-(carboxyphenyl)oxamethyl]methane; bpy = 4,4'-bipyridine; L₂ = 4,4',4'',4'''-benzene-1,2,4,5-tetrayltetrazobenzoic acid; py-CF₃ = 4-(trifluoromethyl)pyridine.

1.5.2 Fluorescence Based Chemical Sensing

Across the globe, various pollutions are rapidly increasing year by year. The development of new technologies, industrial growth, human activities, etc. are responsible for the enhancement of urban pollutions.¹¹² Exposure of these pollutants causes the contamination of water, abnormality on human health and air pollution.¹¹³ The development of efficient and eco-friendly chemical sensors is therefore crucial for the detection of environmental pollutants including toxic metal ions, anions, nitroaromatic explosives, biomolecules and organic compounds.¹¹⁴

Several methods have been reported so far including electrochemistry,^{115, 116} gas chromatography,¹¹⁷ liquid chromatography,¹¹⁸ and GC-MS^{118, 119} for the detection of various analytes. Fluorescent-based chemical sensing has several advantages over above-mentioned traditional analytical methods because of its high selectivity towards the target analyte. Moreover, the fluorescence based method can be applied in various fields including biological system, cell imaging, explosive sensing and industrial application.^{120,}

¹²¹ Due to high solubility of organic molecules in sensing medium, it is difficult to separate them, which prevents their reusability. Sometimes, organic molecules show toxicity towards living cells. This also restricts their use in real biological environment. Recently, the development of fluorescent MOF-based porous materials has attracted over other sensor materials for selective detection of various analytes in many fields including chemical threat detection, bioimaging, food quality control and medical diagnostics.¹²²⁻¹²⁵ The MOF-based fluorescent probes have various advantages over other small organic molecules-based probes because of the following factors: (i) the synthesis of MOF materials is much more straightforward than other probes;¹²⁴ (ii) the exact structures of MOFs can be determined by X-ray diffraction method as the MOFs are crystalline in nature, which is helpful for describing the actual interaction of MOFs with the analytes;¹²⁶ (iii) due to the porous nature of MOFs, the close interactions between MOFs and analytes can occur, which enhance their selectivity towards desired analyte.¹²⁷ Moreover, functional groups, Lewis acid-base and open metal sites within the MOF materials can act as active sites for the detection of different analytes.¹²⁸⁻¹³⁰ The selective interaction of the target analyte with the active metal sites within the MOFs can result in increment in detection performance with lower detection limit up to the level of single molecule. In addition, incorporation of fluorescent organic ligands or fluorescent dyes in the rigid

MOFs can lead to the formation of fluorescent MOF materials which emit stronger fluorescence that might be visible in the naked eye.¹²⁹ The fluorescence properties of MOFs can be generated from either organic ligands or metal ions. The origin of fluorescence in ligand centered fluorescent MOFs have three subtypes: (I) ligand fluorescence; (II) ligand-to-metal charge transfer (LMCT) and (III) metal-to-ligand charge transfer (MLCT) (Figure 1.10).¹³¹ Encouraged by the above-mentioned advantages, a broad-variety of luminescent MOF materials have been synthesized and examined for the detection of various analytes such as cations, anions, explosive compounds, biomolecules, etc.^{125, 128, 129, 132-135}

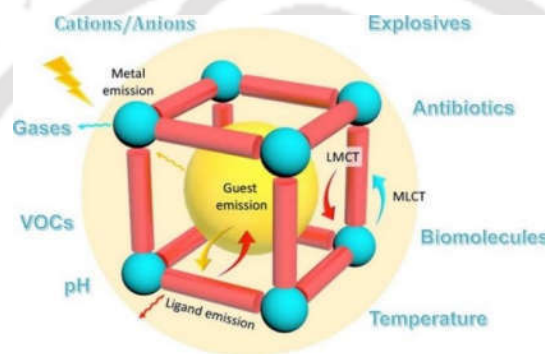


Figure 1.10 Representation of photoluminescence properties in MOFs. SBUs, blue spheres; organic linkers, red cylinders; guest chromophores, inner yellow sphere. Reproduced with permission from ref. 131. Copyright 2017 Elsevier.

In principle, for ‘turn-off’ and ‘turn-on’ fluorescence experiments, the alteration of fluorescence intensity of the fluorescent MOFs can be considered as sensing signal. Depending on the electronic nature of analyte, energy or electron transfer between the fluorescent MOF and analyte or a combination of the two can occur, which lead to either enhancement or quenching of the fluorescence. The nitroaromatic explosives are strong quencher compounds because of high electron affinity.^{136, 137} The Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} ions also show quenching of fluorescence intensity via LMCT or by the relaxation of the excitation energy through non-radiative process. In case of turn-on fluorescence experiments, new emission peaks (typically in the visible range) are generated from a previously dark background after addition of analyte. In order to act as a fluorescent probe, a MOF material must follow the few properties: (i) it must show detectable change in

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fluorescence intensity when it interacts with the analyte and (ii) it must show high selectivity and sensitivity towards target analyte.

Several MOF materials have been investigated for the selective sensing of various anions such as F^- ,¹³⁸ I^- ,¹³⁹ CO_3^{2-} ,¹⁴⁰ ClO_4^- ,¹⁴¹ NO_3^- ,¹⁴¹ MnO_4^- ,¹⁴² $Cr_2O_7^{2-}$,¹⁴³ etc. Recently, a Cd(II)-based MOF $[Cd(L_3)_2(ClO_4)_2] \cdot \text{toluene} \cdot \text{MeOH}]_n$ ($L_3 = 1,4\text{-bis(4-pyridyl)-2,3-diaza-1,3-butadiene}$) has been reported for the detection of N_3^- , ClO_4^- , SCN^- and $N(CN)_2^-$ ions.¹⁴⁴ A water-stable Zr-based MOF ($[Zr_6O_4(OH)_4(2,7\text{-CDC})_6] \cdot 19H_2O \cdot 2DMF$) (2,7-CDC = 9*H*-carbazole-2,7-dicarboxylate) has been reported for the selective detection of CN^- ion.¹³³

In biological systems, cation sensing plays an important role. The fluorescent MOF-based porous materials have been also investigated for the detection of various metal ions. For example, a PCN-224 (PCN = porous coordination network) type Zr-based MOF has been utilized for the detection of heavy metal ion like Hg^{2+} ion in HEPES buffer. An indium-based MOF,¹⁴⁵ $[In_2(OH)_2(H_2TTHA)(H_2O)_2]$ ($H_6TTHA = 1,3,5\text{-triazine-2,4,6-triamine hexaacetic acid}$), has been used for the detection of both UO_2^{2+} and Ru^{3+} cations.¹³² An Al-based MOF, nMOF-253, has been reported for the detection of Fe^{2+} in water medium and bioimaging in live cell.¹⁴⁶

The protonation and deprotonation of the fluorescent organic ligand within the MOF frameworks can change the fluorescence emission spectra which allow detection of the pH of the solution.¹⁴⁷ For example, an Eu(III)-based MOF, UPC-5, has been used for the determination of pH of the solution in range of 7.5 to 10.0.¹⁴⁷ Furthermore, a Zr-based UiO-67-bpyd (bpyd = 2,2-bipyridine-5,5'-dicarboxylate) MOF has been demonstrated for the determination of pH of the solution in the range of 1 to 9.¹⁴⁸

The MOF materials which have been investigated in various fields of chemical sensing are represented in Table 1.2.

Table 1.2 Representative examples of MOF-based chemical sensing of different analytes.

MOFs	Type of Sensing	Analytes	Ref.
A. Anion Sensing			
Ln-MOFs	turn-off fluorescence	F^-	138

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bio-MOF-1 $\supset$ DAAC	turn-on fluorescence	CN ⁻	149
NU-1000	turn-off fluorescence	Cr ₂ O ₇ ²⁻	150
[Mn ₄ (C ₂₀ H ₁₀ N ₂ O ₄ S) ₂ (HCOO) ₄ (DEF) ₂] and [Pb(C ₂₀ H ₁₀ N ₂ O ₄ S)(DMF)]	turn-off fluorescence	CrO ₄ ²⁻ , Cr ₂ O ₇ ²⁻ and MnO ₄ ⁻	151
CAU-10-N ₂ H ₃	turn-on fluorescence	CN ⁻	152
UiO-66-NH ₂	turn-on fluorescence	PO ₄ ³⁻	153
Tb ³⁺ @Zr-MOF	turn-on fluorescence	F ⁻	154
[Zr ₆ O ₄ (OH) ₄ (2,7-CDC) ₆] $\cdot$ 19H ₂ O $\cdot$ 2DMF	turn-on fluorescence	CN ⁻	133
B. Cation Sensing			
Zr-DPTDC, Zr-TDC, Zr-DMTDC, Zr-MPTDC	turn-off fluorescence	Fe ³⁺	155
PCN-224	turn-off fluorescence	Hg ²⁺	145
[Eu(BTB)(phen)] $\cdot$ 4.5DMF $\cdot$ 2H ₂ O	turn-off fluorescence	Al ³⁺	156
MIL-53-L ₆	turn-off fluorescence	Cu ²⁺	157
[Ln(OH) ₂ (H ₂ TTHA)(H ₂ O) ₂]	turn-off fluorescence	UO ₂ ²⁺ and Ru ³⁺	132
FJI-C8	turn-off fluorescence	Fe ³⁺	158
[Eu(BTPCA)(H ₂ O)] $\cdot$ 2DMF $\cdot$ 3H ₂ O	turn-on fluorescence	Zn ²⁺	159
[Eu(BTPCA)(H ₂ O)] $\cdot$ 2DMF $\cdot$ 3H ₂ O	turn-off fluorescence	Fe ³⁺	159
[Zr ₆ O ₄ (OH) ₄ (2,7-CDC) ₆] $\cdot$ 19H ₂ O $\cdot$ 2DMF	turn-off fluorescence	Fe ³⁺	133
Sm ³⁺ @[Al(OH)(btec)] $\cdot$ H ₂ O	turn-on fluorescence	Ag ⁺	160
C. Biomolecules Sensing			
MN-ZIF-90	turn-on fluorescence	cysteine	161

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Al-MIL-53-N ₃	turn-on fluorescence	H ₂ S	162
UiO-66-(NO ₂) ₂	turn-on fluorescence	H ₂ S	163
UiO-66-NH ₂	turn-off fluorescence	DNA	164
UiO-66-N ₃	turn-on fluorescence	H ₂ S	165
NMOF-PVA-BDY	turn-on fluorescence	ONOO ⁻	134

D. NAEs Sensing

[Zn _{1.5} (L ₇)(H ₂ O)]·1.5(C ₆ H ₆)	turn-off fluorescence	DNT, DMNB	135
[Zn ₂ (ndc) ₂ (bpe)]·2.5DMF·0.25H ₂ O	turn-off fluorescence	TNT and RDX	166
[Zn ₂ (ndc) ₂ (bpee)]·2.25DMF·0.5H ₂ O	turn-off fluorescence	TNT and RDX	166
BUT-12	turn-off fluorescence	TNP and 4-NP	167
BUT-13	turn-off fluorescence	TNP and 4-NP	167
[Zn ₂ (L ₈) ₂ (dpyb)]	turn-off fluorescence	TNP	168
Zn(L ₈)(dipb)]·2H ₂ O	turn-off fluorescence	TNP	168
Zn-PDA	turn-off fluorescence	TNP	169
[Zn ₂ (fdc) ₂ (bpee) ₂ (H ₂ O)] _n ·2H ₂ O	turn-off fluorescence	NB	170
Zr-BTDB-MOF	turn-off fluorescence	TNP	171
USTC-7	turn-off fluorescence	TNP	172
[Zr ₆ O ₄ (OH) ₄ (2,7-CDC) ₆]·19H ₂ O·2DMF	turn-off fluorescence	PNP	133

Ligand abbreviations: ndc = 2,6-naphthalenedicarboxylate; L₇ = 4,4',4''-(benzene-1,3,5-triyltris(oxy))tribenzoate; L₈ = 3,3'-(thiophene-2,5-diyl)dibenzoate, dpyb = 1,4-di(pyridin-4-yl)benzene; dipb = 4,4'-di(1H-imidazol-1-yl)-1,10-biphenyl; PDA = 9-phenylcarbazole-3,6-dicarboxylate;fdc = 2,5-furandicarboxylate; BTDB = 4,4'-

(benzo[*c*][1,2,5]thiadiazole-4,7-diyl)dibenzoate; DAAC = 3,6-diaminoacridinium cation; BTC = 1,3,5-benzenetricarboxylate; TDC = thieno[2,3-*b*]thiophene-2,5-dicarboxylate; DMTDC = dimethylthieno[2,3-*b*]thiophene-2,5-dicarboxylate; MPTDC = monophenylthieno[2,3-*b*]thiophene-2,5-dicarboxylate; DPTDC = diphenylthieno[2,3-*b*]thiophene-2,5-dicarboxylate; BTPCA = 1,1',1''-(benzene-1,3,5-triyl)tripiperidine-4-carboxylate; BTB = 1,3,5-benzenetribenzoate; phen = 1,10-phenanthroline; btec = pyromellitate; TTHA = 1,3,5-triazine-2,4,6-triaminehexaacetate; **L**₆ = 2-(pyrene-1-imine)-terephthalate; bpe = 1,2-bis(4-pyridyl)ethane; bpee = 1,2-bis(4-pyridyl)ethylene; TNT = 2,4,6-trinitrotoluene; 4-NP = *p*-nitrophenol; TNP = 2,4,6-trinitrophenol; DMNB = 2,3-dimethyl-2,3-dinitrobutane; RDX = 1,3,5-trinitro-1,3,5-triazine; DNT = dinitrotoluene.

1.5.2.1 Fluorescence Sensing of Nitroaromatic Explosives (NAEs)

Selective detection of NAEs is crucial for security screening, homeland security, environmental safety and human health. The major industrial explosive compounds are 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), nitrobenzene (NB), 2,3-dimethyl-2,3-dinitrobutane (DMNB), *p*-nitrophenol (PNP), 2,6-dinitrotoluene (2,6-DNT) and 2,4,6-trinitrophenol (TNP). Among these, the most explosive compound is TNP than other NAEs which has been used in the manufacture of rocket fuels, landmines, fireworks and matches.^{173, 174} It is also used in the leather, pharmaceutical and dye industries. Excessive use of the TNP in the industrial level causes several problems in environment, human health and wildlife. Therefore, selective sensing of TNP among other NAEs is vital for the reduction of its effect on the environment and living beings. Several fluorescent MOF materials have been used so far as fluorescent probes for the detection of NAEs. In this detection, the electron-rich MOF materials interact with the electron deficient NAEs. The electron transfer mechanism from MOFs to NAEs causes 'turn-off' effect of the fluorescence due to the reduction of fluorescence intensity. Several examples of luminescent MOF materials are available exhibiting fluorescence quenching properties towards NAEs.¹⁷¹

Fluorescent MOFs have been synthesized from π -electron rich organic ligands which can be easily quenched by NAEs.¹⁷¹ Metal ions with d^0 (e.g., Zr^{4+}) or d^{10} (e.g., Zn^{2+} and Cd^{2+}) configuration are very promising candidates for the formation of ligand-centered

fluorescent MOF materials due to their strong luminescent behavior. Several Zn(II)-based fluorescent MOF materials have been reported for the detection of NAEs.^{135, 166, 168-170, 175-177} For example, a Zn(II)-based MOF, $[\text{Zn}_{1.5}(\text{L}_4)(\text{H}_2\text{O})] \cdot 1.5\text{C}_6\text{H}_6$ ($\text{L}_4 = 4,4',4''\text{-(benzene-1,3,5-triyltris(oxy))tribenzoate}$) has been synthesized with a π -conjugated organic ligand. It shows selective sensing behavior towards DMNB over other NAEs (Figure 1.11).¹³⁵ Furthermore, several Cd(II)-based MOFs have been reported for sensing of NAEs.^{178, 179} In addition, the several other metal ions have been used for synthesizing fluorescent MOF materials^{180, 181} for the detection of NAEs. For example, a Zr-BTDB MOF (BTDB = 4,4'-(benzo[*c*][1,2,5]thiadiazole-4,7-diyl)dibenzoate) has been demonstrated for rapid and selective detection of TNP.¹⁷¹ Few Mg-based MOFs have been reported for the detection of NAEs.^{182, 183} A Cu-based MOF, $\text{Cu}_6(\text{L}_5)_3(\text{H}_2\text{O})_6$ ($\text{L}_5 = 5,5'\text{--}((5,7,12,14\text{-tetrahydro-5,14:7,12-bis}([1,2]\text{benzeno)pentacene-6,13-diyl})\text{bis(ethyne-2,1-diyl)})\text{diisophthalate}$) has been reported for the detection of NAEs.¹⁸⁴

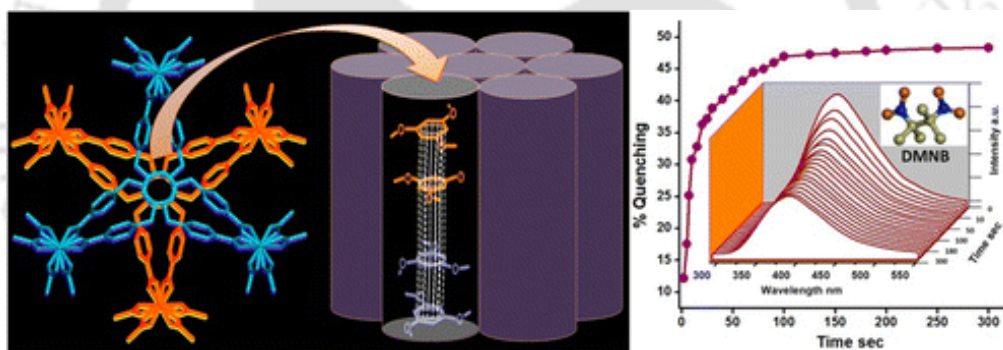


Figure 1.11 Representation of Zn-based MOF for selective sensing of DMNB and DNT. Reproduced with permission from ref. 135. Copyright 2013 American Chemical Society.

In addition, lanthanide-based fluorescent MOF materials have been employed towards the detection of NAEs. The MOFs with other metal ions than lanthanides have major drawbacks due to small Stokes shift which prevents the detection of NAEs by the naked eye. On the other hand, lanthanide MOFs-based sensors exhibit large Stokes shift which is useful for the detection of NAEs. A large number of Tb(III)¹⁸⁵⁻¹⁸⁷ and Eu(III)¹⁸⁸⁻¹⁹⁰ MOFs have been reported for the selective detection of NAEs.

1.5.2.2 Sensing of Reactive Oxygen/Nitrogen Species (ROS/RNS)

In biological systems, both ROS and RNS play very important roles.¹⁹¹ The major ROS/RNS are hydrogen peroxide (H_2O_2), peroxyxynitrite (ONOO^-), singlet oxygen ($^1\text{O}_2$), superoxide ($\text{O}_2^{\bullet-}$), nitric oxide radical ($\bullet\text{NO}$), nitrosonium ion (NO^+), nitrite (NO_2^-), nitrate (NO_3^-), hydroxy radical ($\bullet\text{OH}$), *tert*-butyl hydrogen peroxide (TBHP), peracid (RCO_3H) and hypochlorous acid (HOCl). Excess ROS/RNS in biological system causes several human diseases.¹⁹²⁻¹⁹⁴ Selective detection of ROS/RNS in biological system is crucial for monitoring the concentration of ROS/RNS. Several organic fluorescent probes bearing boronic acid functional group shown selective fluorescence response towards hydrogen peroxide and peroxyxynitrite via Baeyer–Villiger oxidation reaction.¹⁹⁵⁻¹⁹⁷ Few MOF-based sensors for H_2O_2 have been reported using different analytical techniques such as chemiluminescence,¹⁹⁸ electrochemistry^{199, 200} and colorimetry²⁰¹ for the detection of ROS. But, there is no report on MOFs so far for the sensing of ROS using fluorometry. The surface modification or functionalization of the MOF materials with boronate ester or boronic acid groups offers a selective interaction between analyte and functional group.¹³⁴ A boronic acid group functionalized MOF-based material has been recently reported for the detection of RNS. The Zr-based Nano-MOF (NMOF-PVA-BDY) with surface-coated boronic acid group has been reported for the selective sensing of ONOO^- (Figure 1.12).¹³⁴ So, the direct functionalization of ligand with boronic acid functional group can serve as a potential material for the fluorescence based detection of H_2O_2 or ONOO^- . Hence, the synthesis of boronic acid functionalized MOFs are highly interesting for the detection of ROS/RNS.

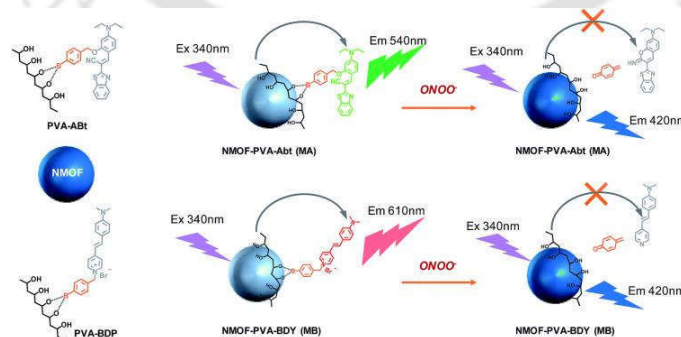


Figure 1.12 Boronic acid functionalized Zr-based NMOF (NMOF-PVA-BDY) for the selective sensing of ONOO^- . Reproduced with permission from ref. 136. Copyright 2017 Royal Society of Chemistry.

1.6 Motivation and Objectives

MOFs are an emerging class of highly crystalline porous materials with potential applications in the field of gas storage, separation and chemical sensing of various analytes (cations, anions, biomolecules, small molecules, nitroaromatic explosives materials, volatile organic compounds, etc.). During synthesis of functionalized MOFs, pre-functionalized organic ligands were utilized. Moreover, functionalization can be achieved by employing the post-synthetic modifications method. The anchored functional groups in the MOF framework play a crucial role in gas storage, separation and sensing application.^{202, 203} The anchored functional groups can act as active sites for adsorption of specific gas molecules or sensing of specific analytes during fluorescence detection, thus increasing the selectivity of the MOF towards target gas or analyte. In spite of numerous advantages, applications of many MOFs are limited due to their low chemical stability under harsh conditions. The synthesis of water-stable MOFs is still a key challenge. Some of the reported MOFs^{204, 205} have shown collapse of their structures after prolonged exposure to moisture. This instability makes MOFs unfeasible in practical applications. For improving the hydrolytic stability, hydrophobic functional groups (e.g., -F, -CH₃, -CF₃, -OCF₃, etc.) have been incorporated into MOF frameworks. In addition to the hydrophobicity, the high valent metal ions (e.g., Zr(IV),^{33, 206} Hf(IV),³³ Ce(IV),³⁴ Ti(IV),³⁵ etc.) have been used for the syntheses of physicochemically stable MOFs. In this dissertation, the gas adsorption and fluorescence sensing applications of water-stable MOFs bearing functionalized organic ligands and high valent metal ions (Zr(IV), Hf(IV) and Ce(IV)) will be presented.

1.7 References

1. F. Perera, *Int. J. Environ. Res. Public Health*, 2018, **15**, 1-17.
2. C. D. Butler, *Int. J. Environ. Res. Public Health*, 2018, **15**, 2266-2287.
3. T. A. Ruda-Eberenz, A. Nagy, W. J. Waldman and P. K. Dutta, *Langmuir*, 2008, **24**, 9140–9147.
4. H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673–674.
5. B. Li, H.-M. Wen, W. Zhou and B. Chen, *J. Phys. Chem. Lett.*, 2014, **5**, 3468–3479.

6. J. E. Efome, D. Rana, T. Matsuura and C. Q. Lan, *J. Mater. Chem. A*, 2018, **6**, 4550–4555.
7. X. Fang, B. Zong and S. Mao, *Nano-Micro Lett.*, 2018, **10**, 1-19.
8. L. Wang, M. Zheng and Z. Xie, *J. Mater. Chem. B*, 2018, **6**, 707-717.
9. S. Kim, K. W. Dawson, B. S. Gelfand, J. M. Taylor and G. K. H. Shimizu, *J. Am. Chem. Soc.*, 2013, **135**, 963–966.
10. C. Wang, B. An and W. Lin, *ACS Catal.*, 2019, **9**, 130–146.
11. H. Li, M. Eddaoudi, M. O’Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276–279.
12. S. S. Kaye, A. Dailly, O. M. Yaghi and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 14176–14177.
13. D. J. Ashworth, A. Cooper, M. Trueman, R. W. M. Al-Saedi, L. D. Smith, A. J. H. M. Meijer and J. A. Foster, *Chem. Eur.J.*, 2018, **24**, 17986-17996.
14. J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400-1417.
15. C. Baerlocher, L. B. McCusker and D. H. Olson, *Atlas of Zeolite Framework Types*, Elsevier, Amsterdam, The Netherlands, 6th rev. edn. edn., 2007.
16. W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev.*, 2014, **43**, 5561-5593.
17. G. F. d. L. Lima, A. Mavrandonakis, H. A. d. Abreu, H. A. Duarte and T. Heine, *J. Phys. Chem. C*, 2013, **117**, 4124–4130.
18. Y. F. Feng, H. Jiang, S. N. Li, J. Wang, X. Y. Jing, Y. R. Wang and M. Chen, *Colloids Surf., A*, 2013, **431**, 87-92.
19. F. Xu, L. Kou, J. Jia, X. Hou, Z. Long and S. Wang, *Anal. Chim. Acta*, 2013, **804**, 240-245.
20. K. K. Yee, N. Reimer, J. Liu, S. Y. Cheng, S. M. Yiu, J. Weber, N. Stock and Z. T. Xu, *J. Am. Chem. Soc.*, 2013, **135**, 7795–7798.
21. A. Shahat, H. M. A. Hassan and H. M. E. Azzazy, *Anal. Chim. Acta*, 2013, **793**, 90-98.
22. K. A. Cychosz and A. J. Matzger, *Langmuir*, 2010, **26**, 17198–17202.
23. S. Devautour-Vinot, C. Martineau, S. Diaby, M. Ben-Yahia, S. Miller, C. Serre, P. Horcajada, D. Cunha, F. Taulelle and G. Maurin, *J. Phys. Chem. C*, 2013, **117**, 11694–11704.
24. S. Yang, C. Chen, Z. Yan, Q. Cai and S. Yao, *J. Sep. Sci.*, 2013, **36**, 1283–1290.

Chapter 1

25. Z. Hasan, J. Jeon and S. H. Jhung, *J. Hazard. Mater.*, 2012, **209**, 151-157.
26. X. Zhao, D. Liu, H. Huang, W. Zhang, Q. Yang and C. Zhong, *Microporous Mesoporous Mater.*, 2014, **185**, 72-78.
27. N. Goel and N. Kumar, *RSC Adv.*, 2018, **8**, 10746-10755.
28. S. Mukherjee, A. V. Desai, A. I. Inamdar, B. Manna and S. K. Ghosh, *Cryst. Growth Des.*, 2015, **15**, 3493-3497.
29. J. J. Low, A. I. Benin, P. Jakubczak, J. F. Abrahamian, S. A. Faheem and R. R. Willis, *J. Am. Chem. Soc.*, 2009, **131**, 15834-15842.
30. J. B. DeCoste, G. W. Peterson, B. J. Schindler, K. L. Killops, M. A. Browe and J. J. Mahle, *J. Mater. Chem. A*, 2013, **1**, 11922-11932.
31. F. Jeremias, V. Lozan, S. K. Henninger and C. Janiak, *Dalton Trans.*, 2013, **42**, 15967-15973.
32. V. Bon, V. Senkovskyy, I. Senkovska and S. Kaskel, *Chem. Commun.*, 2012, **48**, 8407-8409.
33. V. Bon, I. Senkovska, I. A. Baburin and S. Kaskel, *Cryst. Growth Des.*, 2013, **13**, 1231-1237.
34. M. Lammert, M. T. Wharmby, S. Smolders, B. Bart, A. Lieb, K. A. Lomachenko, D. D. Vos and N. Stock, *Chem. Commun.*, 2015, **51**, 12578-12581.
35. M. Dan-Hardi, C. Serre, T. Fort, L. Rozes, G. Maurin, C. Sanchez and G. Férey, *J. Am. Chem. Soc.*, 2009, **131**, 10857-10859.
36. T. Wu, L. Shen, M. Luebbers, C. Hu, Q. Chen, Z. Ni and R. I. Masel, *Chem. Commun.*, 2010, **46**, 6120-6122.
37. J. G. Nguyen and S. M. Cohen, *J. Am. Chem. Soc.*, 2010, **132**, 5244-5246.
38. J. M. Taylor, R. Vaidhyanathan, S. S. Iremonger and G. K. H. Shimizu, *J. Am. Chem. Soc.*, 2012, **134**, 14338-14340.
39. M. SK, S. Banesh, V. Trivedi and S. Biswas, *Inorg. Chem.*, 2018, **57**, 14574-14581.
40. M. SK, S. Bhowal and S. Biswas, *Eur. J. Inorg. Chem.*, 2015, **2015**, 3317-3322.
41. Y. Pan, Y. Liu, G. Zeng, L. Zhao and Z. Lai, *Chem. Commun.*, 2011, **47**, 2071-2073.
42. M. Jian, B. Liu, R. Liu, J. Qu, H. Wang and X. Zhang, *RSC Adv.*, 2015, **5**, 48433-48441.

43. R.-B. Lin, D. Chen, Y.-Y. Lin, J.-P. Zhang and X.-M. Chen, *Inorg. Chem.*, 2012, **51**, 9950–9955.
44. Z.-Q. Jiang, F. Wang and J. Zhang, *Inorg. Chem.*, 2016, **55**, 13035–13038.
45. G.-H. Wang, Z.-G. Li, H.-Q. Jia, N.-H. Hu and J.-W. Xu, *CrystEngComm*, 2009, **11**, 292–297.
46. B. Sakintuna and Y. Yürüm, *Ind. Eng. Chem. Res.*, 2005, **44**, 2893–2902.
47. J. Klinowski, F. A. A. Paz, P. Silva and J. Rocha, *Dalton Trans.*, 2011, **40**, 321–330.
48. M. Taddei, P. V. Dau, S. M. Cohen, M. Ranocchiari, J. A. v. Bokhoven, F. Costantino, S. Sabatinif and R. Vivanif, *Dalton Trans.*, 2015, **44**, 14019–14026.
49. K. Zhou, S. Chaemchuen, Z. Wu and F. Verpoort, *Microporous Mesoporous Mater.*, 2017, **239**, 28–33.
50. D. J. Tranchemontagne, J. R. Hunt and O. M. Yaghi, *Tetrahedron*, 2008, **64**, 8553–8557.
51. D. Lv, Y. Chen, Y. Li, R. Shi, H. Wu, X. Sun, J. Xiao, H. Xi, Q. Xia and Z. Li, *J. Chem. Eng. Data*, 2017, **62**, 2030–2036.
52. W.-J. Li, J. Lü, S.-Y. Gao, Q.-H. Li and R. Cao, *J. Mater. Chem. A*, 2014, **2**, 19473–19478.
53. K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498–519.
54. J. Vermesse, D. Vidal and P. Malbrunot, *Langmuir*, 1996, **12**, 4190–4196.
55. U. Wingenfelder, C. Hansen, G. Furrer and R. Schulin, *Environ. Sci. Technol.*, 2005, **39**, 4606–4613.
56. K. Sahnner, G. Hagen, D. Schönauer, S. Reiß and R. Moos, *Solid State Ion.*, 2008, **179**, 2416–2423.
57. Y. Li, L. Li and J. Yu, *Chem*, 2017, **3**, 928–949.
58. J. Přeck, P. Pizarro, D. P. Serrano and J. Čejka, *Chem. Soc. Rev.*, 2018, **47**, 8263–8306.
59. M. M. Hossain, B. A. Kumar and K. J. Kim, *Int. J. Hydrogen Energy*, 2015, **9**, 2231–2247.
60. R. Millini and G. Bellussi, *Catal. Sci. Technol.*, 2016, **6**, 2502–2527.
61. N. Carrara, C. Betti, F. Coloma-Pascual, M. C. Almansa, L. Gutierrez, C. Miranda, M. E. Quiroga and C. R. Lederhos, *Int. J. Chem. Eng.*, 2018, **2018**, 4307308–4307318.

Chapter 1

62. J. A. Mason, M. Veenstra and J. R. Long, *Chem. Sci.*, 2014, **5**, 32-51.
63. H. Li, K. Wang, Y. Sun, C. T. Lollar, J. Li and H.-C. Zhou, *Mater. Today*, 2018, **21**, 108-121.
64. L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. V. Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105–1125.
65. S. A. Diamantis, A. Margariti, A. D. Pournara, G. S. Papaefstathiou, M. J. Manos and T. Lazarides, *norg. Chem. Front.*, 2018, **5**, 1493-1511.
66. A. Rossin, G. Tuci, L. Luconi and G. Giambastiani, *ACS Catal.*, 2017, **7**, 5035–5045.
67. L. Zhu, X.-Q. Liu, H.-L. Jiang and L.-B. Sun, *Chem. Rev.*, 2017, **117**, 8129–8176.
68. Y. Li, H. Xu, S. Ouyang and J. Ye, *Phys. Chem. Chem. Phys.*, 2016, **18**, 7563-7572.
69. A. Dhakshinamoorthy, Z. Li and H. Garcia, *Chem. Soc. Rev.*, 2018, **47**, 8134-8172.
70. H. Zheng, Y. Zhang, L. Liu, W. Wan, P. Guo, A. M. Nyström and X. Zou, *J. Am. Chem. Soc.*, 2016, **138**, 962–968.
71. R. B. Jackson, C. L. Qere, R. M. Andrew, J. G. Canadell, G. P. Peter, J. Roy and L. Wu, *Environ. Res. Lett.*, 2017, **12**, 110202-110205.
72. Z. Zhang, Y. Zhao, Q. Gong, Z. Lib and J. Li, *Chem. Commun.*, 2013, **49**, 653-661.
73. P. D. C. Dietzel, R. E. Johnsen, H. Fjellvåg, S. Bordiga, E. Groppo, S. Chavan and R. Blom, *Chem. Commun.*, 2008, **0**, 5125–5127.
74. C. Montoro, E. Garcia, S. Calero, M. A. Perez-Fernandez, A. L. Lopez, E. Barea and J. A. R. Navarro, *J. Mater. Chem.*, 2012, **22**, 10155–10158.
75. Z.-R. Jiang, H. Wang, Y. Hu, J. Lu and H.-L. Jiang, *ChemSusChem*, 2015, **8**, 878–885.
76. E. F. d. Silva and H. F. Svendsen, *Int. J. Greenhouse Gas Control*, 2007, **1**, 151-157.
77. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724–781.
78. J. M. Castillo, J. Silvestre-Albero, F. Rodriguez-Reinoso, T. J. H. Vlugt and S. Calero, *Phys. Chem. Chem. Phys.*, 2013, **15**, 17374-17382.
79. R. W. Flaig, T. M. O. Popp, A. M. Fracaroli, E. A. Kapustin, M. J. Kalmutzki, R. M. Altamimi, F. Fathieh, J. A. Reimer and O. M. Yaghi, *J. Am. Chem. Soc.*, 2017, **139**, 12125–12128.

80. A. Ö. Yazaydin, A. I. Benin, S. A. Faheem, P. Jakubczak, J. J. Low, R. R. Willis and R. Q. Snurr, *Chem. Mater.*, 2009, **21**, 1425–1430.
81. A. Ö. Yazaydin, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low and R. R. Willis, *J. Am. Chem. Soc.*, 2009, **131**, 18198–18199.
82. S. R. Caskey, W.-F. A. G. and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870–10871.
83. P. D. C. Dietzel, V. Besikiotis and R. Blom, *J. Mater. Chem.*, 2009, **19**, 7362–7370.
84. J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 38–39.
85. P. D. C. Dietzel, R. E. Johnsen, H. Fjellvåg, S. Bordiga, E. Groppo, S. Chavan and R. Blom, *Chem. Commun.*, 2008, **0**, 5125–5127.
86. P. Chowdhury, C. Bikkina, D. Meister, F. Dreisbach and S. Gumma, *Microporous Mesoporous Mater.*, 2009, **117**, 406–413.
87. A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998–17999.
88. J. W. Yoon, S. H. Jhung, Y. K. Hwang, S. M. Humphrey, P. T. Wood and J. S. Chang, *Adv. Mater.*, 2007, **19**, 1830–1834.
89. K. L. Mulfort, O. K. Farha, C. D. Malliakas, M. G. Kanatzidis and J. T. Hupp, *Chem. Eur. J.*, 2009, **16**, 276–281.
90. H. S. Choi and M. P. Suh, *Angew. Chem. Int. Ed.*, 2009, **48**, 6865–6869.
91. A. Demessence, D. M. D'Alessandro, M. L. Foo and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 8784–8786.
92. B. Arstad, H. Fjellvåg, K. O. Kongshaug, O. Swang and R. Blom, *Adsorption*, 2008, **14**, 755–762.
93. R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939–943.
94. S. R. Miller, G. M. Pearce, P. A. Wright, F. Bonino, S. Chavan, S. Bordiga, I. Margiolaki, N. Guillou, G. Férey, S. Bourrelly and P. L. Llewellyn, *J. Am. Chem. Soc.*, 2008, **130**, 15967–15981.
95. J. A. R. Navarro, E. Barea, J. M. Salas, N. Masciocchi, S. Galli, A. Sironi, C. O. Ania and J. B. Parra, *J. Mater. Chem.*, 2007, **17**, 1939–1946.
96. P. D. Southon, L. Liu, E. A. Fellows, D. J. Price, G. J. Halder, K. W. Chapman, B. Moubaraki, K. S. Murray, J.-F. Létard and C. J. Kepert, *J. Am. Chem. Soc.*, 2009, **131**, 10998–11009.

Chapter 1

97. L. Hamon, P. L. Llewellyn, T. Devic, A. Ghoufi, G. Clet, V. Guillerm, G. D. Pirngruber, G. Maurin, C. Serre, G. Driver, W. v. Beek, E. Jolimaître, A. Vimont, M. Daturi and G. Férey, *J. Am. Chem. Soc.*, 2009, **131**, 17490–17499.
98. Z. Zhao, Z. Li and Y. S. Lin, *Ind. Eng. Chem. Res.*, 2009, **48**, 10015–10020.
99. S. Couck, J. F. M. Denayer, G. V. Baron, T. Rémy, J. Gascon and F. Kapteijn, *J. Am. Chem. Soc.*, 2009, **131**, 6326–6327.
100. C. Serre, S. Bourrelly, A. Vimont, N. A. Ramsahye, G. Maurin, P. L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes and G. Férey, *Adv. Mater.*, 2007, **19**, 2246–2251.
101. E. Neofotistou, C. D. Malliakas and P. N. Trikalitis, *Chem. Eur. J.*, 2009, **15**, 4523–4527.
102. J. Y. Lee, J. M. Roberts, O. K. Farha, A. A. Sarjeant, K. A. Scheidt and J. T. Hupp, *Inorg. Chem.*, 2009, **48**, 9971–9973.
103. B. Wang, A. P. Côté, H. Furukawa, M. O’Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207–211.
104. J. A. R. Navarro, E. Barea, J. M. Salas, N. Masciocchi, S. Galli, A. Sironi, C. O. Ania and J. B. Parra, *Inorg. Chem.*, 2006, **45**, 2397–2399.
105. H. J. Park and M. P. Suh, *Chem. Commun.*, 2010, **46**, 610–612.
106. P. K. Thallapally, J. Tian, M. R. Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren and J. L. Atwood, *J. Am. Chem. Soc.*, 2008, **130**, 16842–16843.
107. B. Mu, F. Li and K. S. Walton, *Chem. Commun.*, 2009, **0**, 2493–2495.
108. Z. Guo, J. Yu, G. Li, Z. Si, H. Guo and H. Zhang, *CrystEngComm*, 2009, **11**, 2254–2256.
109. Y.-S. Bae, O. K. Farha, J. T. Hupp and R. Q. Snurr, *J. Mater. Chem.*, 2009, **19**, 2131–2134.
110. A. Rossin, A. Ienco, F. Costantino, T. Montini, B. D. Credico, M. Caporali, L. Gonsalvi, P. Fornasiero and M. Peruzzini, *Cryst. Growth Des.*, 2008, **8**, 3302–3308.
111. H. Hayashi, A. P. Côté, H. Furukawa, M. O’Keeffe and O. M. Yaghi, *Nat. Mater.*, 2007, **6**, 501–506.
112. Y. Zhou, B. Yan and F. Lei, *Chem. Commun.*, 2014, **50**, 15235–15238.

Chapter 1

113. M. Haseena, M. F. Malik, A. Javed, S. Arshad, N. Asif, S. Zulfiqar and J. Hanif, *Environ. Risk Assess. Rem.*, 2017, **1**, 16-19.
114. C. N. McEwen, F. S. Ligler and T. M. Swager, *Chem. Soc. Rev.*, 2013, **42**, 8581-8583.
115. S. Li, C. Zhang, S. Wang, Q. Liu, H. Feng, X. Ma and J. Huo, *Analyst*, 2018, **143**, 4230-4246.
116. W. C. A. Koh, J. I. Son, E. S. Choe and Y.-B. Shim, *Anal. Chem.*, 2010, **82**, 10075-10082.
117. K. L. McDonald, *Anal. Chem.*, 1972, **44**, 1298-1299.
118. D. Tsikas, *Analyst*, 2011, **136**, 979-987.
119. B. F. Scott, C. A. Moddy, C. Spencer, J. M. Small, D. C. G. Muir and S. A. Maburay, *Environ. Sci. Technol.*, 2006, **40**, 6405-6410.
120. J. Liu, Y. Chen, W. Wang, J. Feng, M. Liang, S. Ma and X. Chen, *J. Agric. Food Chem.*, 2016, **64**, 371-380.
121. D. F. S. Gallis, L. E. S. Rohwer, M. A. Rodriguez, M. C. Barnhart-Dailey, K. S. Butler, T. S. Lukll, J. A. Timlin and K. W. Chapman, *ACS Appl. Mater. Interfaces*, 2017, **9**, 22268-22277.
122. Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815-5840.
123. M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330-1352.
124. Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126-1162.
125. L. V. Meyer, F. Schönfeld and K. Müller-Buschbaum, *Chem. Commun.*, 2014, **50**, 8093-8108.
126. Y. Cui, F. Zhu, B. Chen and G. Qian, *Chem. Commun.*, 2015, **51**, 7420- 7431.
127. Z. Hu, K. Tan, W. P. Lustig, H. Wang, Y. Zhao, C. Zheng, D. Banerjee, T. J. Emge, Y. J. Chabal and J. Li, *Chem. Sci.*, 2014, **5**, 4873- 4877.
128. B. Chen, S. Xiang and G. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115-1124.
129. S. S. Nagarkar, A. V. Desai, P. Samanta and S. K. Ghosh, *Dalton Trans.*, 2015, **44**, 15175-15180.
130. J. Lei, R. Qian, P. Ling, L. Cui and H. Ju, *Trends Analyt. Chem.*, 2014, **58**, 71-78.
131. Y. Zhang, S. Yuan, G. Day, X. Wang, X. Yang and H.-C. Zhou, *Coord. Chem. Rev.*, 2018, **354**, 28-45.

Chapter 1

132. N. Du, J. Song, S. Li, Y.-X. Chi, F.-Y. Bai and Y.-H. Xing, *ACS Appl. Mater. Interfaces*, 2016, **8**, 28718–28726.
133. A. Das and S. Biswas, *Sens. Actuators, B.*, 2017, **250**, 121-131.
134. Z. Ding, J. Tan, G. Feng, Z. Yuan, C. Wuband and X. Zhan, *Chem. Sci.*, 2017, **8**, 5101–5106.
135. A. K. Chaudhari, S. S. Nagarkar, B. Joarder and S. K. Ghosh, *Cryst. Growth Des.*, 2013, **13**, 3716–3721.
136. M. E. Germain and M. J. Knapp, *Chem. Soc. Rev.*, 2009, **38**, 2543-2555.
137. S. J. Toal and W. C. Trogler, *J. Mater. Chem.*, 2006, **16**, 2871-2883.
138. J.-M. Zhou, W. Shi, N. Xu and P. Cheng, *Inorg. Chem.*, 2013, **52**, 8082–8090.
139. P. F. Shi, H. C. Hu, Z. Y. Zhang, G. Xiong and B. Zhao, *Chem. Commun.*, 2015, **51**, 3985–3988.
140. H. Liu, H. Wang, T. Chu, M. Yu and Y. Yang, *J. Mater. Chem. C*, 2014, **2**, 8683–8690.
141. A. Karmakar, B. Manna, A. V. Desai, B. Joarder and S. K. Ghosh, *Inorg. Chem.*, 2014, **53**, 12225–12227.
142. X. Li, Y. Gong, H. Zhao and R. Wang, *Inorg. Chem.*, 2014, **53**, 12127–12134.
143. X. Li, H. Xu, F. Kong and R. Wang, *Angew. Chem., Int. Ed.*, 2013, **52**, 13769–13773.
144. B. Manna, S. Sing, A. Karmakar, A. V. Desai and S. K. Ghosh, *Inorg. Chem.*, 2015, **54**, 110–116.
145. J. Yang, Z. Wang, Y. Li, Q. Zhuang, W. Zhao and J. Gu, *RSC Adv.*, 2016, **6**, 69807–69814.
146. Y. Lu, B. Yan and J.-L. Liu, *Chem. Commun.*, 2014, **50**, 9969-9972.
147. Q. Meng, X. Xin, L. Zhang, F. Dai, R. Wang and D. S. Sun, *J. Mater. Chem. A*, 2015, **3**, 24016-24021.
148. S.-H. Wu, S. Wang, W.-L. Fang, X.-F. Guo and H. Wang, *Anal. Methods*, 2019, **11**, 36-43.
149. A. Karmakar, B. Joarder, A. Mallick, P. Samanta, A. V. Desai, S. Basu and S. K. Ghosh, *Chem. Commun.*, 2017, **53**, 1253-1256.
150. Z.-J. Lin, H.-Q. Zheng, H.-Y. Zheng, L.-P. Lin, Q. Xin and R. Cao, *Inorg. Chem.*, 2017, **56**, 14178–14188.
151. A. K. Jana and S. Natarajan, *ChemPlusChem*, 2017, **82**, 1153 – 1163.

152. R. Dalapati, S. Nandi, H. Reinsch, B. K. Bhunia, B. B. Mandal, N. Stock and S. Biswas, *CrystEngComm*, 2018, **20**, 4194-4201.
153. J. Yang, Y. Dai, X. Zhu, Z. Wang, Y. Li, Q. Zhuang, J. Shia and J. Gu, *J. Mater. Chem. A*, 2015, **3**, 7445-7452.
154. H.-Y. Zheng, X. Lian, S.-J. Qin and B. Yan, *ACS Omega*, 2018, **3**, 12513-12519.
155. R. Dalapati, Ü. Kökçam-Demir, C. Janiakb and S. Biswas, *Dalton Trans.*, 2018, **47**, 1159-1170.
156. H. Xu, B. Zhai, C.-S. Cao and B. Zhao, *Inorg. Chem.*, 2016, **55**, 9671-9676.
157. C. Liu and B. Yan, *Sens. Actuators, A*, 2016, **235**, 541-546.
158. C.-H. Chen, X.-S. Wang, L. Li, Y.-B. Huang and R. Cao, *Dalton Trans.*, 2018, **47**, 3452-3458.
159. Q. Tang, S. Liu, Y. Liu, J. Miao, S. Li, L. Zhang, Z. Shi and Z. Zheng, *Inorg. Chem.*, 2012, **52**, 2799-2801.
160. J.-N. Hao and B. Yan, *J. Mater. Chem. A*, 2015, **3**, 4788-4792.
161. H. LI, X. Feng, Y. Guo, D. Chen, R. Li, X. Ren, X. Jiang, Y. Dong and B. Wang, *Sci. Rep.*, 2014, **4**, 4366-4370.
162. A. Das, S. Banesh, V. Trivedi and S. Biswas, *Dalton Trans.*, 2018, **47**, 2690-2700.
163. S. Nandi, S. Banesh, V. Trivedi and S. Biswas, *Analyst*, 2018, **143**, 1482-1491.
164. H.-T. Zhang, J.-W. Zhang, G. Huang, Z.-Y. D. Du and H.-L. Jiang, *Chem. Commun.*, 2014, **50**, 12069-12072.
165. S. S. Nagarkar, T. Saha, A. V. Desai, P. Talukdar and S. K. Ghosh, *Sci. Rep.*, 2014, **4**, 7053-7058.
166. Z. Hu, S. Pramanik, K. Tan, C. Zheng, W. Liu, X. Zhang, Y. J. Chabal and J. LI, *Cryst. Growth Des.*, 2013, **13**, 4204-4207.
167. B. Wang, X.-L. Lv, D. Feng, L.-H. Xie, J. Zhang, M. Li, Y. Xie, J.-R. Li and H.-C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 6204-6216.
168. h.-Q. Shi, Z.-J. Guo and H.-G. Zheng, *Chem. Commun.*, 2015, **51**, 8300-8303.
169. X. Jiang, Y. Liu, P. Wu, L. Wang, Q. Wang, G. Zhu, X.-l. L. Lia and J. Wang, *RSC Adv.*, 2014, **4**, 47357-47360.
170. D. Singh and C. M. Nagaraj, *Dalton Trans.*, 2014, **43**, 17912-17915.
171. M. SK and S. Biswas, *CrystEngComm*, 2016, **18**, 3104-3113.
172. Y. Hu, M. Ding, X.-Q. Liu, L.-B. Sunb and H.-L. Jiang, *Chem. Commun.*, 2016, **52**, 5734-5737.

Chapter 1

173. G. He, H. Peng, T. Liu, M. Yang, Y. Zhang and Y. Fang, *J. Mater. Chem.*, 2009, **19**, 7347-7353.
174. Y. Peng, A.-J. Zhang, M. Donga and Y.-W. Wang, *Chem. Commun.*, 2011, **47**, 4505-4507.
175. Z. Hu, B. J. Deibert and J. LI, *Chem. Soc. Rev.*, 2014, **43**, 5815-5840.
176. S. Pramanik, Z. Hu, X. Zhang, C. Zheng, S. Kelly and J. Li, *Chem. Eur. J.*, 2013, **19**, 15964-15971.
177. S. Sanda, S. Parshamoni, S. Biswas and S. Konar, *Chem. Commun.*, 2015, **51**, 6576-6579.
178. H. He, Y. Song, F. Sun, N. Zhao and G. Zhu, *Cryst. Growth Des.*, 2015, **15**, 2033–2038.
179. A. K. Chaudhari, S. S. Nagarkar, B. Joarder, S. Mukherjee and S. K. Ghosh, *Inorg. Chem.*, 2013, **52**, 12784–12789.
180. S. Shanmugaraju, S. A. Joshi and P. S. Mukherjee, *Inorg. Chem.*, 2011, **50**, 11736–11745.
181. J.-F. Song, Y. Li, R.-S. Zhou, T.-P. Hu, Y.-L. Wen, J. S. Shao and X.-B. Cui, *Dalton Trans.*, 2016, **45**, 545-551.
182. D. Liu, X. Liu, Y. Liu, Y. Yu, F. Chen and C. Wang, *DaltonTrans.*, 2014, **43**, 15237–15244.
183. Z.-F. Wu, B. Tan, M.-L. Feng, A.-J. Lan and X.-Y. Huang, *J. Mater. Chem. A*, 2014, **2**, 6426-6431.
184. M. Zhang, L. Zhang, Z. Xiao, Q. Zhang, R. Wang, F. Dai and D. Sun, *Sci. Rep.*, 2016, **6**, 20672-20681.
185. D. K. Shing, S. Bhattacharya, P. Majee, S. K. Mondal, M. Kumar and P. Mahata, *J. Mater. Chem. A*, 2014, **2**, 20908-20915.
186. J. Wang, W. Sun, S. Chang, H. Liu, G. Zhang, Y. Wang and Z. Liu, *RSC Adv.*, 2015, **5**, 48574-48579.
187. J.-J. Qian, L.-G. Qiu, Y.-M. Wang, Y.-P. Yuan, A.-J. Xiea and Y.-H. Shen, *Dalton Trans.*, 2014, **43**, 3978-3983.
188. M. Jurcic, W. J. Peveler, C. N. Savory, D. O. Scanlon, A. J. Kenyone and I. P. Parkin, *J. Mater. Chem. A*, 2015, **3**, 6351-6359.
189. X.-H. Zhou, L. Li, H.-H. Li, A. Li, T. Yang and W. Huang, *Dalton Trans.*, 2013, **42**, 12403-12409.

190. H. Xu, F. Liu, Y. Cui, B. Chen and G. Qian, *Chem. Commun.*, 2011, **47**, 3153-3155
191. D. Gius and D. R. Spitz, *Antioxid. Redox Signaling*, 2006, **8**, 1249– 1252.
192. J. S. Richman and J. R. Moorman, *Am. J. Physiol.: Heart Circ. Physiol.*, 2000, **278**, H2039– H2049.
193. G. Supinski, D. Stofan, L. A. Callahan, D. Nethery, T. M. Nosek and A. DiMarco, *J. Appl. Physiol.*, 1999, **87**, 783–779.
194. A. M. Shah and K. M. Channon, *Br. Heart J.*, 2004, **90**, 486–487.
195. X. Wang, Y. Huang, W. Lv, C. Li, W. Zeng, Y. Zhang and X. Feng, *Anal. Methods*, 2017, **9**, 1872-1875.
196. N. Karton-Lifshin, E. Segal, L. Omer, M. Portnoy, R. Satchi-Fainaro and D. Shabat, *J. Am. Chem. Soc.*, 2011, **133**, 10960–10965.
197. X. Sun, Q. Xu, G. Kim, S. E. Flower, J. P. Lowe, J. Yoon, J. S. Fossey, X. Qian, S. D. Bull and T. D. James, *Chem. Sci.*, 2014, **5**, 3368–3373.
198. F. Luo, Y. Lin, L. Zheng, X. Lin and Y. Chi, *ACS Appl. Mater. Interfaces*, 2015, 11322–11329.
199. D. Zhang, J. Zhang, H. Shi, X. Guo, Y. Guo, R. Zhang and B. Yuan, *Sens. Actuators, B*, 2015, **221**, 224–229.
200. L. Yang, C. Xu, W. Ye and W. A. Liu, *Sens. Actuators, B*, 2015, **215**, 489–496.
201. C. Gao, H. Zhu, J. Chen and H. Qiu, *Chin. Chim. Lett.*, 2017, **28**, 1006-1012.
202. V. Colombo, C. Montoro, A. Maspero, G. Palmisano, N. Masciocchi, S. Galli, E. Barea and J. A. R. Navarro, *J. Am. Chem. Soc.*, 2012, **134**, 12830–12843.
203. M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, *Chem. Mater.*, 2010, **22**, 6632–6640.
204. J. A. Greathouse and M. D. Allendorf, *J. Am. Chem. Soc.*, 2006, **128**, 10678–10679.
205. L. Huang, H. Wang, J. Chen, Z. Wang, J. Sun, D. Zhao and Y. Yan, *Microporous Mesoporous Mater.*, 2003, **58**, 105-114.
206. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850–13851.

2.1 Introduction

In the last two decades, research activities on high crystalline porous metal-organic frameworks (MOFs)¹⁻⁵ have grown exponentially. Due to porosity nature of MOFs, they are used in different areas such as gas storage/separation,⁶⁻¹⁰ heterogeneous catalysis,¹¹⁻¹³ chemical sensing,¹⁴⁻¹⁹ drug delivery²⁰⁻²² and polymerization.²³ MOFs are a new class of highly crystalline and porous materials. They are built up of inorganic secondary building blocks (SBUs). The interconnection of the inorganic SBUs by polytopic organic ligand molecules results in 1D, 2D and 3D framework structures having well-defined pore systems (channels, cages, etc.). Since an almost infinite combination of metal ions and organic ligands are possible, a huge variety of porous and topologies of MOF structures have been reported until today. It is possible to tune the pore dimensions (hence specific surface area and pore volume) and pore surface characteristics of MOFs by varying the sizes²⁴ of the organic ligands and by grafting various functional groups²⁵⁻³⁰ to the organic ligands, respectively.

MOF materials having high surface areas, high pore sizes, thermal and chemical stabilities are suitable for their applications in industry. Several famous MOF compounds³¹⁻³⁵ have shown low stability and therefore they are not suitable for industrial applications, although they have displayed great potential^{10, 36-40} for gas adsorption and separation. Synthesis of MOFs with high oxidation states metal ions (such as, Ti(IV),⁴¹ Zr(IV),⁴² Hf(IV),⁴³ etc.) is one of the approaches for synthesizing MOF materials having relatively higher thermal and chemical stabilities. Among numerous Zr(IV)-based MOF materials are reported till date,⁴⁴⁻⁴⁶ the microporous UiO-66 compound⁴² has attracted the attention of researchers owing to its high thermal and chemical stability as well as promising performances for CO₂/CH₄ separation.^{47, 48} The three-dimensional (3D) cubic framework of this MOF material is constructed from [Zr₆O₄(OH)₄]¹²⁺ building units which are interconnected by 1,4-benzenedicarboxylate (BDC) ligands. The use of longer 2,6-naphthalenedicarboxylate (NDC) ligand instead of BDC resulted in the formation of Zr(IV) and Hf(IV)-based DUT-52 (DUT = Dresden University of Technology)⁴³ framework compounds, which possess the same framework topology as that of UiO-66. Zr-DUT-52 material has been also termed as Zr-NDC⁴⁹ and Zr₆-NDC⁵⁰ in other reports. This MOF compound also exhibits high physiochemical stability and significant microporosity like UiO-66 (UiO = University of Oslo). The presented Zr(IV) (**1**) and

Ce(IV) (**2**) based MOF compounds consisting of 4-carboxycinnamate (CCA) ligands are isostructural with DUT-52 and hence both of them bear UiO-66 framework topology. It is noteworthy that, only a handful examples of Ce(IV)-based MOF compounds have been reported till date. Very recently, the synthesis, properties and redox catalytic activities of nine Ce(IV)-based MOF materials with UiO-66 structures containing ligands of different sizes and functionalities have been reported by Stock *et al.*⁵¹ More recently, we have employed the Ce(IV)-based azide and nitro-functionalized UiO-66 materials as turn-on fluorescence probes for the sensing of H₂S.⁵² Although the CCA ligand has been formerly employed for the construction of few MOFs with divalent metal ions,⁵³⁻⁵⁹ it has never been incorporated into MOFs having tetravalent metal ions such as Zr(IV) and Ce(IV). Therefore, we hypothesized that the employment of the CCA ligand and tetravalent metal ions would give rise to MOFs having high physiochemical stability. In this report, we present the synthesis, complete characterization, thermal and chemical stability as well as gas sorption behavior of the new Zr(IV) (**1**) and Ce(IV) (**2**) based MOF compounds containing the CCA ligand.

2.2 Experimental

2.2.1 Materials and General Methods

The H₂CCA ligand was synthesized according to a previously published procedure.⁵⁶ All other starting materials were of reagent grade and used as received from the commercial suppliers. Fourier transform infrared (FT-IR) spectra were recorded in the region of 440-4000 cm⁻¹ with a Perkin Elmer Spectrum Two FT-IR spectrometer. The following indications are used to characterize absorption bands: very strong (vs), strong (s), medium (m), weak (w), shoulder (sh), and broad (br). Elemental analyses (C, H, N) were carried out on a Thermo Scientific Flash 2000 CHNS-O analyzer equipped with a TCD detector. Thermogravimetric (TG) analyses were performed with a Mettler-Toledo TGA/SDTA 851e thermogravimetric analyzer in a temperature range of 30-600 °C under air atmosphere at a heating rate of 5 °C min⁻¹. Ambient temperature X-ray powder diffraction (XRPD) patterns were recorded on a Bruker D2 Phaser X-ray diffractometer (30 kV, 10 mA) or a Bruker D8 Advance θ -2 θ diffractometer (40 kV, 40 mA) in transmittance Bragg-Brentano geometry equipped with a LYNXEYE 1D detector and Göbel mirror, using Cu-K α (λ = 1.5406 Å) radiation. Le Bail fits of the XRPD patterns of

as-synthesized **1** and **2** were performed by using the Jana2006 program.⁶⁰ The solution ¹H-NMR spectra were recorded on a Bruker AM 300 spectrometer at 300 MHz. Before the NMR measurements, the compounds (20 mg each) were digested in 500 μ L of 1M NaOH in D₂O for 24 h. The nitrogen sorption isotherms up to 1 bar were measured using a Quantachrome Autosorb iQ-MP gas sorption analyzer at -196 °C. The carbon dioxide adsorption measurements were performed using a Quantachrome iSorb-HP gas sorption analyzer at 0 °C. Prior to the sorption experiments, the samples of **1** and **2** were degassed by heating (190 °C, 6 h for **1**; 50 °C, 4 h for **2**) under dynamic vacuum.

2.2.2 Procedure for Le Bail Fitting

The lattice models **1** and **2** were constructed by transforming the crystallographic unit cell of UiO-66 from space group $F\bar{4}3m$ into P23. The latter setting allowed us to transform the H₂BDC ligand into the less symmetric H₂CCA ligand while retaining a cubic crystal system. Both lattice models were fully geometry optimized by force-field calculations employing the UFF force field provided in the Forcite module of BIOVIA Materials Studio V8.0 (Accelrys Software, Inc., San Diego, CA, USA) software package. Materials Studio contains a full implementation of the Universal force field, including bond order assignment. The Materials Studio implementation has been rigorously tested and results are in agreement with published work on this force field.⁶¹⁻⁶³ Once fully relaxed lattice models were obtained, the lattice constants of both compounds were adjusted to the values as given in Table 2.1 and a constrained geometry optimization was performed to yield the final structural parameters which are given in this chapter.

2.2.3 Synthesis of [Zr₆O₄(OH)₄(C₁₀H₆O₄)₆] $\cdot$ 1.5DMF $\cdot$ 17H₂O (as-synthesized **1**)

A mixture of ZrCl₄ (100 mg, 0.43 mmol), H₂CCA ligand (82 mg, 0.43 mmol) and acetic acid (0.25 mL, 4.37 mmol) in 2 mL of *N,N'*-dimethylformamide (DMF) was heated in a sealed glass tube at 150 °C for 24 h using an aluminum block heater. After spontaneous cooling to room temperature, the white precipitate was collected by filtration, washed with acetone (4 $\times$ 2 mL) and dried in air. The yield was 137 mg (0.06 mmol, 83%) based on the Zr salt. Anal. calcd for C_{64.5}H_{84.5}N_{1.5}O_{50.5}Zr₆: C, 34.64 H, 3.80 N, 0.93. Found: C, 34.31 H, 3.74 N, 0.76%. FT-IR (KBr, cm⁻¹): 3418 (br), 1692 (s), 1640 (s), 1588 (s), 1532 (s),

1410 (vs), 1289 (w), 1254 (m), 1208 (w), 1180 (w), 1145 (w), 1111 (w), 1018 (w), 978 (m), 857 (m), 783 (s), 725 (sh), 662 (s), 570 (w), 472 (s).

Synthesis of $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{C}_{10}\text{H}_6\text{O}_4)_6]\cdot 6\text{DMF}\cdot 16\text{H}_2\text{O}$ (as-synthesized **2**)

A mixture of H_2CCA ligand (40 mg, 0.21 mmol) in DMF (2 mL) and an aqueous solution of ammonium cerium (IV) nitrate (400 μL , 0.5333 M) was sealed in a glass tube and heated using an oil bath under magnetic stirring at 100 $^\circ\text{C}$ for 20 min. The yellow precipitate was collected by centrifugation, washed with acetone (4×2 mL) and dried in air. The yield was 35 mg (0.02 mmol, 78%) based on the Ce salt. Anal. calcd for $\text{C}_{78}\text{H}_{114}\text{Ce}_6\text{N}_6\text{O}_{54}$: C, 32.98 H, 4.04 N, 2.95. Found: C, 32.71 H, 4.27 N, 2.75%. FT-IR (KBr, cm^{-1}): 3363 (br), 1647 (vs), 1586 (s), 1536 (s), 1388 (vs), 1288 (w), 1255 (w), 1205 (w), 1183 (w), 1144 (w), 1106 (m), 1012 (sh), 984 (m), 863 (m), 786 (m), 714 (m), 681 (w), 659 (w), 582 (s), 537 (sh), 454 (w).

2.2.4 Activation of As-Synthesized **1** and **2**

For activation, the as-synthesized sample of **1** was directly heated at 190 $^\circ\text{C}$ under vacuum for 6 h. In order to activate **2**, the as-synthesized form of the compound was stirred in acetone at room temperature for 3 h, during which period, the solvent was discarded and fresh acetone was added after each 1 h. In the second step, the acetone-exchanged form of the compound was heated at 50 $^\circ\text{C}$ under vacuum for 4 h. The thermally activated forms of **1** and **2** are denoted as **1'** and **2'**, respectively.

2.3 Results and Discussion

2.3.1 Synthesis and Activation

Compound **1** was synthesized by using similar synthesis conditions as described recently for several Ce(IV)-based MOF materials.^{51, 52} For optimizing the synthesis conditions of **1**, reactions were performed using mixtures of Zr(IV) salts (ZrCl_4 , $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ or $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and H_2CCA ligand in amide solvents like DMF, *N,N'*-diethylformamide (DEF) and *N,N'*-dimethylacetamide (DMA). Various modulators/additives⁶⁴ (benzoic acid (BA), formic acid (FA), acetic acid (AA), trifluoroacetic acid (TFA), H_2O or conc. HCl) were added in the reaction mixtures in order to enhance the crystallinity of the compound. All possible combinations of the reactants were employed in these reactions. **1** was

obtained with high crystallinity by using ZrCl_4 as the metal source and acetic acid as the modulator in DMF. For this combination, $\text{ZrCl}_4/\text{H}_2\text{CCA}$ ligand/acetic acid molar ratio of 1:1:10 was used. Reactions with all other combinations of reactants led to either amorphous products or products having lower crystallinity than **1** with optimum crystallinity. For investigating the effect of varying the ZrCl_4 /acetic acid ratio on the crystallinity and phase-purity of **1**, various ZrCl_4 /acetic acid molar ratios ranging from 1:10 to 1:100 were employed. Compound **1** was obtained with high crystallinity and phase-purity when ZrCl_4 /acetic acid molar ratio was 1:10 (Figure 2.1). With increase in the ZrCl_4 /acetic acid molar ratio, either the crystallinity of the compound decreased or additional peaks in the XRPD patterns due to an unknown crystalline phase were observed.

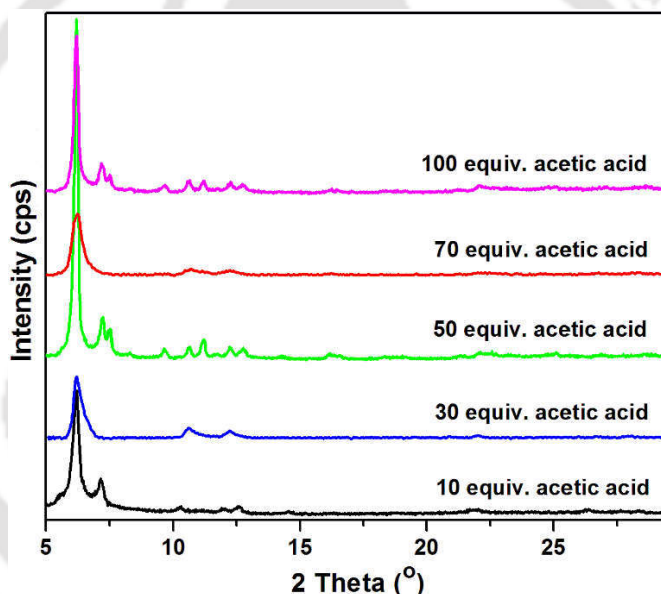


Figure 2.1 XRPD patterns of the samples of compound **1** prepared with different equivalents (with respect to ZrCl_4) of acetic acid as a modulator.

The physisorbed DMF molecules from the external surface of the as-synthesized samples of **1** and **2** were removed by washing the samples with acetone after filtration. After that, **1** was directly heated under vacuum in order to remove the occluded molecules encapsulated inside the pores. For activating **2**, a two-step procedure was employed. At first, the as-synthesized form of **2** was stirred in acetone for exchanging the guest molecules entrapped within the pores with more volatile acetone molecules. In the second step, the acetone-exchanged form of **2** was heated under vacuum for removing the acetone

molecules from the pores. The thermally activated compounds exhibit similar XRPD patterns (Figures 2.2 and 2.3) as those of the as-synthesized compounds. Therefore, both compounds retain their structural integrity after thermal activation.

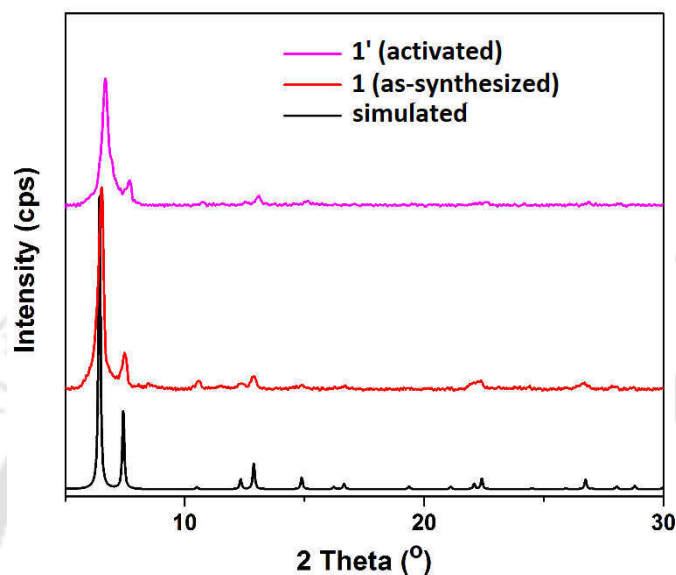


Figure 2.2 XRPD patterns of compound 1 in different forms: simulated (black), as-synthesized (red) and thermally activated (pink).

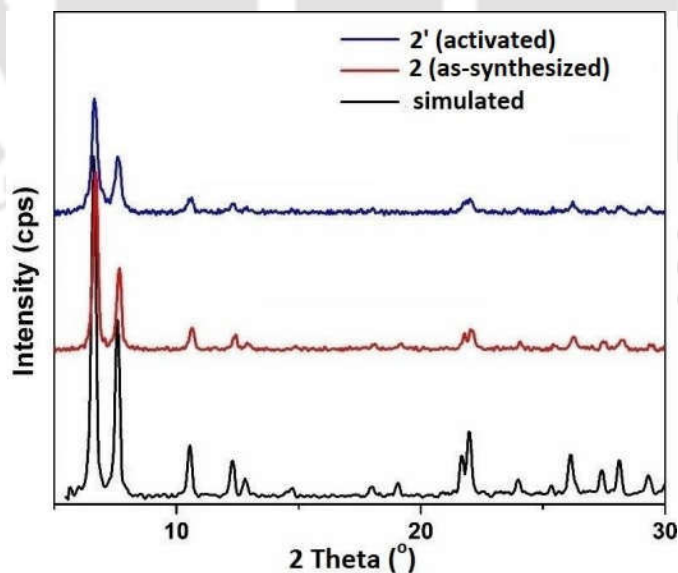


Figure 2.3 XRPD patterns of compound 2 in different forms: simulated (black), as-synthesized (red) and thermally activated (violet).

2.3.2 Infrared Spectroscopy

The FT-IR spectra of the as-synthesized and thermally activated samples of **1** and **2** (Figures 2.4 and 2.5) reveal strong absorption bands at around 1590 and 1390 cm^{-1} , which can be attributed to the asymmetric and symmetric $-\text{CO}_2$ stretching vibrations of the coordinated CCA ligand molecules, respectively.^{25-29, 65} In the IR spectrum of the as-synthesized and activated **1** and **2**, the strong absorption bands observed at around 1640 cm^{-1} can be ascribed to the $\text{C}=\text{C}$ stretching vibration of the coordinated CCA ligand molecules.⁶⁶ The strong absorption band at around 1690 cm^{-1} in the IR spectrum of as-synthesized **1** and **2** can be attributed to the $\text{C}=\text{O}$ stretching vibration of the occluded DMF molecules.

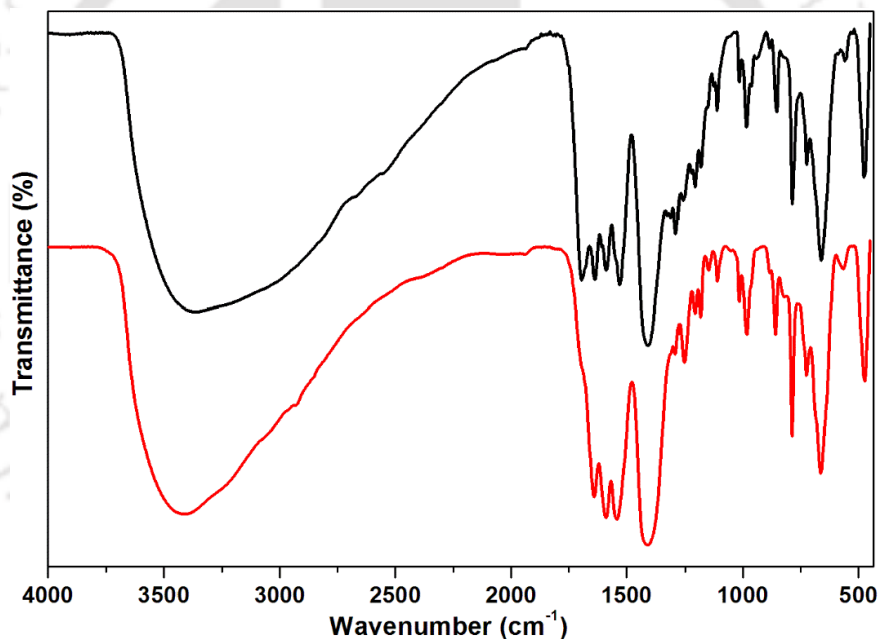


Figure 2.4 FT-IR spectra of the as-synthesized (black) and activated (red) samples of compound **1**.

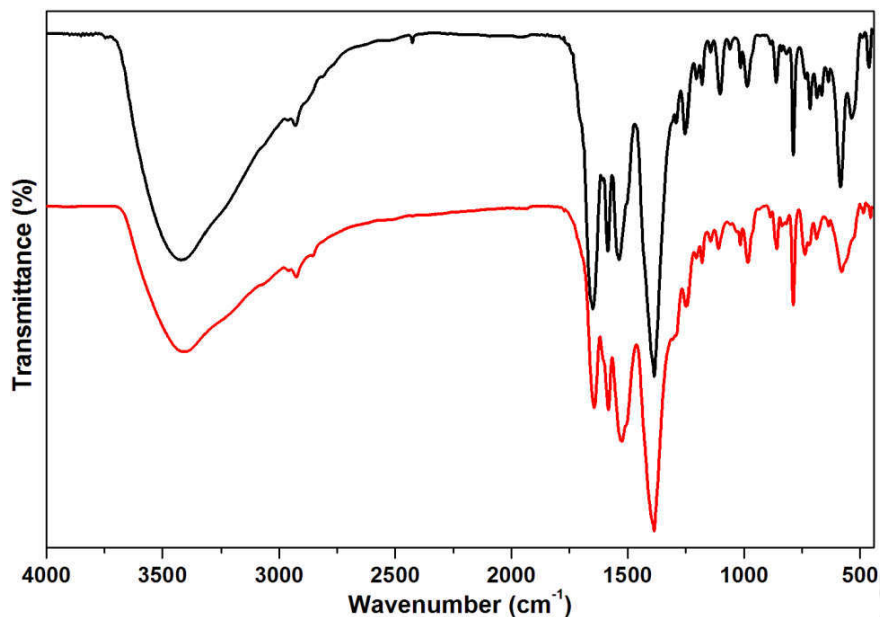


Figure 2.5 FT-IR spectra of the as-synthesized (black) and activated (red) samples of compound **2**.

2.3.3 Structure Description

Determination of the lattice parameters of the as-synthesized samples of **1** and **2** were carried out from their XRPD patterns measured at ambient conditions. The lattice parameters displayed in Table 2.1 clearly indicate that both compounds possess cubic structures. The values of the unit cell parameters of the present compounds are close to those of the formerly reported, structurally related DUT-52 framework material.^{43, 49, 50, 67}

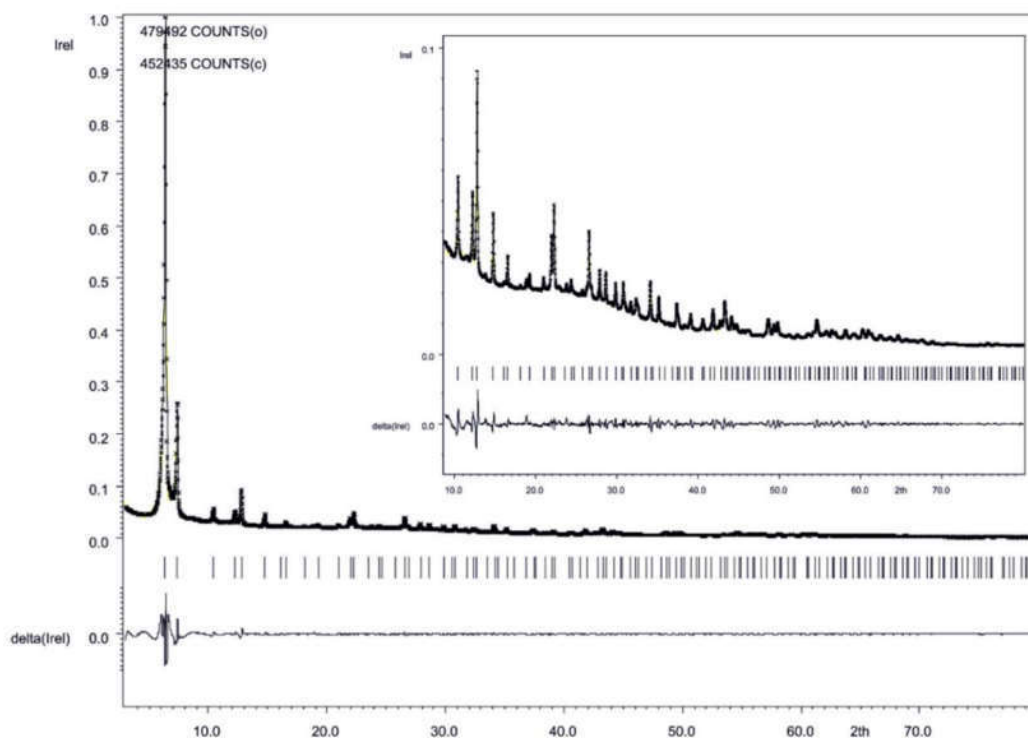


Figure 2.6 Le Bail fit of the XRPD pattern of as-synthesized **1**. Dotted and solid lines denote observed and calculated patterns, respectively. The peak markers and the difference plot are displayed at the bottom. $R_p = 5.51$, $R_{wp} = 7.82$.

Le Bail fits of the experimental XRPD patterns of as-synthesized **1** and **2** are presented as Figures 2.6 and 2.7, respectively. Good reliability factors were obtained from the fits, which indicated that the experimental XRPD patterns matched well with the calculated ones. The similarity between the theoretical and experimental XRPD patterns for both compounds (Figures 2.2 and 2.3) confirms their phase-purity. Since the frameworks of **1** and **2** are isostructural with DUT-52,^{43, 49, 50, 67} the framework structures (Figure 2.8) of the hydroxylated forms of the present compounds are composed of $[M_6O_4(OH)_4]^{12+}$ ($M = \text{Zr}$ for **1** or Ce for **2**) building units. In these building units, the $\mu_3\text{-O}$ and $\mu_3\text{-OH}$ groups alternatively cap the triangular faces of the M_6 octahedron. The cross-linking of the $[M_6O_4(OH)_4]^{12+}$ building blocks by the carboxylate groups of 12 CCA ligand molecules leads to the formation of cubic, 3D frameworks. In these network structures, both octahedral and tetrahedral shaped microporous cages exist. Each Zr or Ce atom adopts a square-antiprismatic geometry, coordinating with eight O atoms. Four O atoms from carboxylate groups occupy the corners of one square face of the square antiprism, whereas

the O atoms from the μ_3 -O and μ_3 -OH groups are located at the corners of the second square face. In the network structures, every octahedral cage (free diameter ~ 14 Å) at the center is linked with eight tetrahedral cages (free diameter ~ 11 Å) at the corners through narrow trigonal windows (free diameter ~ 8 Å).⁴⁹

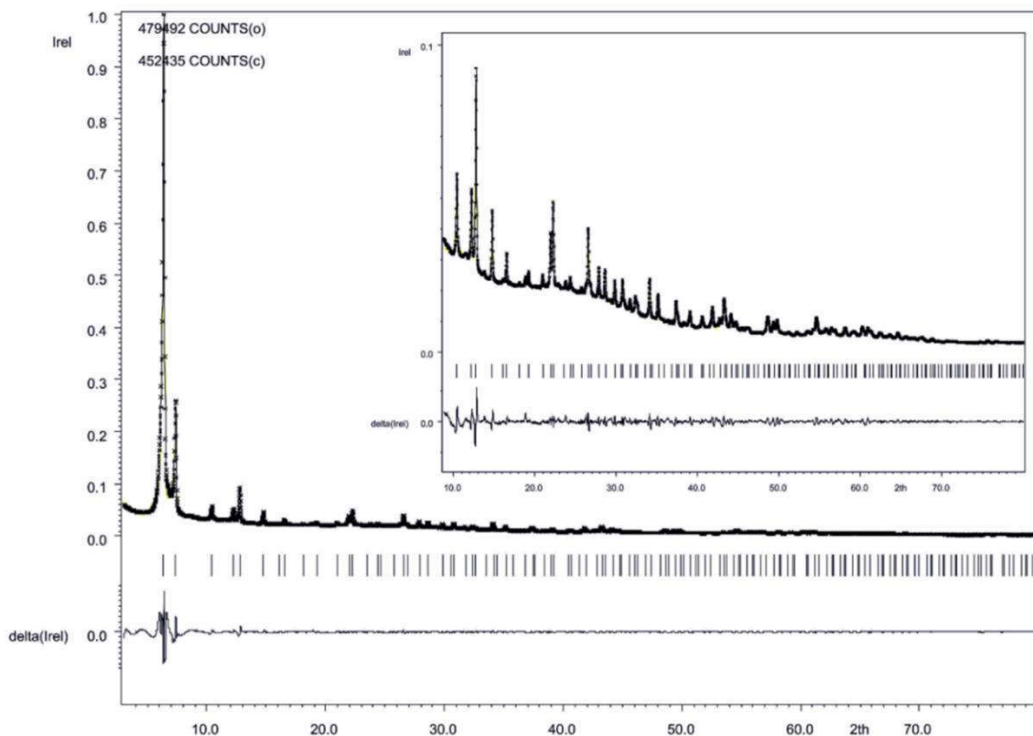


Figure 2.7 Le Bail fit of the XRPD pattern of as-synthesized **2**. Dotted and solid lines denote observed and calculated patterns, respectively. The peak markers and the difference plot are displayed at the bottom. $R_p = 1.33$, $R_{wp} = 1.97$.

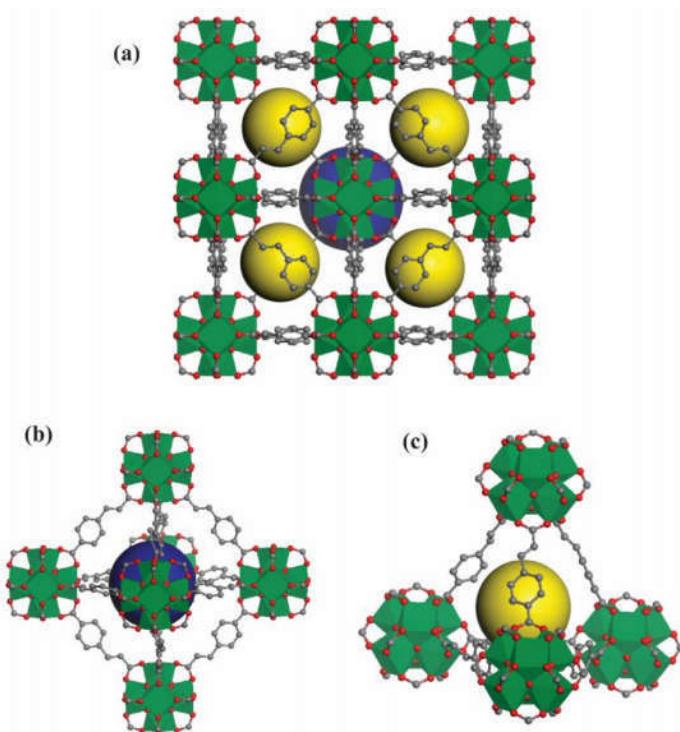


Figure 2.8 (a) Ball-and-stick representation of the 3D cubic structures of **1** and **2** showing arrangements of the octahedral (blue spheres) and tetrahedral (yellow spheres) cages in the framework. (b,c) Enlarged representation of the octahedral and tetrahedral cages. Zr and Ce atoms are shown as polyhedra (color codes: Zr/Ce, green; C, dark grey and O, red). The hydrogen atoms and occluded molecules have been omitted for clarity.

Table 2.1 Refined lattice parameters for as-synthesized **1** and **2** having cubic unit cells.

Compounds	a (Å)	V (Å ³)
1 (as-synthesized)	23.809 (2)	13497 (1)
2 (as-synthesized)	24.6349 (8)	14950.3 (5)
Zr-DUT-52 ⁴³	23.910(3)	13669(3)
Hf-DUT-52 ⁴³	23.74391(24)	13395.6(2)
Zr-NDC ⁴⁹	23.7853	-
Zr ₆ -NDC ⁵⁰	23.808(1)	13495(2)

2.3.4 Thermal Stability

The thermal stability of the compounds was determined by performing TG analyses with the as-synthesized as well as activated samples of **1** and **2** in an air atmosphere. The TG analyses (Figure 2.9) reveal that **1** and **2** are thermally stable up to 390 and 300 °C, respectively. The high thermal stability of **1** is comparable with those of Zr-UiO-66 and several other Zr(IV)-based MOF materials.^{27, 44-46, 65, 68-70} Similarly, the lower thermal stability of **2** than **1** compares well with those of Ce-UiO-66 and few other Ce(IV)-based MOF compounds.^{51, 52}

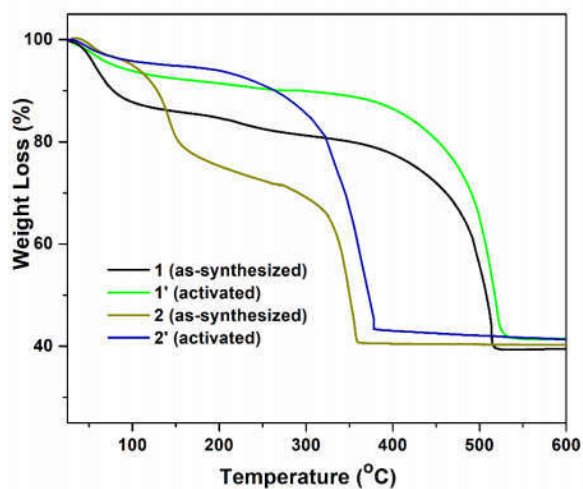


Figure 2.9 TG curves of the different forms of **1** and **2** measured in an air atmosphere in the temperature range of 30-600 °C.

In the TG traces of as-synthesized **1** and **2** (Figure 2.9), the first weight loss steps of 13.5 and 10.5 wt% in the temperature range of 40-130 °C can be ascribed to the removal of 17 and 16 uncoordinated H₂O molecules per formula unit (calcd.: 13.6 wt%, **1**; 10.1 wt%, **2**), respectively. The second weight loss steps of 5.0 and 16.0 wt% in the temperature ranges of 130-280 and 130-230 °C can be assigned to the removal of 1.5 and 6 occluded DMF molecules per formula unit of **1** and **2** (calcd.: 4.9 wt%, **1**; 15.4 wt%, **2**), respectively. Owing to the removal of organic linker molecules from the framework, the decomposition of **1** and **2** occurs above 390 and 300 °C, respectively.

In the TG curves of **1'** and **2'**, the first weight loss step can be ascribed to the removal of the adsorbed water molecules. The occurrence of this weight loss step can be related to the

exposure of the compounds to air after thermal activation, resulting in hydration of the materials.

2.3.5 Chemical Stability

For determination of the chemical stability of the thermally activated samples (0.05 g for each) of **1'** and **2'**, the samples were stirred in water, methanol, acetic acid and 1M HCl solutions (10 mL for each) under ambient conditions for 12 h. After collecting the samples by filtration, the crystallinity of the filtered solids were examined by XRPD measurements (Figures 2.10 and 2.11). **1'** retained its crystallinity (and hence structural integrity) after treatment with methanol. The crystallinity of **1'** was reduced slightly after treatment with water and acetic acid. However, the treatment of **1'** with 1M HCl solution lead to substantial reduction in crystallinity. In case of **1'**, the crystallinity was greatly reduced after treatment with methanol and water. The crystallinity of **2'** was completely lost when treated with acetic acid and 1M HCl solutions. Therefore, **1'** exhibited relatively lower chemical stability compared to several other Zr(IV)-based MOF materials.^{27, 44, 45, 68, 69} On the other hand, the low chemical stability of **2'** is comparable with few other recently reported Ce(IV)-based MOF compounds.^{51, 52}

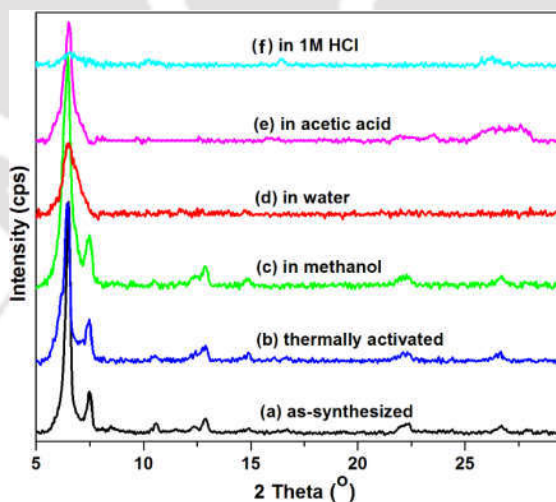


Figure 2.10 XRPD patterns of compound **1'** in different forms: as-synthesized (a), thermally activated (b), treated with methanol (c), water (d), acetic acid (e), and 1M HCl (f).

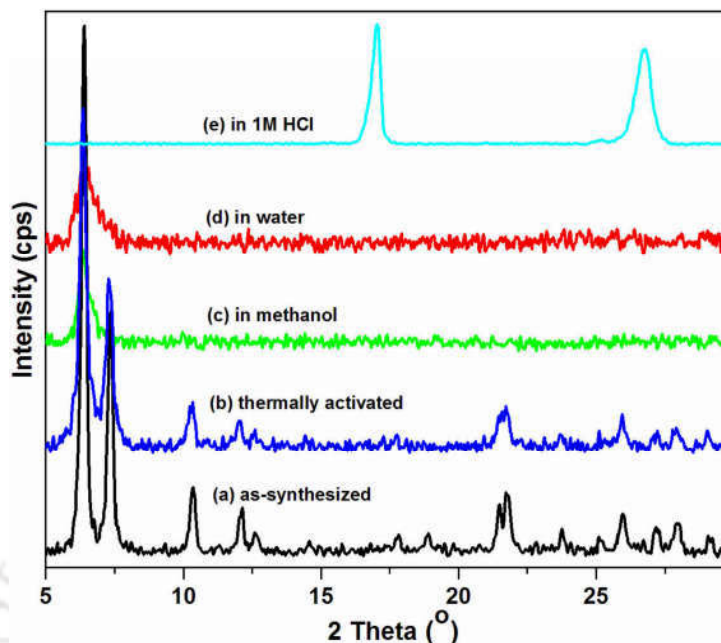


Figure 2.11 XRPD patterns of compound **2'** in different forms: as-synthesized (a), thermally activated (b), treated with methanol (c), water (d), and 1M HCl (e).

2.3.6 Gas Adsorption Properties

In order to verify the permanent microporosity of the framework materials, N₂ sorption measurements were performed with **1'** and **2'**. As displayed in Figure 2.12, the adsorption isotherms of the compounds followed type-I behavior. From the N₂ adsorption isotherms, the specific BET surface areas and micropore volumes of the materials were calculated. The specific BET surface areas and micropore volumes of **1'** and **2'** are summarized in Table 2.2. The BET surface area and micropore volume of **2'** are comparable with the structurally related Zr(IV) and Hf(IV)-based DUT-52 compounds, although these values are much lower compared to the isostructural Zr-NDC material. On the other side, the BET surface area and micropore volume of **1'** are lower compared to **2'**. This fact can be attributed to the difficulty in activating the as-synthesized sample of **1** by the two-step procedure which has been applied for activating the as-synthesized **1** (i.e., solvent-exchange followed by heating under vacuum).

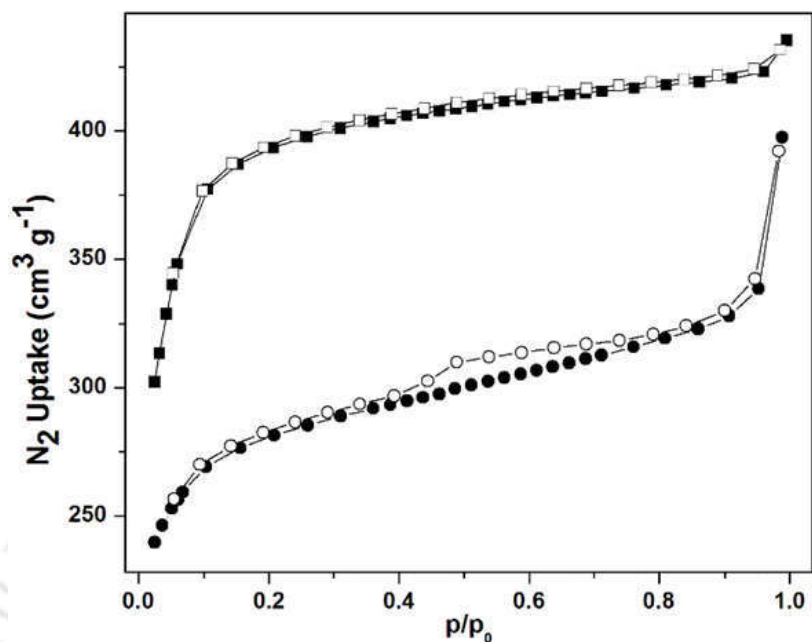


Figure 2.12 N_2 adsorption (filled symbols) and desorption (empty symbols) isotherms of 1' (circles) and 2' (squares) measured at $-196\text{ }^{\circ}\text{C}$.

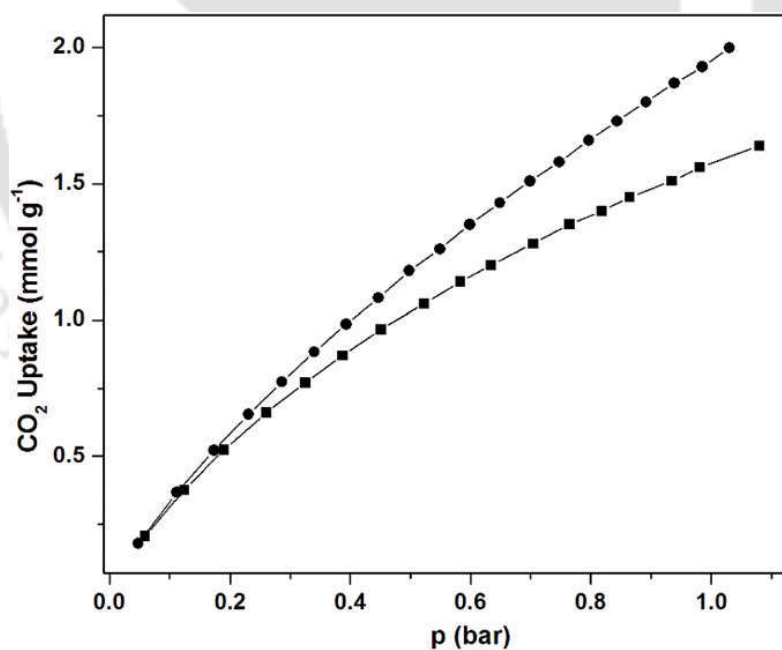


Figure 2.13 Low-pressure CO_2 adsorption isotherms of 1' (circles) and 2' (squares) recorded at $0\text{ }^{\circ}\text{C}$.

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Table 2.2 Specific BET surface areas^[a] and micropore volumes^[b] of **1'** and **2'** determined from the N₂ adsorption isotherms.

Compounds	BET Surface Area (m ² g ⁻¹)	Micropore Volume (cm ³ g ⁻¹)
1'	870	0.62
2'	1210	0.67
Zr-DUT-52 ⁴³	1399	0.60
Hf-DUT-52 ⁴³	1097	0.47
Zr-NDC ⁴⁹	1720	0.67
Zr ₆ -NDC ⁵⁰	1287	0.54

[a] Specific BET surface areas were estimated in the p/p_0 range of 0.05-0.1.

[b] Micropore volumes were determined at $p/p_0 = 0.99$.

The accessible surface areas of **1'** and **2'** have been calculated by using the Poreblazer software.⁷¹ The accessible surface areas of **1'** and **2'** have been estimated to be 1421 and 1242 m² g⁻¹, respectively. On the other hand, the experimental BET surface areas of **1'** and **2'** are 870 and 1210 m² g⁻¹, respectively. Thus, the theoretical surface area of **2'** is close to the experimental value, which supports the structural model of this compound. Since **1'** and **2'** are isostructural, they are expected to show similar experimental surface areas. The lower experimental surface area of **1'** as compared to the theoretical value suggests the incomplete activation of the compound.

The permanent microporosity of the framework structures of **1'** and **2'** was also verified by low-pressure CO₂ adsorption measurements at 0 °C. The occurrence of type-I adsorption isotherms (Figure 2.13) confirmed microporous nature of both compounds. The CO₂ adsorption capacities of **1'** and **2'** at 0 °C and 1 bar reached 2.0 and 1.6 mmol g⁻¹, respectively. These CO₂ uptake values are comparable with that of the isostructural DUT-52 material.⁶⁷

2.4 Conclusions

We have presented the synthesis, complete characterization, thermal and chemical stability as well as gas sorption characteristics of new Zr(IV) and Ce(IV)-based MOF materials consisting of H₂CCA ligand. Both compounds have been synthesized under solvothermal conditions (150 °C, 24 h for **1**; 100 °C, 20 min for **2**). The phase purity of the compounds were examined by a combination of XRPD analysis, FT-IR spectroscopy, thermogravimetric and elemental analyses. As confirmed by the XRPD measurements, both compounds are isostructural with DUT-52 framework material. Based on the thermogravimetric analyses, **1** and **2** are thermally stability up to 390 and 300 °C in air atmosphere, respectively. As revealed from the XRPD experiments, both materials display moderate stability in water and methanol, however they lose their crystallinity when exposed to 1M HCl. N₂ sorption analyses indicate that **1'** and **2'** exhibit specific BET surface areas of 870 and 1210 m² g⁻¹, respectively. The CO₂ uptake values of **1'** and **2'** at 0 °C and 1 bar correspond to 2.0 and 1.6 mmol g⁻¹, respectively.

2.5 References

1. Themed issue on MOFs, *Chem. Soc. Rev.*, 2009, **38**, 1201-1508.
2. Special issue on MOFs, *Chem. Rev.*, 2012, **112**, 673-1268.
3. O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705-714.
4. G. Férey and *Chem. Soc. Rev.*, 2008, **37**, 191-214.
5. S. Kitagawa, R. Kitaura and S. S. Noro, *Angew. Chem. Int. Ed.*, 2004, **43**, 2334-2375.
6. R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 3875-3877.
7. S. Couck, E. Gobechiya, C. E. A. Kirschhock, P. S. Crespo, J. J. AlcaÇiz, A. M. Joaristi, E. Stavitski, J. Gascon, F. Kapteijn, G. V. Baron and J. F. M. Denayer, *ChemSusChem*, 2012, **15**, 740-750.
8. L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294-1314.
9. J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.

10. L. Hamon, P. L. Llewellyn, T. Devic, A. Ghoufi, G. Clet, V. Guillermin, G. D. Pirngruber, G. Maurin, C. Serre, G. Driver, W. VanBeek, E. Jolimaite, A. Vimont, M. Daturi and G. Férey, *J. Am. Chem. Soc.*, 2009, **131**, 17490-17499.
11. L. Ma, J. M. Falkowski, C. Abney and W. Lin, *Nat. Chem.*, 2010, **2**, 838-846.
12. J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450-1459.
13. K. Manna, T. Zhang, M. Carboni, C. W. Abney and W. Lin, *J. Am. Chem. Soc.*, 2012, **136**, 13182-13185.
14. L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. V. Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105-1125.
15. K. Müller-Buschbaum, F. Beuerle and C. Feldmann, *Microporous Mesoporous Mater.*, 2015, **216**, 171-199.
16. Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815-5840.
17. M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330-1352.
18. Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126-1162.
19. Y. Cui, B. Chen and G. Qian, *Coord. Chem. Rev.*, 2014, **273-274**, 76-86.
20. D. Liu, C. Poon, K. Lu, C. He and W. Lin, *Nat. Commun.*, 2014, **5**, 4182-4192.
21. K. M. L. Taylor-Pashow, J. D. Rocca, Z. G. Xie, S. Tran and W. B. Lin, *J. Am. Chem. Soc.*, 2009, **131**, 14261-14263.
22. P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J. S. Chang, Y. K. Hwang, V. Marsaud, Y.-N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur and R. Gref, *Nat. Mater.*, 2010, **9**, 172-178.
23. T. Uemura, N. Yanai and S. Kitagawa, *Chem. Soc. Rev.*, 2009, **38**, 1228-1236.
24. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469-472.
25. S. Biswas, T. Ahnfeldt and N. Stock, *Inorg. Chem.*, 2011, **50**, 9518-9526.
26. S. Biswas, D. E. P. Vanpoucke, T. Verstraelen, M. Vandichel, S. Couck, K. Leus, Y.-Y. Liu, M. Waroquier, V. V. Speybroeck, J. F. M. Denayer and P. V. D. Voort, *J. Phys. Chem. C*, 2013, **117**, 22784-22796.
27. S. Biswas and P. V. D. Voort, *Eur. J. Inorg. Chem.*, 2013, **2013**, 2154-2160.

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28. A. Buragohain, P. V. D. Voort and S. Biswas, *Microporous Mesoporous Mater.*, 2015, **215**, 91-97.
29. A. Buragohain, S. Couck, P. V. D. Voort, J. F. M. Denayer and S. Biswas, *J. Solid State Chem.*, 2016, **238**, 195-202.
30. S. Biswas, J. Zhang, Z. Li, Y.-Y. Liu, M. Grzywa, L. Sun, D. Volkmer and P. V. D. Voort, *Dalton Trans.*, 2013, **42**, 4730-4737.
31. L. M. Huang, H. T. Wang, J. X. Chen, Z. B. Wang, J. Y. Sun, D. Y. Zhao and Y. S. Yan, *Microporous Mesoporous Mater.*, 2003, **58**, 105-114.
32. J. A. Greathouse and M. D. Allendorf, *J. Am. Chem. Soc.*, 2006, **128**, 10678-10679.
33. Y. Li and R. T. Yang, *Langmuir*, 2007, **23**, 12937-12944.
34. S. S. Kaye, A. Dailly, O. M. Yaghi and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 14176-14177.
35. D. Ma, Y. Li and Z. Li, *Chem. Commun.*, 2011, **47**, 7377-7379.
36. B. Wang, A. P. Cote, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207-211.
37. L. Hamon, E. Jolimaître and G. D. Pirngruber, *Ind. Eng. Chem. Res.*, 2010, **49**, 7497-7503.
38. Y.-S. Bae, B. G. Hauser, O. M. Farha, J. T. Hupp and R. Q. Snurr, *Microporous Mesoporous Mater.*, 2011, **141**, 231-235.
39. S. Keskin, T. M. VanHeest and D. S. Sholl, *ChemSusChem*, 2010, **3**, 879-891.
40. R. Babarao, S. Dai and J. Jiang, *Langmuir*, 2011, **27**, 3451-3460.
41. M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez and G. Ferey, *J. Am. Chem. Soc.*, 2009, **131**, 10857-10859.
42. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850-13851.
43. V. Bon, I. Senkovska, M. S. Weiss and S. Kaskel, *CrystEngComm*, 2013, **15**, 9572-9577.
44. M. Kim and S. M. Cohen, *CrystEngComm*, 2012, **14**, 4096-4104.
45. S. Wang, J. Wang, W. Cheng, X. Yang, Z. Zhang, Y. Xu, H. Liu, Y. Wu and M. Fang, *Dalton Trans.*, 2015, **44**, 8049-8061.
46. Y. Bai, Y. Dou, L.-H. Xie, W. Rutledge, J.-R. Li and H.-C. Zhou, *Chem. Soc. Rev.*, 2016, **45**, 2327-2367.

47. Q. Yang, H. Jobic, F. Salles, D. Kolokolov, V. Guillermin, C. Serre and G. Maurin, *Chem. Eur. J.*, 2011, **17**, 8882-8889.
48. Q. Yang, A. D. Wiersum, H. Jobic, V. Guillermin, C. Serre, P. L. Llewellyn and G. Maurin, *J. Phys. Chem. C*, 2011, **115**, 13768-13774.
49. W. Zhang, H. Huang, D. Liu, Q. Yang, Y. Xiao, Q. Ma and C. Zhong, *Microporous Mesoporous Mater.*, 2013, **171**, 118-124.
50. V. Guillermin, F. Ragon, M. Dan-Hardi, T. Devic, M. Vishnuvarthan, B. Campo, A. Vimont, G. Clet, Q. Yang, G. Maurin, G. Férey, A. Vittadini, S. Gross and C. Serre, *Angew. Chem. Int. Ed.*, 2012, **51**, 9267-9271.
51. M. Lammert, M. T. Wharmby, S. Smolders, B. Bueken, A. Lieb, K. A. Lomachenko, D. D. Vos and N. Stock, *Chem. Commun.*, 2015, **51**, 12578-12581.
52. A. Buragohain and S. Biswas, *CrystEngComm*, 2016, **18**, 4374-4381.
53. W. Zhang, Y. Liu, G. Lu, Y. Wang, S. Li, C. Cui, J. Wu, Z. Xu, D. Tian, W. Huang, J. S. DuCheneu, W. D. Wei, H. Chen, Y. Yang and F. Huo, *Adv. Mater.*, 2015, **27**, 2923-2929.
54. M.-J. Dong, M. Zhao, S. Ou, C. Zou and C.-D. Wu, *Angew. Chem. Int. Ed.*, 2014, **53**, 1575-1579.
55. H. Kumagai, Y. Oka, K. Inoue and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 2002, **2002**, 3442-3446.
56. T. K. Prasad and M. P. Suh, *Chem. Eur. J.*, 2012, **18**, 8673-8680.
57. B. Wu, Z.-G. Ren, H.-X. Li, M. Dai, D.-X. Li, Y. Zhang and J.-P. Lang, *Inorg. Chem. Commun.*, 2009, **12**, 1168-1170.
58. A. Modrow, M. Feyand, D. Zargarani, R. Herges and N. Stock, *Z. Anorg. Allg. Chem.*, 2012, **638**, 2138-2143.
59. M. Xue, S. Ma, Z. Jin, R. M. Schaffino, G.-S. Zhu, E. B. Lobkovsky, S.-L. Qiu and B. Chen, *Inorg. Chem.*, 2008, **47**, 6825-6828.
60. V. Petricek, M. Dusek and L. Palatinus, Jana2000 – The Crystallographic Computing System Institute of Physics, Czech Republic, Praha, 2000.
61. A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. GoddardIII and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024-10035.
62. C. J. Casewit, K. S. Colwell and A. K. Rappe, *J. Am. Chem. Soc.*, 1992, **114**, 10046-10053.
63. A. K. Rappe, K. S. Colwell and C. J. Casewit, *Inorg. Chem.*, 1993, **32**, 3438-3450.

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64. N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933-969.
65. S. Biswas, J. Zhang, Z. Li, Y.-Y. Liu, M. Grzywa, L. Sun, D. Volkmer and P. V. D. Voort, *Dalton Trans.*, 2013, **42**.
66. C. N. Banwell and E. M. McCash, *Fundamentals of Molecular Spectroscopy* McGraw Hill, New York, 1994.
67. J. H. Cavka, C. A. Grande, G. Mondino and R. Blom, *Ind. Eng. Chem. Res.*, 2014, **53**, 15500-15507.
68. M. SK, M. Grzywa, D. Volkmer and S. Biswas, *J. Solid State Chem.*, 2015, **232**, 221-227.
69. M. SK, S. Bhowal and S. Biswas, *Eur. J. Inorg. Chem.*, 2015, **2015**, 3317-3322.
70. M. SK and S. Biswas, *CrystEngComm*, 2016, **18**, 3104-3113.
71. L. Sarkisov and A. Harrison, *Mol. Simul.*, 2011, **37**, 1248-1257.



3.1 Introduction

In recent years, research activity on MOFs¹⁻⁶ has undergone a renaissance owing to their potential applications in a wide range of areas such as gas storage/separation,⁷⁻¹⁰ heterogeneous catalysis,¹¹⁻¹³ polymerization¹⁴ and drug delivery.¹⁵⁻¹⁷ This new class of highly crystalline and extremely porous materials are constructed from inorganic building units which are cross-linked by polytopic aromatic ligands. Different functional groups can be introduced into their frameworks in order to achieve the goal for a specific application. For the functionalization of MOFs, either pre-functionalized ligands can be used during the synthesis or a post-synthetic modification strategy¹⁸ can be applied. For luminescent MOFs, the functional groups (such as pyridyl,¹⁹ amine,²⁰ amide,^{21, 22} functionalized dye,²³ etc.) attached with the organic ligands provide interaction sites for the detection of various analytes.

Fluorescent MOF-based probes for the detection of various analytes.^{24, 25, 26-34} Due to their huge porosity and highly crystalline structures bearing definite pore sizes and pore shapes, fluorescent MOF compounds exhibit advantages over other sensor materials in sensing applications. The tuneable nature of their porosity (pore sizes and pore volumes) allow highly size-selective detection of analytes. Moreover, the extent of sensitivity of the detection process is enhanced due to the confinement of the analytes within the large cavities of the MOF materials. In addition, the analytes can interact with the pore surface of MOF compounds through the Lewis acidic or basic as well as coordinatively unsaturated metal sites. As a result of these interactions, the target analytes can be selectively gathered inside the MOF pores, which increases the sensing performance. Furthermore, the luminescence emissions of the MOF materials can be increased by the incorporation of π -conjugated aromatic ligands into the frameworks. Most importantly, the optical band gaps of MOF materials can be tuned in a systematic way because of the virtually infinite combinations of metal ions and organic ligands. Consequently, numerous fluorescent MOF materials have been investigated so far in the literature for the sensing of various analytes such as cations, anions, biomolecules, small molecules, volatile organic compounds and nitroaromatic explosives (NAEs).²⁶⁻³⁴

The fast, selective and sensitive sensing of NAEs is crucial for homeland security, battlefield protection, security screening, industrial and environmental safety as well as human health.³⁵⁻³⁸ Among various military and industrial NAEs, 2,4,6-trinitrophenol

(TNP) is very powerful. This NAE, which is even stronger than its well-known counterpart 2,4,6-trinitrotoluene (TNT), has been extensively employed in the manufacture of fireworks, matches, rocket fuels and landmines as well as in leather, pharmaceutical and dye industries.^{39, 40} In addition, the mutagenic and/or carcinogenic activities of TNP can result in several health issues like anaemia, skin irritation and abnormal liver functions.⁴¹ In order to reduce the harmful effects of TNP on the environment, its fast, sensitive and selective detection in presence of other NAEs is highly demanding. Expensive and sophisticated instruments having low selectivity and poor portability are currently being utilized as the detection methods for NAEs.⁴² On the other hand, fluorescence-based chemical sensors have appeared as one of the most potential candidates in recent years for sensing of NAEs because of their simplicity, portability, low cost, rapid response time, high sensitivity as well as dual compatibility in solid and solution media. Next to other fluorescent sensor materials such as conjugated polymers³⁶⁻³⁸ and nanoparticles,^{43, 44} MOF-based²⁶⁻³⁴ luminescent probes have already shown great potential for the sensing of a broad variety of NAEs.

Herein, we have presented a Zr-based MOF having strong luminescent behaviour. The MOF material (**3**) bearing UiO-68 framework topology and incorporating the thiadiazole-functionalized BTDB ligand. The thermally activated form of the material (termed as **3'** hereafter) is able to detect TNP in methanol suspension with high selectivity and sensitivity. It is noteworthy that the luminescent BTDB ligand has been recently employed to construct a Zn-based MOF, which has exhibited highly selective sensing behaviour towards Cd²⁺ ions.⁴⁵ Despite the fact that many MOF-based²⁶⁻³⁴ fluorescent probes have been examined until today for the sensing of NAEs, only a handful of MOFs^{19, 20, 22, 25, 46-51} have demonstrated fast, selective and sensitive detection behaviour towards TNP.

3.2 Experimental Section

3.2.1 Materials and General Methods

The H₂BTDB ligand was synthesized according to a previously reported procedure.⁴⁵ All other chemicals were commercially available and used without further purification. FT-IR spectra were recorded in the region of 440-4000 cm⁻¹ with a Perkin Elmer Spectrum Two FT-IR spectrometer. The following indications are used to characterize absorption bands: very strong (vs), strong (s), medium (m), weak (w), shoulder (sh) and broad (br).

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TG analysis was performed with a SDT Q600 V20.9 Build 20 thermogravimetric analyzer in a temperature range of 25-600 °C under air atmosphere at a heating rate of 10 °C min⁻¹. Ambient temperature XRPD patterns were recorded on a Bruker D2 Phaser X-ray diffractometer operated at 30 kV, 10 mA using Cu-K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The nitrogen sorption isotherms up to 1 bar were measured using a Quantachrome Autosorb iQ-MP gas sorption analyzer at -196 °C. The compound was degassed at 120 °C for 24 h under dynamic vacuum prior to the sorption experiments. Fluorescence emission studies were performed with a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. Fluorescence lifetimes were measured using time correlated single-photon counting (TCSPC) method on an Edinburgh Instrument Life-Spec II instrument. The samples were excited at 370 nm keeping the emission wavelength at 494 nm using a pulsed diode laser. The fluorescence decays were analyzed by reconvolution method using the FAST software provided by Edinburgh Instruments.

Safety note! *TNP and TNT are potentially explosives, and caution should be exercised when dealing with such materials. However, the small quantities used in this investigation were not found to present a hazard.*

3.2.2 Synthesis of MOF and its Activation

Synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BTDB})_6] \cdot 8\text{H}_2\text{O} \cdot 6\text{DMF}$ (3)

A mixture of ZrCl_4 (50 mg, 0.21 mmol), H_2BTDB ligand (79 mg, 0.21 mmol) and trifluoroacetic acid (TFA) (0.49 mL, 6.40 mmol) in DMF (3 mL) was sealed in a glass tube and heated using a block heater at 150 °C for 24 h. The light-yellow precipitate was collected by filtration and washed with acetone. The solid was first dried in air at room temperature and then at 60 °C for 1 h in a conventional oven. The yield was 82 mg (0.02 mmol, 66%) based on the Zr salt. Anal. calcd. for $\text{C}_{138}\text{H}_{122}\text{N}_{18}\text{O}_{46}\text{S}_6\text{Zr}_6$ (3508.27 g mol⁻¹): C, 47.24 H, 3.50 N, 7.18%. Found: C, 46.95 H, 3.63 N, 7.34%. FT-IR (KBr, cm⁻¹): 3420 (br), 2916 (w), 2853 (w), 1650 (s), 1600 (vs), 1422 (s), 1418 (vs), 1188 (m), 1153 (w), 1096 (w), 1026 (m), 880 (sh), 845 (s), 782 (vs), 711 (sh), 663 (vs), 558 (w), 495 (s).

Activation of the MOF Material

The as-synthesized form of the material was activated in a two-step process. In the first step, the as-synthesized material (150 mg) was stirred in methanol (25 mL) at room

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temperature for 24 h. In the next step, the methanol-exchanged form of the material was heated at 120 °C under dynamic vacuum for 24 h.

3.2.3 Preparation of the Suspension of 3' in Methanol

Compound 3' (3 mg) was placed in a 5 mL glass vial and 3 mL methanol was added. Then, the mixture was sonicated for 1 h and kept for 3 days in order to obtain a stable suspension for fluorescence titration measurements.

3.2.4 Fluorescence Titration Experiments

100 μ L of the suspension of 3' in methanol was taken in quartz cuvette and 2900 μ L methanol was added to it. During the fluorescence titration experiments, 3 mM solution of different nitroaromatic explosives was added in an incremental fashion (25 μ L in each step) to a 3 mL methanol suspension of 3'. The emission intensity was monitored after each addition. For all the fluorescence titration experiments, the excitation wavelength was 370 nm and the emission spectra were recorded in the range of 380-700 nm. The estimation of the quenching efficiency was carried out by employing $(1 - I/I_0) \times 100\%$, where I_0 is the initial luminescence intensity of the suspension of 3' in methanol and I is the luminescence intensity after addition of the analyte.

3.3 Results and Discussion

3.3.1 Synthesis and Characterization

The synthesis of 3 was optimized by carrying out solvothermal reactions of the H₂BTDB ligand with three Zr(IV) salts (ZrCl₄, ZrO(NO₃)₂·xH₂O and ZrOCl₂·8H₂O) in three amide solvents such as DMF, DEF and DMA in presence of different additives⁵² and modulators (H₂O, conc. HCl, benzoic acid, formic acid, acetic acid and trifluoroacetic acid). Solvothermal reactions were performed in all possible combinations of the Zr(IV) salts, modulators/additives and amide solvents. The combination of ZrCl₄ as the metal source and trifluoroacetic acid in DMF resulted in the formation of light-yellow powder of 3 having very high crystallinity. The optimum crystallinity was achieved by employing the ZrCl₄/H₂BTDB/TFA molar ratio of 1:1:30. No crystalline product was obtained when the reactions were carried out in all other combination of the reactants.

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In order to remove the guest molecules entrapped within the pores of the as-synthesized sample of **3**, a two-step activation procedure was applied. At first, the occluded molecules (H_2O and DMF) were exchanged with more volatile (and thus easily removable) methanol molecules. Then, heating of the methanol-exchanged form of the sample under vacuum led to the thermally activated form (**3'**) of the compound.

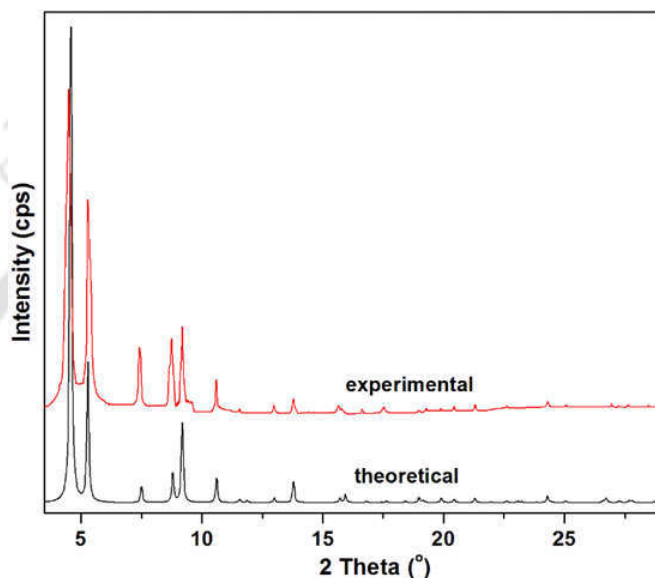


Figure 3.1 Calculated (black) and experimental (red) XRPD patterns of compound **3**.

The experimental XRPD pattern of the as-synthesized sample of **3** matches quite nicely with the theoretical XRPD pattern of the UiO-68 MOF material (Figure 3.1). This result confirms that **3** possesses UiO-68 framework structure. Lillerud's group has previously described the structure of the UiO-68 compound.² In brief, the material bears 3D cubic framework structure, which is built up of $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ building units cross-linked by the carboxylate groups of twelve terphenyl dicarboxylate (TPDC) linker molecules. The microporous network comprises larger octahedral and smaller tetrahedral cages. In case of the UiO-68 compound with TPDC- NH_2 ligand, the two kinds of microporous cages are linked via triangular windows (free diameter ~ 10 Å).⁵³ In the presented MOF material, the thiadiazole functional groups attached with the BTDB linker molecules point towards interior of the cages.

The FT-IR spectra (Figure 3.2) of the as-synthesized and activated samples of **3** reveals the presence of strong absorption bands due to the asymmetric and symmetric $-\text{CO}_2$

stretching vibrations of the coordinated BTDB linker molecules at 1600 and 1410 cm^{-1} , respectively.^{54, 55} In the IR spectrum of the as-synthesized sample of **3**, the strong absorption band owing to the carbonyl stretching vibration of the guest DMF molecules are located at 1650 cm^{-1} . The absence of this absorption band in the IR spectrum of the activated sample of **3** indicates the complete activation of the material.

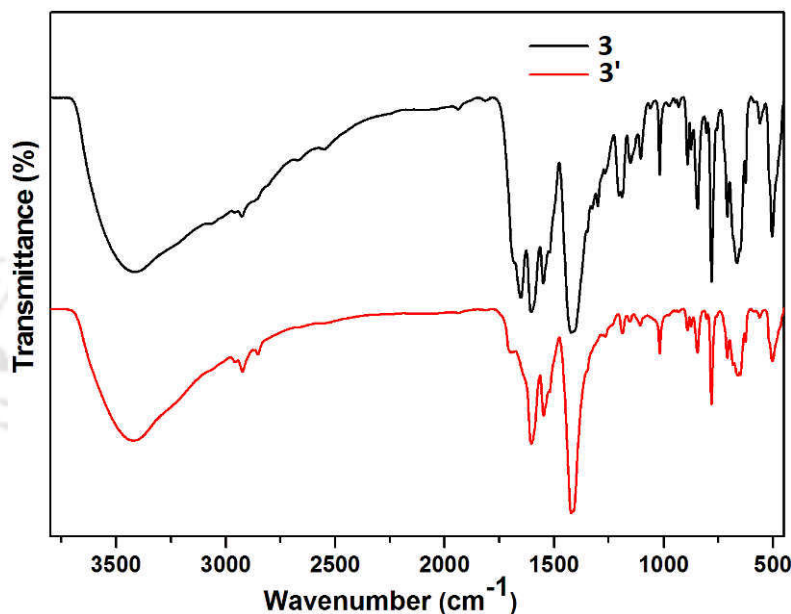


Figure 3.2 FT-IR spectra of the as-synthesized (black) and activated (red) samples of compound **3**.

The permanent porosity of the framework of **3'** was verified by the N_2 adsorption measurements. The N_2 adsorption isotherms (Figure 3.3) exhibited type-I behaviour, which is a characteristic for microporous materials. The values of specific BET surface area and micropore volume (at $p/p_0 = 0.5$), which were determined from the N_2 adsorption isotherms, correspond to 430 $\text{m}^2 \text{g}^{-1}$ and 0.24 $\text{cm}^3 \text{g}^{-1}$, respectively. These values are significantly lower than the formerly reported un-functionalized UiO-68 material.²

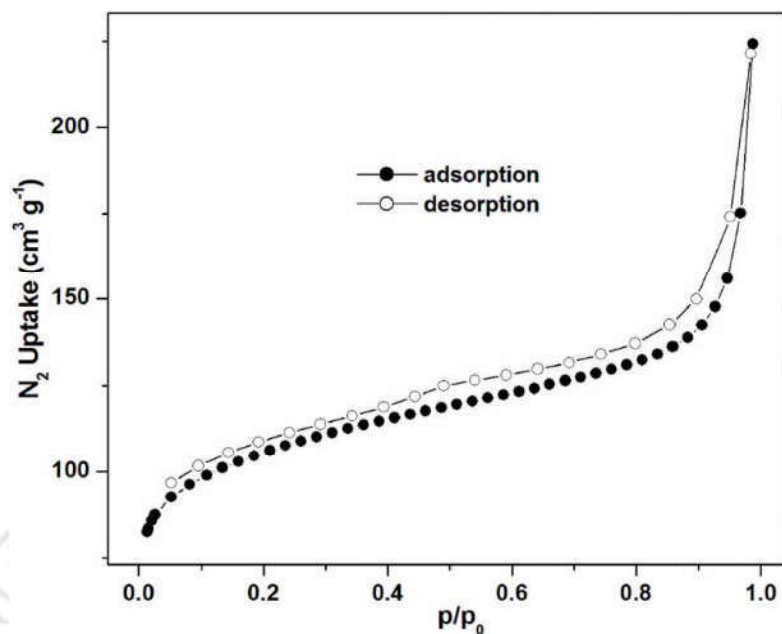


Figure 3.3 N₂ adsorption (filled circles) and desorption (empty circles) isotherms of compound **3'** measured at $-196\text{ }^{\circ}\text{C}$.

3.3.2 Thermal and Chemical Stability

The thermal stability of the as-synthesized and thermally activated samples of **3** was investigated by performing thermogravimetric analyses (TGA) under air atmosphere in the temperature range of $25\text{--}600\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Based on the TG analyses (Figure 3.4), the compound bears very high thermal stability up to $400\text{ }^{\circ}\text{C}$. In the TG trace of as-synthesized **3**, the first weight loss step of 4.4 wt% in the temperature range of $30\text{--}140\text{ }^{\circ}\text{C}$ can be assigned to the loss of 8 occluded water molecules per formula unit (calcd.: 4.1 wt%). The second weight loss step of 13.1 wt% in the temperature range of $140\text{--}400\text{ }^{\circ}\text{C}$ can be ascribed to the removal of 6 guest DMF molecules per formula unit (calcd.: 12.5 wt%). In the TG curve of the thermally activated sample (**3'**), the one weight loss step that occurs below the decomposition temperature can be attributed to the removal of the adsorbed water molecules. This weight loss step is observed because of the exposure of the thermally activated sample to moisture (from air) before the TG analysis, which resulted in hydration of the compound.

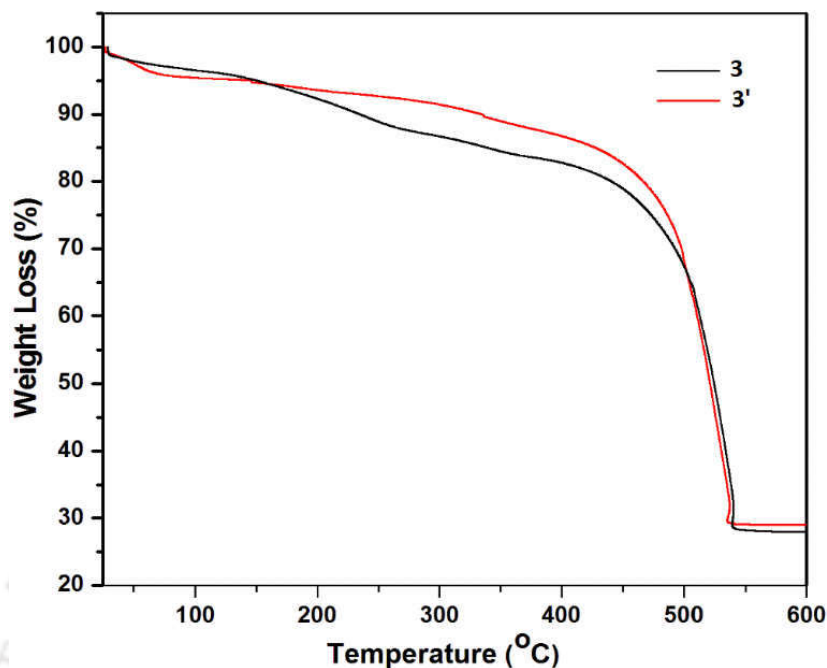


Figure 3.4 TG curves of the as-synthesized (black) and activated (red) samples of compound **3** recorded in an air atmosphere in the temperature range of 25-600 °C with a heating rate of 10 °C min⁻¹.

The chemical stability of the activated sample of **3** was checked by stirring the sample in water, methanol, acetic acid, 1 M HCl and 1 M NaOH solutions at room temperature for 24 h. Subsequently, material was collected by filtration and the crystallinity of the filtered compound was verified by XRPD experiments. After treatment with 1 M NaOH solution, the material lost its crystallinity and became fully amorphous. Fortunately, the compound retained its crystallinity after treating with water, methanol, acetic acid and 1 M HCl solutions (Figure 3.5), thus confirming structural integrity of the material in these liquids.

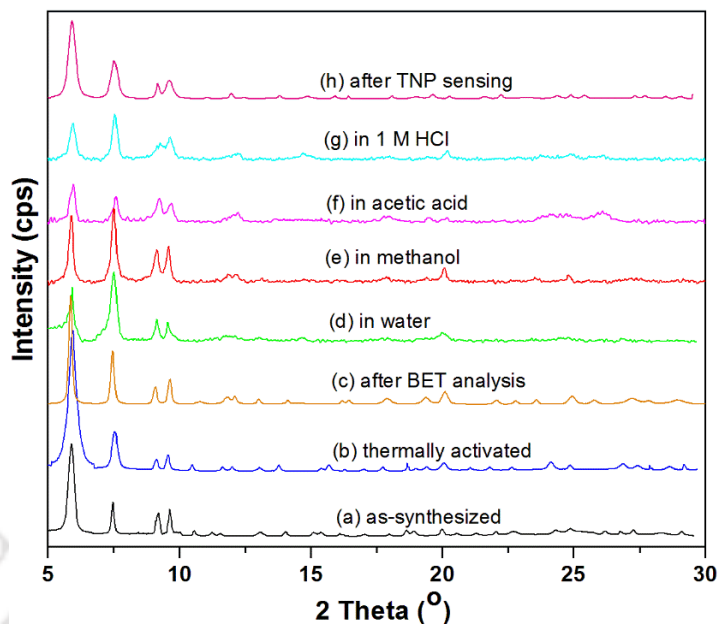


Figure 3.5 XRPD patterns of **3'** in different forms: as-synthesized (a); thermally activated (b); after BET analysis (c); treated with water (d); with methanol (e); with acetic acid (f); with 1M HCl (g); after 5 cycles of fluorescence titration experiments with TNP (h).

3.3.3 Fluorescence Behaviour

Zr(IV) ion (d^0) is electronically inert as Zn(II) and Cd(II) ions (both d^{10}) and thus Zr(IV)-based MOF materials containing luminescent organic ligands have been previously reported to exhibit strong photoluminescence properties.^{20, 56-59} Excellent photoluminescence properties of 2,1,3-benzothiadiazole-based organic dyes,^{60, 61} organic polymers^{62, 63} and a MOF material⁴⁵ have already been demonstrated in the literature. Moreover, highly luminescent small-molecule 2,1,3-benzothiadiazole derivatives have been recognized as potential fluorescent probes for bioimaging applications.⁶⁴

Encouraged by the above-mentioned observations, we have investigated the fluorescence properties of **3'** in the solid state as well as in different organic solvents at ambient conditions. The solid-state luminescence emission spectrum of H₂BTDB ligand (Figure 3.6) exhibits a broad emission band centred at 522 nm, when excited at 370 nm. This emission band can be attributed to the π - π^* transition of the organic ligand.²⁹ On the contrary, **3'** (Figure 3.6) showed an emission band centred at 510 nm upon excitation at 370 nm. Since the fluorescence emission spectra of the H₂BTDB ligand and **3'** are similar, the luminescence properties of **3'** can be ascribed to the ligand-centred electronic

transition.²¹ Nevertheless, the emission band of the compound is slightly blue-shifted ($\Delta\lambda = 12$ nm) and the fluorescence intensity of the emission band is enhanced by 69%, as compared to the pristine organic ligand. The blue shift in the emission band can be assigned to the perturbation in the π - π^* transition due to the coordination of the BTDB ligand with Zr(IV) ions, forming a 3D cubic framework structure.^{21, 65, 66} The enhancement in the luminescence intensity of **3'** as compared to the free H₂BTDB ligand in the solid-state can be ascribed to the strong electronic communication between adjacent coordinated ligand molecules through Zr(IV) ions.^{21, 67, 68} Such an increment in the fluorescence intensity has been previously reported for a Zn(II)-based MOF incorporating BTDB ligand.²¹

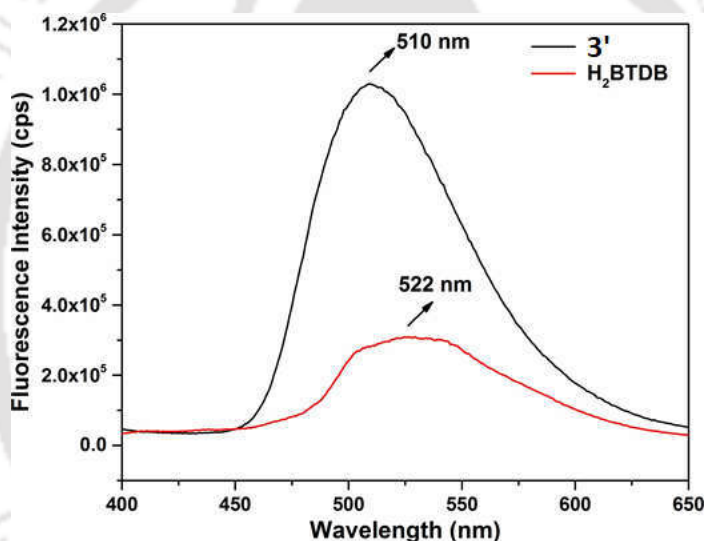


Figure 3.6 Solid-state fluorescence emission spectra of H₂BTDB ligand and **3'** recorded at room temperature ($\lambda_{\text{ex}} = 370$ nm).

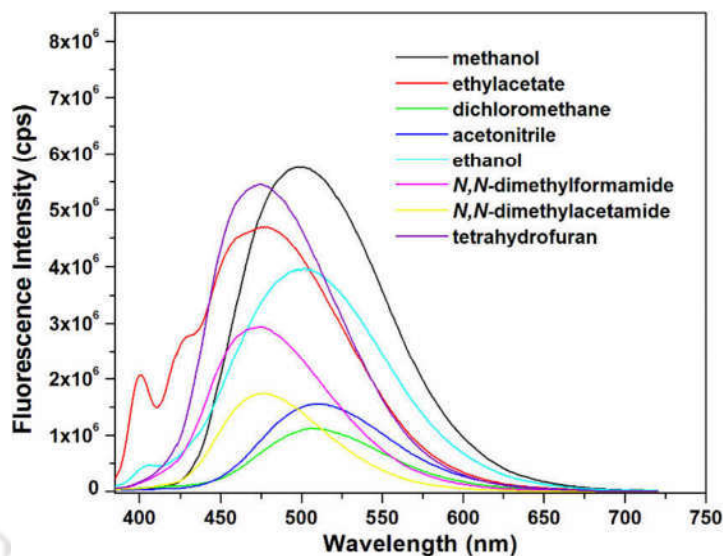


Figure 3.7 Fluorescence emission spectra of compound **3'** in different organic solvents ($\lambda_{\text{ex}} = 370$ nm).

The fluorescence behaviour of **3'** (Figure 3.7) was also investigated in various organic solvents including methanol, ethanol, acetonitrile, dichloromethane, ethyl acetate, tetrahydrofuran, DMF and DMA. A stable suspension of the compound (3 mg) in 3 mL of each organic solvent was employed in all the fluorescence emission measurements. Among all the selected solvents, the methanol suspension of **3'** displayed the strongest emission at 494 nm when excited at 370 nm at ambient conditions. Therefore, all the luminescence measurements were performed with the well-dispersed suspension of **3'** in methanol. Although the compound is stable in water (as corroborated by the XRPD experiments), we were unable to prepare stable suspension of the material in water. Thus, the fluorescence characteristics of the MOF compound in water was not examined.

3.3.4 Selective Detection of Nitroaromatic Explosive Compounds

Since **3'** is strongly luminescent both in the solid and liquid state, we have investigated its potentiality as a fluorescent probe for the selective and sensitive detection of NAEs. For luminescence sensing studies, the following NAEs were chosen: TNP, 2,4-dinitrophenol (2,4-DNP), *p*-nitrophenol (PNP), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), *m*-dinitrobenzene (*m*-DNB), 4-nitrotoluene (4-NT), TNT and nitrobenzene (NB). In all the sensing experiments, 3 mM suspension of each NAE

compound was added in an incremental manner to a well-dispersed suspension of **3'** in methanol and the fluorescence emission intensity of **3'** was monitored at ambient conditions. With increase in the concentration of TNP, the fluorescence intensity of **3'** decreased drastically (Figure 3.8a). Among all the NAE compounds, **3'** displayed the highest quenching efficiency (~98%) for TNP. The emission band of **3'** is blue-shifted ($\Delta\lambda = 20$ nm) upon incremental addition of TNP, which can be assigned to the formation of exciplexes (which stabilize the excited state) between **3'** and TNP.⁶⁹⁻⁷¹ The quenching efficiencies of **3'** towards other NAE compounds (Figure 3.8b) were very low. The descending order of the quenching efficiencies of the selected analytes is: TNP > 2,4-DNP > PNP > 2,4-DNT > 4-NT > 2,6-DNT > *m*-DNB > NB > TNT. These results clearly indicate that **1'** shows high selectivity towards TNP over other potentially interfering NAE compounds.

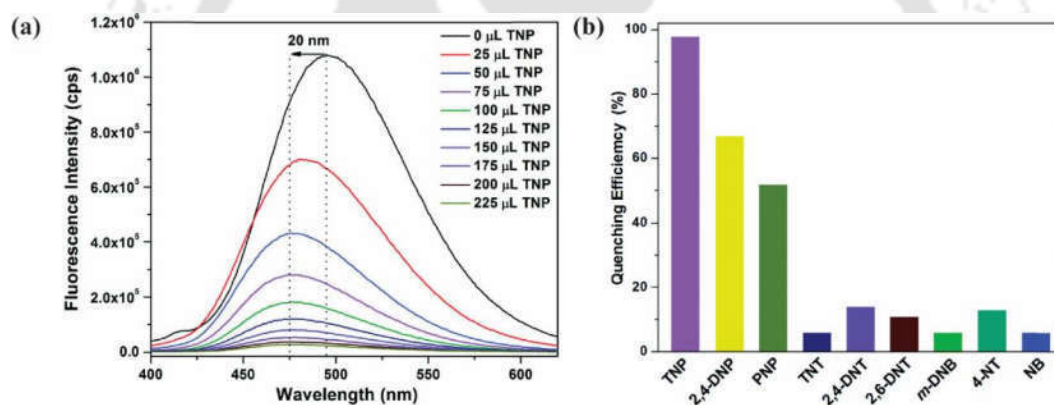


Figure 3.8 (a) Quenching of the fluorescence intensity of **3'** by gradual addition of 3 mM TNP solution to a 3 mL well-dispersed methanol suspension of **3'** ($\lambda_{\text{ex}} = 370$ nm and $\lambda_{\text{max}} = 494$ nm). (b) Fluorescence quenching efficiencies of various nitroaromatic explosives towards **3'** at 3 mM concentration ($\lambda_{\text{ex}} = 370$ nm and $\lambda_{\text{max}} = 494$ nm).

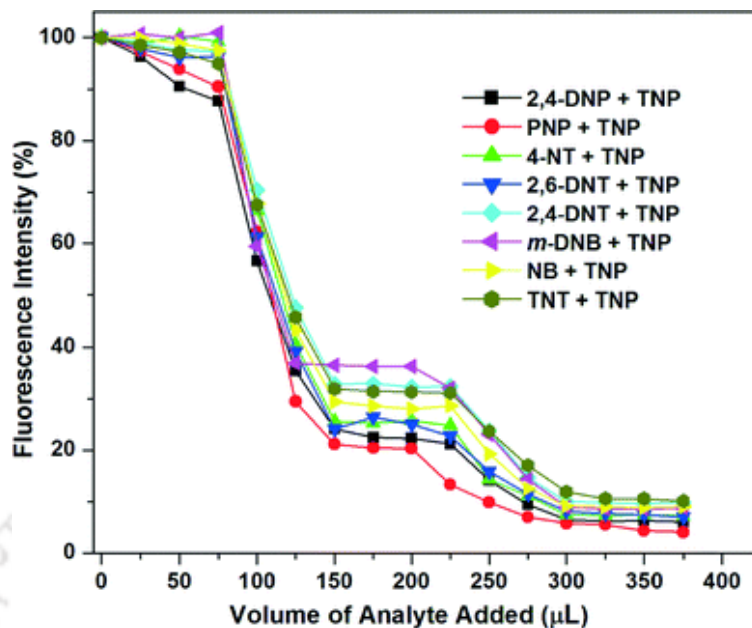


Figure 3.9 Fluorescence quenching response of 3' upon addition of methanol solutions of various nitroaromatic explosives followed by addition of TNP solution.

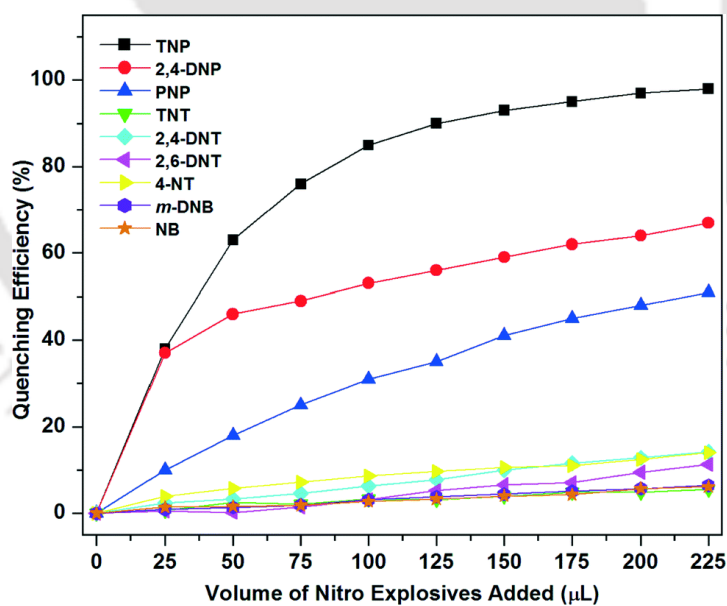


Figure 3.10 Variation of the fluorescence quenching efficiencies upon incremental addition of 3 mM solution of various nitroaromatic explosives to a 3 mL methanol suspension of 3'.

For real-world applications, the selective detection of a NAE compound in presence of other competing NAE materials is highly required. Encouraged by the fact that **3'** displayed the highest quenching efficiency for TNP among the chosen NAEs, the selectivity of the MOF material towards TNP in the presence of other NAEs was investigated. In a specially designed experiment, the luminescence emission spectrum of a well-dispersed suspension of **3'** was initially collected and 3 mM of 2,4-DNP solution (75 μ L) was added to the suspension, which was followed by the addition of TNP solution (75 μ L). Negligible quenching of the fluorescence of **3'** was observed after the addition of 2,4-DNP solution. However, the addition of only 75 μ L of TNP solution to the suspension of **3'** containing the 2,4-DNP solution led to significant quenching of the fluorescence. The same trend (i.e., reduction in fluorescence intensity) was observed in the subsequent addition sequences (i.e., addition of 2,4-DNP solution, followed by the addition of TNP solution). The fluorescence intensity was also decreased in an analogous, step-wise manner upon addition of the solutions of other NAEs, followed by the addition of TNP solution to a methanol suspension of **3'**. In Figure 3.9, the results of these competitive luminescence quenching experiments are summarized. The results shown in this figure, which is a plot of the percentage of the fluorescence intensity versus the volume of the NAEs added, clearly demonstrate that **3'** shows high selectivity for TNP, even in the presence of higher concentrations of other potentially interfering NAEs.

A distinct fluorescence response towards the analyte at a specific concentration is highly demanding for the efficient quenching of a fluorescent probe. In Figure 3.10, the fluorescence quenching efficiencies of the selected NAEs are plotted as a function of their concentrations. The figure reveals that the fluorescence quenching of **3'** by TNP solution is significant even at lower concentrations and considerable increase in the quenching efficiency occurs at higher concentrations. However, the quenching efficiencies of other NAEs are insignificant at lower concentrations and increase only slightly at higher concentrations.

The fluorescence quenching data were analyzed by the Stern-Volmer (S-V) equation:⁷²

$$(I_0/I) = K_{sv} [A] + 1$$

Where, I_0 is the initial fluorescence intensity of **3'** before the addition of analyte, I is the fluorescence intensity of **3'** in the presence of analyte, $[A]$ is the molar concentration of analyte, and K_{sv} is the quenching constant (unit: M^{-1}). The analysis by the S-V equation

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was performed for quantification of the quenching and identification of the nature of quenching process (static versus dynamic). In Figure 3.11, the S-V plots for the chosen NAEs for the luminescence quenching of **3'** are displayed. For TNP, the S-V plots are linear at lower concentrations, which indicates that either static or dynamic quenching is taking place. On the other hand, significant deviation of the same S-V plot from linearity is noticed at higher concentrations. This deviation suggests the existence of both static and dynamic quenching processes. For all other NAEs, the S-V plots are linear in nature. The value of K_{sv} for TNP was determined from the linear part of the respective S-V plot. This value was found to be $1.15 \times 10^3 \text{ M}^{-1}$, which is comparable with other MOF-based fluorescent probes reported (Table 3.1)^{19, 40, 46-49, 51, 73, 74} so far.

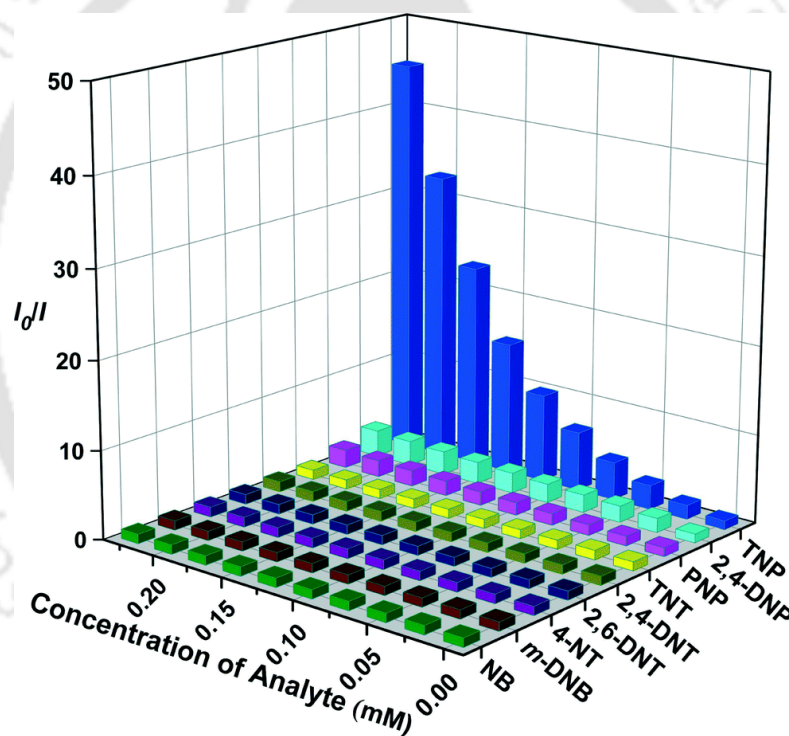


Figure 3.11 Stern-Volmer plots for the fluorescence quenching of **3'** (as a stable suspension in methanol) upon gradual addition of various nitroaromatic explosives.

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Table 3.1 A comparison of the Stern-Volmer constant (K_{sv}), detection limit and medium used for the detection of TNP by luminescent MOFs reported till date.

Sl. No.	MOFs	$K_{sv} (\times 10^4 \text{ M}^{-1})$	Detection Limit	Medium Used	Ref.
1	$[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BTDB})_6] \cdot 8\text{H}_2\text{O} \cdot 6\text{DMF}$	0.115	$1.63 \times 10^{-6} \text{ M}$	methanol	this work
2	$[\text{Cd}_5\text{Cl}_6(\text{L})(\text{HL})_2] \cdot 7\text{H}_2\text{O}$	4.05	$1.87 \times 10^{-7} \text{ M}$	ethanol	22
3	$[\text{Cd}_3(\text{TPT})_2(\text{DMF})_2] \cdot (\text{H}_2\text{O})_{0.5}$	6.56		ethanol	48
4	$\text{Zr}_6\text{O}_4(\text{OH})_4(\text{L})_6$ (UiO-67@N)	2.9		water	56
5	$\text{Cd}(\text{NDC})_{0.5}(\text{PCA})$	3.5		ACN	46
6	$[\text{Zn}_2(\text{NDC})_2(\text{bpy})] \cdot \text{G}_x$	0.422		ethanol	75
7	Bio-MOF-1	4.6	2.9 ppb	water	47
8	$[\text{Tb}(1,3,5\text{-BTC})]$	3.41	$8.1 \times 10^{-8} \text{ M}$	ethanol	51
9	$\text{Zn}_2(\text{PAM})_2(1,3\text{-PDA})_2$		$1.27 \times 10^{-8} \text{ M}$	DMSO	20
10	$[\text{Eu}_2(\text{MFDA})_2(\text{HCOO})_2$ $(\text{H}_2\text{O})_6] \cdot (\text{H}_2\text{O})_n$		$4.5 \times 10^{-7} \text{ M}$	DMF	40

Time-resolved fluorescence quenching experiments were carried out in order to distinguish between the two quenching processes (static versus dynamic). In these experiments, the fluorescence decays of **3'** were monitored at different concentrations of TNP. The lifetime decay profile of **3'** is shown in Figure 3.12. The decay profile evidently reveals that the continuing addition of TNP resulted in only slight change in the lifetime values (Table 3.2). The average excited state lifetime $\langle \tau \rangle$ values were found to be 2.95 and 1.78 ns before and after the addition of 225 μL of TNP solution, respectively. These lifetime values strongly suggest that static rather than dynamic quenching process is occurring in these systems.

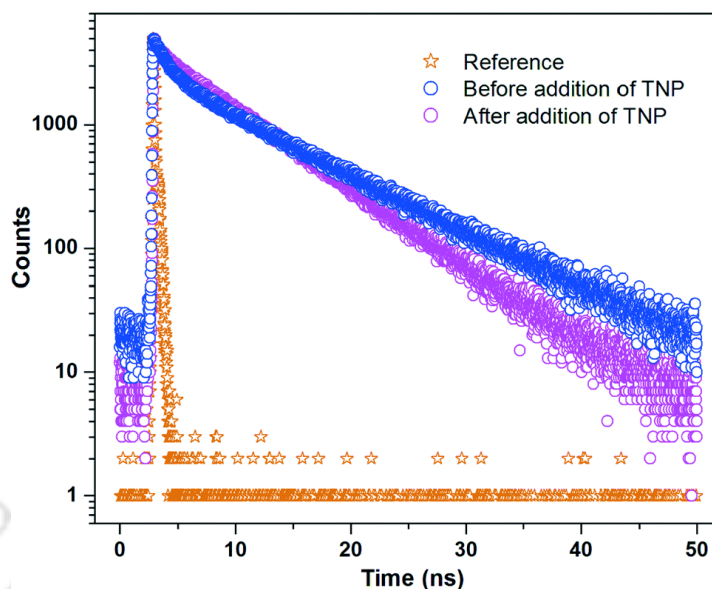


Figure 3.12 Fluorescence lifetime decay profile of **3'** before and after addition of 225 μL of TNP solution ($\lambda_{\text{ex}} = 370 \text{ nm}$ and $\lambda_{\text{max}} = 494 \text{ nm}$).

Table 3.2 Average excited state lifetime ($\langle\tau\rangle$) values of compound **3'** before and after addition of different volumes of 3 mM TNP solution ($\lambda_{\text{ex}} = 370 \text{ nm}$, $\lambda_{\text{em}} = 494 \text{ nm}$).

Volume of TNP Added (μL)	B_1	B_2	a_1	a_2	τ_1 (ns)	τ_2 (ns)	$\langle\tau\rangle^*$ (ns)
0	0.080	0.041	0.79	0.21	1.238	9.039	2.949
45	0.093	0.061	0.81	0.19	1.057	6.888	2.165
90	0.104	0.067	0.82	0.18	0.974	6.868	2.034
135	0.066	0.066	0.88	0.12	0.967	6.864	1.674
180	0.054	0.067	0.90	0.10	0.979	6.799	1.561
225	0.096	0.072	0.85	0.15	0.900	6.743	1.776

$$*\langle\tau\rangle = a_1\tau_1 + a_2\tau_2$$

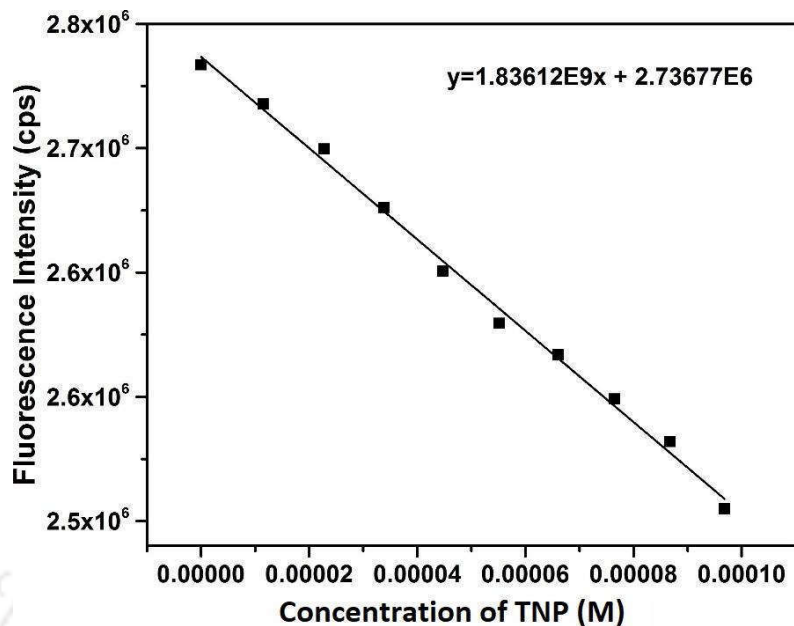


Figure 3.13 Change in the fluorescence intensity of 3' in methanol suspension as a function of TNP concentration.

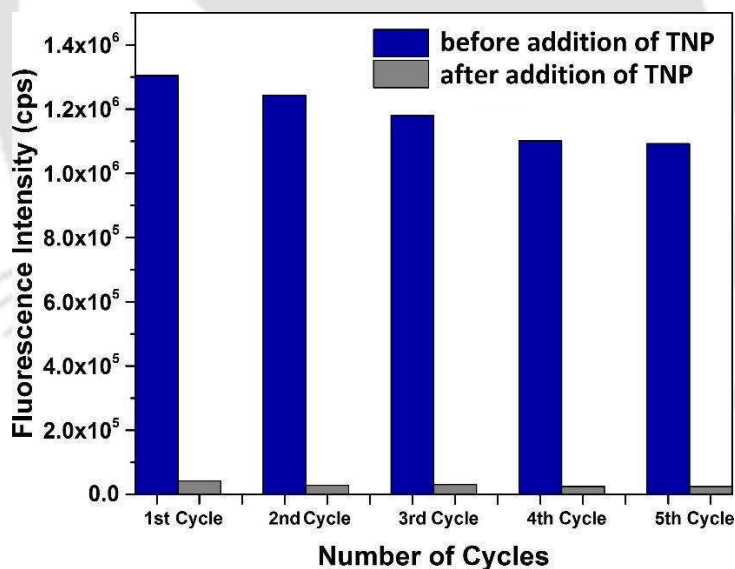


Figure 3.14 Reproducibility of quenching efficiency of the methanol suspension of 3' towards 3 mM TNP solution.

The limit of detection (LOD) for TNP towards 3' was obtained by monitoring the fluorescence quenching upon gradual addition of very low concentrations of TNP solution to the methanol suspension of 3'. When the fluorescence intensity of 3' was plotted against

the concentration of TNP solution, a linear curve (Figure 3.13) was obtained. The LOD value was determined by employing the equation: $\text{LOD} = 3\sigma/K$, where σ denotes the standard deviation of the initial intensity of **3'** without analytes and K represents the slope of the above-mentioned linear curve. The estimated LOD value of **3'** for the detection of TNP was 1.63×10^{-6} M. This value compares quite nicely with other MOF-based fluorescent probes documented in the literature (Table 3.1)^{19, 40, 46-49, 51, 73, 74} till date.

The reusability of a sensor material is a key issue for long-term real-life applications. The recyclability of the performance of **3'** for sensing TNP was investigated up to five cycles. After each fluorescence titration measurement (with 3 mM TNP solution), the material was recovered by centrifugation and then washed several times with methanol. After five cycles of repetition, the initial fluorescence intensity of **3'** did not alter significantly (Figure 3.14). Thus, the compound showed excellent recyclability of its detection performance towards TNP. The XRPD experiment (Figure 3.5), verified that the crystallinity (and thus structural integrity) of **3'** was retained after five repeated cycles of fluorescence titration experiments. The results of the recyclability tests reveal that the fluorescent probe is highly photostable as well as reusable. Therefore, **3'** is a potential candidate for the long-term in-field detection of NAEs.

3.3.5 Mechanism for the Detection of Nitroaromatic Explosive Compounds

In order to understand the high selectivity of **3'** towards TNP over various other NAEs, the sensing mechanism was examined. We speculate that the larger pore apertures of **3'** having microporous UiO-68 structure allow the passage of the selected NAEs into cages where the NAE molecules interact with the inner pore walls of the framework. Three possible mechanisms for quenching the luminescence of electron-rich **3'** by electron-deficient TNP can be proposed based on the steady-state fluorescence measurements. They include: (1) photo-induced electron transfer (PET), (2) fluorescence resonance energy transfer (FRET) and (3) molecular interactions (such as electrostatic interactions).

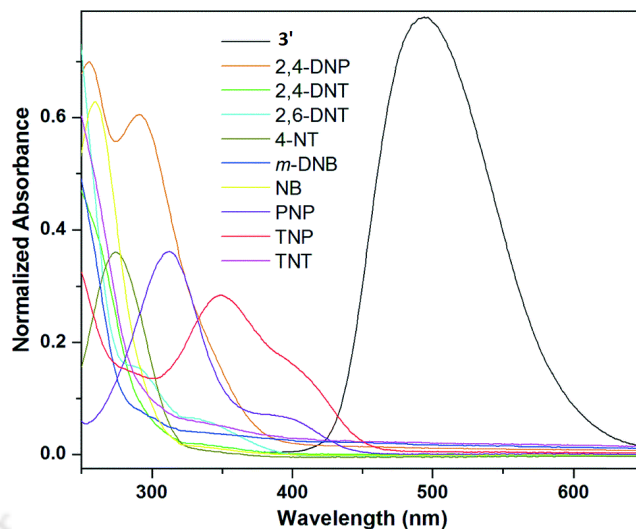


Figure 3.15 Overlap between the emission spectrum of **3'** and the absorption spectra of different nitroaromatic explosives.

The highly selective detection of NAEs by **3'** might be attributed to a PET mechanism. It is noteworthy that the same mechanism has been hypothesized previously for many other MOFs in order to account for their highly selective sensing behaviour towards NAEs. Usually, the lowest unoccupied MOs (LUMOs) of the electron-deficient NAEs reside between the valence band (VB) and conduction band (CB) of the MOF materials.⁷⁶ Consequently, the transfer of electrons can easily take place from the CB of **3'** to the LUMO of the electron-deficient NAEs, leading to the quenching of the photoluminescence intensity of **3'** upon excitation. We have determined the HOMO and LUMO orbital energies of the selected analytes by using the density functional theory (DFT) at B3LYP/6-31G* accuracy level using Gaussian 09 package of programs.⁷⁷ The estimated LUMO energy values of the NAEs increase in the sequence: TNP < TNT < *m*-DNB < 2,4-DNT < 2,6-DNT < DNP < NB < 4-NT < PNP. The reverse of this order is applicable when considering the ease of electron transfer from the electron-rich **3'** to the electron-deficient NAEs. Consequently, the highest quenching efficiency of TNP correlates well with its lowest LUMO energy value. However, the experimental sequence of the quenching efficiencies (i.e., TNP > 2,4-DNP > PNP > 2,4-DNT > 4-NT > 2,6-DNT > *m*-DNB > NB > TNT) of other NAEs does not match completely with the trend of their calculated LUMO energy values. These results indicate that the observed quenching properties cannot be

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explained by considering only the PET mechanism. The quenching behaviour of the NAEs might be also governed by the FRET mechanism.

In order for the FRET mechanism from the fluorophore of the organic ligand to the non-emissive NAEs to occur, the absorption bands of the NAEs must overlap efficiently with the emission band of the fluorophore.⁷⁸ The fluorescence quenching efficiency of the NAEs is increased by the effective energy transfer process. It can be seen from Figure 3.15 that TNP possesses a considerable overlap with the fluorescence emission band of **3'**, whereas relatively less or almost no overlap is observed for other NAEs. The largest spectral overlap between the absorption band of TNP and the emission band of **3'** correlates well with the highest quenching efficiency of TNP. Therefore, the efficient spectral overlap provides evidence in favour of the energy transfer mechanism. This mechanism can also be evidenced by the non-linearity of the S-V plot (Figure 3.11) at higher concentrations.⁴⁶

In addition to PET and FRET mechanisms, the highest fluorescence quenching efficiency of TNP can be attributed to the electrostatic interactions between the Lewis basic N-donor sites of the thiadiazole ring attached with the BTDB linker and the acidic hydroxyl group of TNP.^{46,46} Notably, the Lewis basicity of the N atoms in the thiadiazole ring has previously been demonstrated for conjugated polymers containing 2,1,3-benzothiadiazole moieties.⁷⁹ The surface area of interaction of **3'** with the acidic hydroxyl groups of TNP is enhanced by the presence of two basic N-donor sites per BTDB linker molecule.^{24, 80} Such enhancement in the surface interaction between the host MOF and guest TNP leads to reduction in the photoluminescence intensity of the former. The involvement of the electrostatic interactions in the fluorescence quenching process was confirmed by comparing the quenching efficiencies of three NAEs bearing one hydroxyl group, namely TNP, 2,4-DNP and PNP. The decreasing order of the quenching efficiencies was: TNP > 2,4-DNP > PNP (Figure 3.10), which correlates well with the sequence of acidity of the three NAEs. Thus, the highly effective quenching of TNP towards **3'** can be attributed to the presence of strong electrostatic interactions between TNP and **3'**.

3.4 Conclusions

We have demonstrated the successful synthesis, thorough characterization, thermal and chemical stability as well as fluorescence sensing properties of a new, highly luminescent

3D Zr(IV)-based MOF material (**3**) having UiO-68 framework topology and containing the thiadiazole-functionalized BTDB ligand. Highly crystalline **3** was synthesized by the solvothermal reaction of a mixture of ZrCl₄, H₂BTDB ligand and trifluoroacetic acid in DMF at 150 °C for 24 h. As confirmed by the steady-state fluorescence titration measurements, the activated **3'** showed selective detection behaviour towards TNP (via fluorescence quenching mechanism), even in the presence of other potentially interfering nitroaromatic explosive compounds. The detection limit of the material for sensing TNP was found to be 1.63×10^{-6} M, which compares well with the previously reported MOF-based fluorescent probes. As verified by the recyclability experiments, **3'** is highly photostable and reusable, thus fulfilling the essential criteria of the MOF sensor for long-term practical applications. Both energy and electron transfer mechanisms could be attributed for the highest fluorescence quenching efficiency of TNP. In addition, the electrostatic interactions between the Lewis basic N-donor sites of the BTDB ligand and the acidic –OH group of TNP might be ascribed for the increased selectivity of **3'** towards detection of TNP. Owing to its excellent detection performance, the strongly fluorescent MOF probe is a promising candidate for the in-field sensing of TNP.

3.5 References

1. G. Ferey, C. M. Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science*, 2005, **309**, 2040-2042.
2. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850-13851.
3. Themed issue on MOFs, *Chem. Soc. Rev.*, 2009, **38**, 1201-1508.
4. Special issue on MOFs, *Chem. Rev.*, 2012, **112**, 673-1268.
5. O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705-714.
6. S. Kitagawa, R. Kitaura and S. S. Noro, *Angew. Chem. Int. Ed.*, 2004, **43**, 2334-2375.
7. R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 3875-3877.

Chapter 3

8. S. Couck, E. Gobechiya, C. E. A. Kirschhock, P. S. Crespo, J. J. AlcaÇiz, A. M. Joaristi, E. Stavitski, J. Gascon, F. Kapteijn, G. V. Baron and J. F. M. Denayer, *ChemSusChem*, 2012, **15**, 740-750.
9. L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248-1256.
10. L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294-1314.
11. L. Ma, J. M. Falkowski, C. Abney and W. Lin, *Nat. Chem.*, 2010, **2**, 838-846.
12. K. Manna, T. Zhang, M. Carboni, C. W. Abney and W. Lin, *J. Am. Chem. Soc.*, 2012, **136**, 13182-13185.
13. J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450-1459.
14. T. Uemura, N. Yanai and S. Kitagawa, *Chem. Soc. Rev.*, 2009, **38**, 1228-1236.
15. D. Liu, C. Poon, K. Lu, C. He and W. Lin, *Nat. Commun.*, 2014, **5**, 4182-4192.
16. K. M. L. Taylor-Pashow, J. D. Rocca, Z. G. Xie, S. Tran and W. B. Lin, *J. Am. Chem. Soc.*, 2009, **131**, 14261-14263.
17. P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J. S. Chang, Y. K. Hwang, V. Marsaud, Y.-N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur and R. Gref, *Nat. Mater.*, 2010, **9**, 172-178.
18. K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498-519.
19. S. S. Nagarkar, A. V. Desai and S. K. Ghosh, *Chem. Commun.*, 2014, **50**, 8915-8918.
20. S. S. Nagarkar, A. V. Desai, P. Samanta and S. K. Ghosh, *Dalton Trans.*, 2015, **44**, 15175-15180.
21. G.-Y. Wang, C. Song, D.-M. Kong, W.-J. Ruan, Z. Chang and Y. Li, *J. Mater. Chem. A*, 2014, **2**, 2213-2220.
22. A. Buragohain, M. Yousufuddin, M. Sarma and S. Biswas, *Cryst. Growth Des.*, 2016, **16**, 842-851.
23. C. Dietl, H. Hintz, B. Ruhle, J. S. a. d. Gunne, H. Langhals and S. Wuttke, *Chem. Eur. J.*, 2015, **21**, 10714-10720.
24. S. Mukherjee, A. V. Desai, B. Manna, A. I. Inamdar and S. K. Ghosh, *Cryst. Growth Des.*, 2015, **15**, 4627-4634.
25. X. H. Zhou, L. Li, H. H. Li, A. Li, T. Yang and W. Huang, *Dalton Trans.*, 2013, **42**, 12403-12409.

26. L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. V. Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105–1125.
27. K. Müller-Buschbaum, F. Beuerle and C. Feldmann, *Microporous Mesoporous Mater.*, 2015, **216**, 171-199.
28. Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815-5840.
29. M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330–1352.
30. Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126-1162.
31. Y. Cui, B. Chen and G. Qian, *Coord. Chem. Rev.*, 2014, **273-274**, 76-86.
32. L. V. Meyer, F. Schonfeld and K. Muller-Buschbaum, *Chem. Commun.*, 2014, **50**, 8093-8108.
33. B. Chen, S. Xiang and G. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115-1124.
34. J. Lei, R. Qian, P. Ling, L. Cui and H. Ju, *Trends Analyt. Chem.*, 2014, **58**, 71-78.
35. Y. Wang, A. La, Y. Ding, Y. Liu and Y. Lei, *Adv. Funct. Mater.*, 2012, **22**, 3547–3555.
36. Y. Salinas, R. Martinez-Manez, M. D. Marcos, F. Sancenon, A. M. Costero, M. Parraad and S. Gil, *Chem. Soc. Rev.*, 2012, **41**, 1261-1296.
37. D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537-2574.
38. S. W. Thomas, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339-1386.
39. G. He, H. Peng, T. Liu, M. Yang, Y. Zhang and Y. Fang, *J. Mater. Chem.*, 2009, **19**, 7347-7353.
40. Y. Peng, A.-J. Zhang, M. Dong and Y.-W. Wang, *Chem. Commun.*, 2011, **47**, 4505-4507.
41. D. Udhayakumari, S. Velmathi, P. Venkatesan and S. P. Wu, *Anal. Methods*, 2015, **7**, 1161-1166.
42. M. E. Germain and M. J. Knapp, *Chem. Soc. Rev.*, 2009, **38**, 2543-2555.
43. D. Gao, Z. Wang, B. Liu, L. Ni, M. Wu and Z. Zhang, *Anal. Chem.*, 2008, **80**, 8545-8553.
44. Y. Jiang, H. Zhao, N. Zhu, Y. Lin, P. Yu and L. Mao, *Angew. Chem. Int. Ed.*, 2008, **47**, 8601-8604.
45. N. Wei, Y.-R. Zhang and Z.-B. Han, *CrystEngComm*, 2013, **15**, 8883-8886.

Chapter 3

46. S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem. Int. Ed.*, 2013, **52**, 2881-2885.
47. B. Joarder, A. V. Desai, P. Samanta, S. Mukherjee and S. K. Ghosh, *Chem. Eur. J.*, 2015, **21**, 965-969.
48. X.-Z. Song, S.-Y. Song, S.-N. Zhao, Z.-M. Hao, M. Zhu, X. Meng, L.-L. Wu and H.-J. Zhang, *Adv. Funct. Mater.*, 2014, **24**, 4034-4041.
49. T. Wen, D.-X. Zhang, J. Liu, R. Lin and J. Zhang, *Chem. Commun.*, 2013, **49**, 5660-5662.
50. X. Zhu, J. Gu, Y. Wang, B. Li, Y. Li, W. Zhao and J. Shi, *Chem. Commun.*, 2014, **50**, 8779-8782.
51. J.-D. Xiao, L.-G. Qiu, F. Ke, Y.-P. Yuan, G.-S. Xu, Y.-M. Wang and X. Jiang, *J. Mater. Chem. A.*, 2013, **1**, 8745-8752.
52. N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933-969.
53. A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. Eur. J.*, 2011, **17**, 6643-6651.
54. S. Biswas, T. Ahnfeldt and N. Stock, *Inorg. Chem.*, 2011, **50**, 9518-9526.
55. S. Biswas, D. E. P. Vanpoucke, T. Verstraelen, M. Vandichel, S. Couck, K. Leus, Y.-Y. Liu, M. Waroquier, V. V. S. broeck, J. F. M. Denayer and P. V. D. Voort, *J. Phys. Chem. C*, 2013, **117**, 22784-22796.
56. S. S. Nagarkar, A. V. Desai and S. K. Ghosh, *Chem. Commun.*, 2014, **50**, 8915-8918.
57. J. Yang, Z. Wang, K. Hu, Y. Li, J. Feng, J. Shi and J. Gu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 11956-11964.
58. Y.-A. Li, C.-W. Zhao, N.-X. Zhu, Q.-K. Liu, G.-J. Chen, J.-B. Liu, X.-D. Zhao, J.-P. Ma, S. Zhang and Y.-B. Dong, *Chem. Commun.*, 2015, **51**, 17672-17675.
59. W. Zhang, H. Huang, D. Liu, Q. Yang, Y. Xiao, Q. Ma and C. Zhong, *Microporous Mesoporous Mater.*, 2013, **171**, 118-124.
60. X. Zhang, H. Gorohmaru, M. Kadowaki, T. Kobayashi, T. Ishi-i, T. Thiemann and S. Mataka, *J. Mater. Chem.*, 2004, **14**, 1901-1904.
61. X. Zhang, R. Yamaguchi, K. Moriyama, M. Kadowaki, T. Kobayashi, T. Ishi-i, T. Thiemann and S. Mataka, *J. Mater. Chem.*, 2006, **16**, 736-740.
62. Y. Dong, B. Koken, X. Ma, L. Wang, Y. Cheng and C. Zhu, *Inorg. Chem. Commun.*, 2011, **14**, 1719-1722.

Chapter 3

63. M. J. Edelmann, J.-M. Raimundo, N. F. Utesch and F. Diederich, *Helv. Chim. Acta*, 2002, **85**, 2195-2213.
64. B. A. D. Neto, P. H. P. R. Carvalho and J. R. Correa, *Acc. Chem. Res.*, 2015, **48**, 1560-1569.
65. S. Wang, J. Wang, W. Cheng, X. Yang, Z. Zhang, Y. Xu, H. Liu, Y. Wu and M. Fang, *Dalton Trans.*, 2015, **44**, 8049-8061.
66. K. S. Asha, K. Bhattacharyya and S. Mandal, *J. Mater. Chem. C*, 2014, **2**, 10073-10081.
67. F. Guo, F. Wang, H. Yang, X. Zhang and J. Zhang, *Inorg. Chem.*, 2012, **51**, 9677-9682.
68. B. Gole, A. K. Bar and P. S. Mukherjee, *Chem. Commun.*, 2011, **47**, 12137-12139.
69. H. He, Y. Song, F. Sun, Z. Bian, L. Gao and G. Zhu, *J. Mater. Chem. A*, 2015, **3**, 16598-16603.
70. S.-R. Zhang, D.-Y. Du, J.-S. Qin, S.-J. Bao, S.-L. Li, W.-W. He, Y.-Q. Lan, P. Shen and Z.-M. Su, *Chem. Eur. J.*, 2014, **20**, 3589-3594.
71. S. Pramanik, Z. Hu, X. Zhang, C. Zheng, S. Kelly and J. Li, *Chem. Eur. J.*, 2013, **19**, 15964-15971.
72. R.-B. Lin, F. Li, S.-Y. Liu, X.-L. Qi, J. P. Zhang and X.-M. Chen, *Angew. Chem. Int. Ed.*, 2013, **52**, 13429-13433.
73. P. Valvekens, D. Jonckheere, T. De Baerdemaeker, A. V. Kubarev, M. Vandichel, K. Hemelsoet, M. Waroquier, V. Van Speybroeck, E. Smolders, D. Depla, M. B. J. Roefsaers and D. De Vos, *Chem. Sci.*, 2014, **5**, 4517-4524.
74. B. Gole, A. K. Bar and P. S. Mukherjee, *Chem. Eur. J.*, 2014, **20**, 13321-13336.
75. K. S. Asha, K. Bhattacharyya and S. Mandal, *J. Mater. Chem. C*, 2014, **2**, 10073-10081.
76. S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li, *J. Am. Chem. Soc.*, 2011, **133**, 4153-4155.
77. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N.

- Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. N. Rega, M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.1*. Gaussian, Inc.: Wallingford CT, 2009.
78. S. Hussain, A. H. Malik, M. A. Afroz and P. K. Iyer, *Chem. Commun.*, 2015, **51**, 7207-7210.
79. G. C. Welch and G. C. Bazan, *J. Am. Chem. Soc.*, 2011, **133**, 4632-4644.
80. P. Vishnoi, M. G. Walawalkar, S. Sen, A. Datta, G. N. Patwaria and R. Murugavel, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10651-10658.

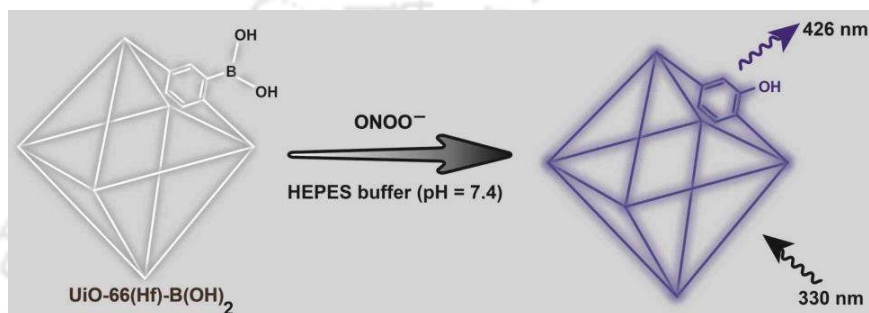


4.1 Introduction

In biological system, the oxidative stress components play very important roles.^{1, 2} All the reactive oxygen species (ROS) or nitrogen species (RNS) such as hydrogen peroxide (H_2O_2), peroxynitrite (ONOO^-), singlet oxygen ($^1\text{O}_2$), superoxide ($\text{O}_2^{\cdot-}$), nitric oxide radical ($\cdot\text{NO}$), nitrosonium ion (NO^+), nitrite (NO_2^-), nitrate (NO_3^-), hydroxy radical ($\cdot\text{OH}$), *tert*-butyl hydrogen peroxide (TBHP) and hypochlorous acid (HOCl) are the major oxidative stress components for the living organisms. They harmful to biomolecules and result in cytotoxicity.³ In living systems, generally ONOO^- is formed from the reaction between nitric oxide ($\cdot\text{NO}$) and superoxide ($\text{O}_2^{\cdot-}$),⁴ which was proposed by Beckman and co-workers in 1990.⁴ At biological condition ($\text{pH} = 7.4$), ONOO^- equilibrates with HONOO ($\text{pK}_a = 6.8$).⁵ Due to its high oxidizing ability power, peroxynitrite can cause severe damage to numerous biomolecules such as nucleic acids, proteins and lipids.^{6, 7} Hence, the excessive concentration of peroxynitrite in the biological medium causes several human diseases including diabetes,⁸ sepsis,⁹ chronic inflammatory processes,¹⁰ atherosclerosis,¹¹ and neurodegenerative disorders.¹² In spite of its detrimental effects, the beneficial role of peroxynitrite (when produced in a controlled manner) includes signal transduction which is helpful for carrying out several regular cellular functions.¹³ Several analytical techniques have been reported so far for the sensing of peroxynitrite, including liquid chromatography,¹⁴ GS-MS,¹⁴ electrochemistry^{15, 16} and chemiluminescence.^{17, 18} Pretreatment of sample is a crucial requirement for these techniques. On the contrary, fluorescence method has been found as an efficient tool for the sensing and imaging of small biomolecules in living cells due to its non-destructive nature, great sensitivity, high selectivity and in-situ monitoring. For the reaction-based sensing of peroxynitrite by fluorescence method, several reaction strategies have been reported so far such as oxidative cleavage of boronate or boronic acid to phenol,^{19, 20} generation of dioxirane with reactive ketone,²¹ oxidation of organotellurium²² or organoselenium²³ compounds, nitration of aromatic compounds,²⁴ oxidation of phenol,²⁵ generation of nitrosoamine and its hydrolysis,²⁶ etc. Among these reaction-based approaches, the chemoselective oxidation of aryl boronates or boronic acids to phenols has been found to be a common strategy for the sensing and imaging of peroxynitrite in both extracellular and intracellular media.²⁷

MOFs are porous materials having high surface area, high pore sizes, high thermal and chemical stability. They have been utilized in different fields including chemical sensing,²⁸⁻³³ selective gas adsorption,³⁴ proton conductivity,³⁵ photocatalysis,³⁶ heterogeneous catalysis,³⁷ light harvesting,³⁸ electrical conductivity,³⁹ separation,⁴⁰ etc. Recently, MOF materials have been employed in several biological applications including pH dependent drug delivery,⁴¹ small biomolecules sensing,⁴² cellular imaging, etc. Due to have capability of incorporation of fluorophore ligands in framework structures make MOFs favorable candidates for the sensing of target analytes. These functional groups can interact with the target analytes selectively and thus change in fluorescence intensity of the MOF probe containing fluorophore moieties is observed. By virtue of these methods, several MOFs have been exploited so far by us and others for the extracellular and intracellular sensing of biologically relevant metal ions,^{43, 44} anions,⁴⁵ gas molecules (i.e., gasotransmitters such as H_2S ^{42, 46-48} and NO ⁴⁹), etc. Luminescent MOF materials have several advantages for sensing application over small organic molecule-based fluorescence sensors. Firstly, the protocol of synthesis of MOFs is much straight-forward than other luminescent probes.⁵⁰ Furthermore, the exact structure of MOFs can be determined by X-ray diffraction as MOF materials are crystalline in nature, which is very much helpful for describing the possible interactions between MOFs and targeted analytes.⁵¹ Moreover, close interactions between the MOF and analyte can occur as the distance between the MOF and analyte decreases due to the porous nature of MOFs.⁵² Until today, only one surface-coated MOF anchored with molecular probe possessing boronic acid group has been reported for the sensing of peroxynitrite. Herein, we demonstrate the synthesis and characterization of Hf-UiO-66-B(OH)₂ MOF (**4'**), and its applicability for imaging both extracellular and intracellular peroxynitrite (Scheme 4.1). Both Zr and Hf can form UiO-66 type of structure during solvothermal reaction with $\text{H}_2\text{BDC-B(OH)}_2$ (2-borono-1,4-benzenedicarboxylic acid), but we have selected Hf-based MOF over Zr-based MOF for the sensing experiment because the Hf-based UiO-66 MOFs are expected to be more stable as compared to the Zr-based UiO-66 MOFs. These may be due to the greater dissociation energy of the Hf-O (802 kJ mol⁻¹) bond as compared to that of the Zr-O (776 kJ mol⁻¹) bond.⁵³ Hence, the hydrolytic stability will be greater for Hf-based MOF than Zr-based MOF. In case of aqueous-phase sensing experiment, the hydrolytic stability of the MOF material is an important factor. Furthermore, Hf is much more oxophilic than Zr. Hence, Hf-cluster-based MOF has greater catalytic activity for

nucleophilic ring opening than Zr-cluster-based MOF.⁵⁴ We hypothesized that due to greater oxophilicity of the Hf-O cluster in Hf-based MOF, the boron center of the ligand can become more electrophilic and thus the nucleophilic attack of peroxyxynitrite at the boron center can occur much rapidly in Hf-based MOF than Zr-based MOF. It is noteworthy that material **4'** is the first example of a MOF probe for peroxyxynitrite, which does not require any additional surface modification step during the synthesis.



Scheme 4.1 Selective sensing of peroxyxynitrite by using Hf-UiO-66-B(OH)₂ MOF (**4'**) in 10 mM HEPES buffer at physiological pH.

4.2 Experimental Section

4.2.1 Materials and General Methods

The organic linker H₂BDC-B(OH)₂ was prepared according to the reported literature⁵⁵ and the other reagents were collected from various chemical suppliers. For the confirmation of Hf-based UiO-66-B(OH)₂ MOF formation, XRPD measurements at room temperature were performed with a Bruker D2 Phaser X-ray diffractometer (30 kV, 10 mA) utilizing Cu-K α ($\lambda = 1.5406$ Å) radiation. DICVOL program⁵⁶ was used to determine the lattice parameter and refinement was performed by STOE's WinXPow software package.⁵⁷ For exploring the thermal stability of the material, TG measurements were performed with a SDT Q600 V20.9 Build 20 thermogravimetric instrument in the range of 25-600 °C under air atmosphere at a heating rate of 5 °C min⁻¹. We conducted the EDX experiments with a Zeiss Supra 55VP SEM-EDX (SEM = scanning electron microscope) equipment. For collecting the mass spectrum of the digested material **4'**, an Agilent 6520 Q-TOF high-resolution mass spectrometer (HR-MS) was used. The mass spectrum of **4'** (15 mg) was recorded after digestion by adding 48% HF (60 μ L) to methanol (1.0 mL). A

Bruker AM 600 spectrometer was utilized for recording the ^1H NMR spectrum of **4'** (20 mg) after digestion in 48% HF/DMSO- d_6 (50 μL /500 μL). For carrying out the N_2 adsorption experiments -196°C , a Quantachrome Autosorb iQ-MP volumetric gas adsorption instrument was used. The sample was degassed at 110°C under high vacuum for 24 h before performing the gas adsorption experiments. For investigating the RNS sensing ability of **4'**, all the fluorescence emission spectra data were collected by utilizing a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. For the fluorescence experiments, the excitation and emission wavelengths were 330 and 426 nm, respectively.

4.2.2 Synthesis Procedure for Hf-Based UiO-66-B(OH) $_2$ (**4**)

A mixture of HfCl_4 (100 mg, 0.31 mmol) and $\text{H}_2\text{BDC-B(OH)}_2$ ligand (65 mg, 0.31 mmol) in 10 mL DMF/formic acid (9:1, v/v) was placed in a 25 mL Teflon-lined autoclave. Then, the stainless steel autoclave was heated at 130°C for 48 h. Afterwards, the autoclave was cooled down to room temperature spontaneously. The white precipitate was filtered off and washed repeatedly with acetone. It was first dried in air and then inside an air-oven at 80°C for overnight. Yield: 62 mg (0.017 mmol, 34%). Elemental analysis calculated for $\text{C}_{60}\text{H}_{112}\text{B}_6\text{N}_4\text{O}_{73}\text{Hf}_6$ (3193.32 g mol^{-1}): C 22.56, H 3.50, N 1.75%. Found: C 22.92, H 3.58, N 1.88%. FT-IR (KBr, cm^{-1}): 3440 (br), 2960 (w), 2927 (w), 1658 (s), 1600 (vs), 1473 (m), 1398 (vs), 1280 (w), 1254 (w), 1100 (m), 1030 (m), 826 (m), 760 (s), 724 (w), 675 (s), 560 (m), 470 (m).

4.2.3 Activation of As-Synthesized Hf-UiO-66-B(OH) $_2$

The as-synthesized form of **4** was activated through a three-step process. Briefly, 150 mg of **4** was heated with 30 mL of DMF at 80°C for 20 h under stirring conditions. After filtration, the white material was stirred in 40 mL of methanol at room temperature for 24 h and again filtered off. The material obtained after filtration was heated under vacuum at 110°C for 24 h. The guest-free form of the compound is denoted as **4'**.

4.2.4 Preparation of 0.5 mM ROS/RNS Solutions

For the fluorescence sensing of ROS/RNS, 0.5 mM aqueous solutions of various ROS/RNS (ONOO^- , TBHP, $\text{HO}^\bullet$, $^1\text{O}_2$, $\text{HO}^\bullet$, $^t\text{BuO}^\bullet$, $\text{O}_2^{\bullet-}$, $\text{NO}^\bullet$, NO^+ , NO_2^- , NO_3^- and ClO^-) were prepared according to the reported procedures.⁵⁸⁻⁶¹

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Caution! Peroxynitrite (ONOO^-) is highly reactive with a short lifetime. For every fluorescence titration and cellular imaging experiment, fresh solution of peroxynitrite was prepared and used.

4.2.5 Preparation of 10 mM HEPES Buffer Having pH = 7.4

This buffer solution was prepared as described by us in earlier reports.^{47, 62, 63} HEPES (1.191 g) was placed in a 250 mL volumetric flask and 100 mL of Milli-Q water was added to it. After that 0.25 (M) NaOH solution was added drop wise until the pH of the solution becomes 7.4. Finally, the volume of the volumetric flask was made up to 250 mL by the addition of require amount of Milli-Q water.

4.2.6 Preparation of the Suspension of 4' in 10 mM HEPES Buffer (pH = 7.4)

A suspension of 4' was prepared by adding 2.0 mg of 4' in 20 mL of 10 mM HEPES buffer, followed by sonication for 20 min. After getting a homogeneous suspension, it was used for the entire fluorescence titration experiments.

4.2.7 Procedure for the Fluorescence Sensing of Peroxynitrite in HEPES Buffer (pH = 7.4)

All the fluorescence titration and cellular imaging measurements were conducted under conditions mimicking biological medium (pH = 7.4). The complete fluorescence titration measurements were carried out with an excitation wavelength of 330 nm and the emission spectra were collected in the range of 350-600 nm. In order to perform the concentration dependent fluorescence detection studies, 0.5 mM aqueous solution of each ROS/RNS was added (10 μL in each addition) to the suspension of 4' in 10 mM HEPES buffer (2 mL) in a quartz cuvette. Turn-on fluorescence behavior of 4' was observed upon incremental addition of peroxynitrite solution and saturation in fluorescence intensity was observed upon the introduction of 100 μL of 0.5 mM peroxynitrite solution. For the time-dependent fluorescence detection investigations, the peroxynitrite solution (100 μL) was added to the HEPES suspension of 4' in 10 mM HEPES buffer and the fluorescence intensity was monitored until the attainment of saturation. The selectivity of peroxynitrite over other ROS/RNS was investigated after the addition of interfering ROS/RNS solution (100 μL) to the 10 mM HEPES suspension of 4', followed by the addition peroxynitrite solution

(100 μ L) to the mixture. The turn-on fluorescence response of **4'** was recorded upon the addition of peroxynitrite solution.

4.2.8 Cell Viability Assay

The toxic effect of Hf-UiO-66-B(OH)₂ or peroxynitrite on macrophage J774A.1 cells was tested as described previously.⁶⁴ Cells were seeded at 10 000 per well in a 96-well plate in 200 μ L of complete media. Cells were treated with different concentrations (0–1 mg/mL) of Hf-UiO-66-B(OH)₂ or peroxynitrite (0–50 μ M) for 12 h in triplicate at 37 °C. Post treatment, cells were observed for morphological change due to toxicity and images were captured using cytell imaging system (GE healthcare). Finally, MTT assay was performed to measure the cellular viability. The viability of the untreated cells was considered as 100% and used to express the viability of treated cells.

4.2.9 Cell Culture and Cellular Imaging Experiments for the Sensing of Peroxynitrite

The J774A.1 macrophage cells were cultured in DMEM:F12 media comprising 10% FBS and 1% antibiotic cocktail, which has been reported earlier.⁶⁵ The cells were loaded with probe **4'** (1 mg/mL) for 10 h in the serum-containing media. These probe-loaded cells were washed with PBS three times to remove the excess probe and then treated with the reactive nitrogen species peroxynitrite, ONOO[−] (5 μ M), for 10 min at 37 °C in PBS. The cells were observed in the bright-field and blue channels (λ_{ex} = 390 nm, λ_{em} = 430 nm) using Cytell cell imaging system (GE Healthcare), and images were captured from randomly selected fields.

4.3 Results and Discussion

4.3.1 Synthesis and Characterization

Compound **4** was synthesized under solvothermal conditions. An equimolar mixture of HfCl₄ and H₂BDC-B(OH)₂ ligand was heated in a mixture of DMF/formic acid. The field-emission-scanning electron microscopy (FE-SEM) analysis of **4'** revealed that nanosized monodispersed particles were formed during the synthesis (Figure 4.1) Mostly, compound **4'** exhibited quasi-spherical shaped crystals.

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The formation of UiO-66 type MOF was confirmed by comparison of the XRPD pattern of the as-synthesized form (**4**) of the compound with the calculated XRPD pattern of Hf-UiO-66 material. It can be seen from Figure 4.2 that there is noticeable similarity between the two XRPD patterns. This result verified the formation of the highly crystalline, as-synthesized **4** in pure phase. The unit cell parameters (Table 4.1) determined from the XRPD pattern of as-synthesized **4** are very similar with the reported Hf-UiO-66 material.⁶⁶ The values of the lattice parameters clearly suggest that both compounds possess cubic structures. Moreover, a Pawley fit of the XRPD pattern of as-synthesized **4** showed close resemblance with the theoretical peak positions of Hf-UiO-66 MOF (Figure 4.3).

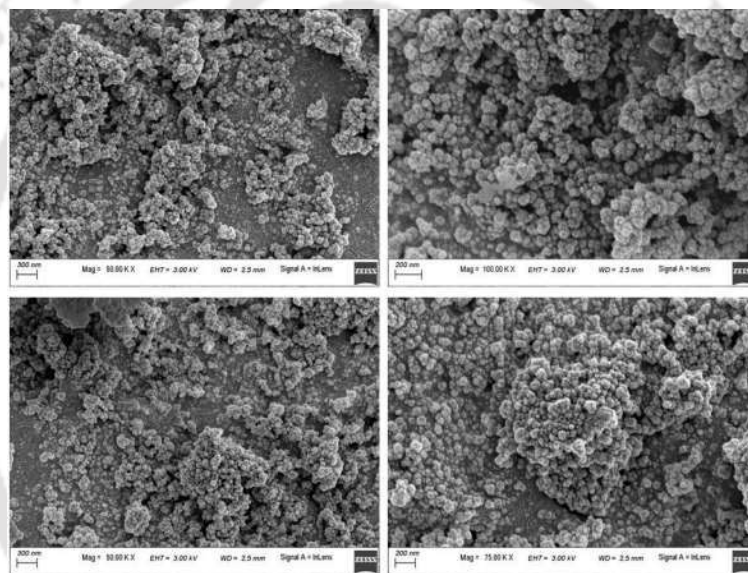


Figure 4.1 FE-SEM images of **4'**.

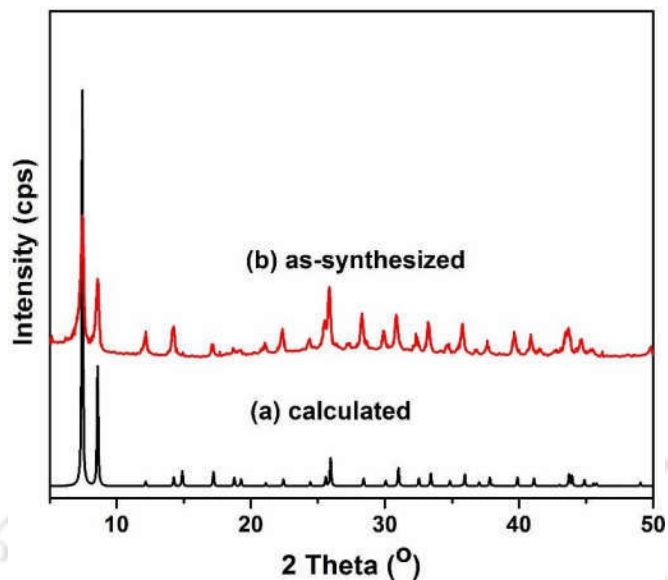


Figure 4.2 calculated XRPD pattern of Hf-UiO-66 and (b) experimental XRPD pattern of as-synthesized **4**.

Table 4.1 Unit cell parameters of the as-synthesized Hf-UiO-66-B(OH)₂ MOF. The obtained values were compared with those of the previously reported Hf-UiO-66 MOF.

Compound Name	Hf-UiO-66-B(OH) ₂ (This Work)	Hf-UiO-66 (Reported) ⁶⁷
Space Group	$Fm\bar{3}m$ (225)	$Fm\bar{3}m$ (225)
Crystal System	Cubic	Cubic
$a = b = c$ (Å)	20.733 (8)	20.7006 (3)
$\alpha = \beta = \gamma$ (°)	90	90
V (Å ³)	8912.3(58)	8870.5(4)
Radiation	Cu K _{α1}	Cu K _{α1}
Figure of Merit (FOM)	16.7	~

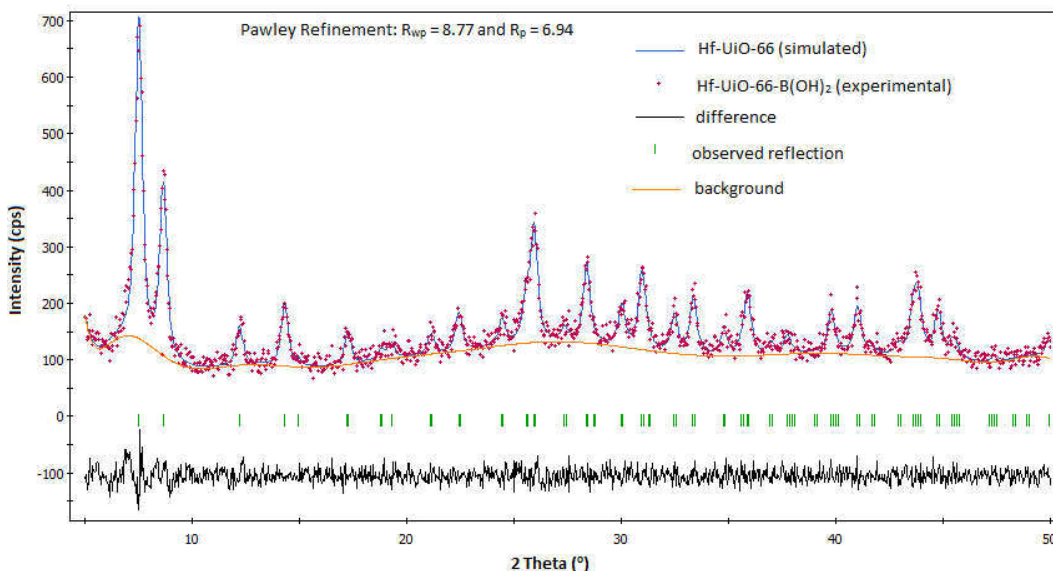


Figure 4.3 Pawley refinement of the as-synthesized **4**. Red dot and blue lines denote observed and calculated patterns, respectively. The peak position and difference plot are displayed at the bottom ($R_p = 6.94$, $R_{wp} = 8.77$).

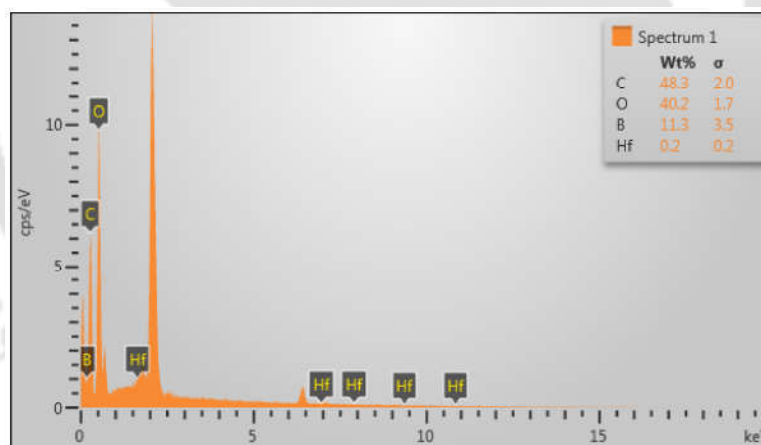


Figure 4.4 EDX spectrum of **4'**.

Owing to its low polarity, the C-B bond can be readily ruptured. We have confirmed the presence of the boronic acid group attached with the ligand molecules in the framework of **4'** by EDX analysis and mass spectrometry. It can be concluded from the EDX spectrum of **4'** (Figures 4.4) that B atoms are present in the framework of the compound, which can be associated with the boronic acid functional group grafted with the coordinated ligand molecules. The mass spectrum of **4'** digested in HF/MeOH was also recorded to verify the

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existence of pendant -B(OH)_2 functional group. As shown in Figure 4.5, the mass spectrum contains a peak at $m/z = 209.003$, which can be assigned to the $[\text{M-H}]^-$ ion (M = mass of $\text{H}_2\text{BDC-B(OH)}_2$ ligand). It becomes evident from these results that the boronic acid group remains attached with the framework ligand molecules during the synthesis and activation of the MOF compound.

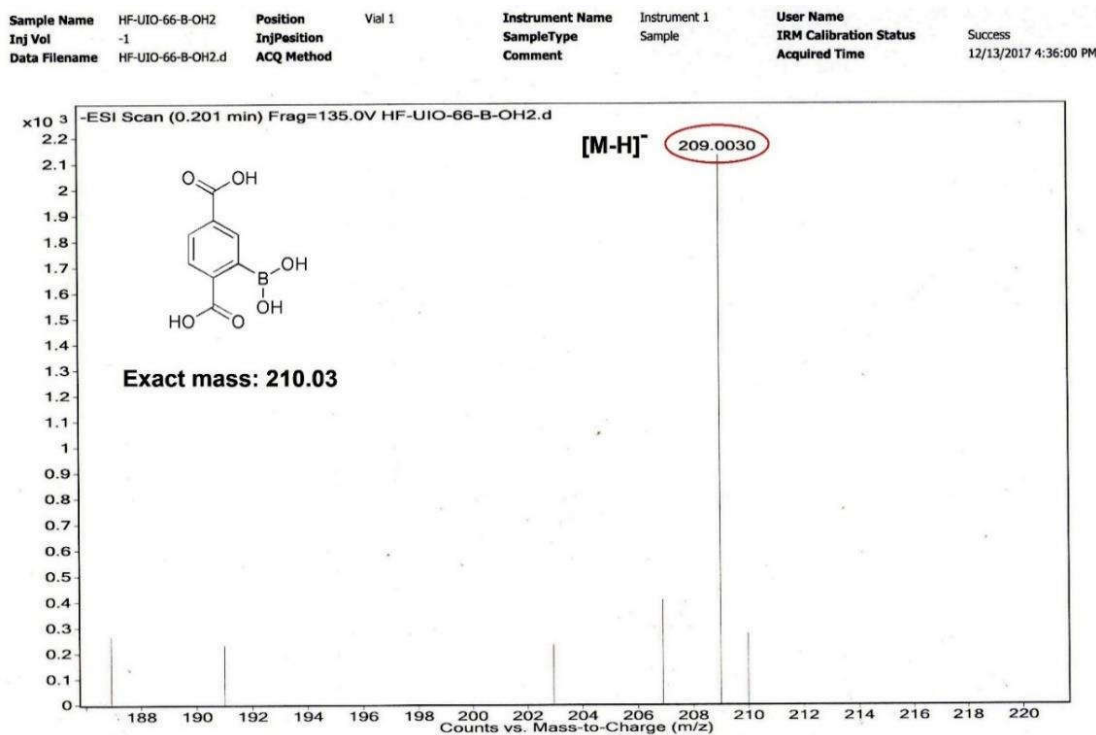


Figure 4.5 Mass spectrum of **4'** after digestion in HF/MeOH.

4.3.2 Infrared Spectroscopy

FT-IR analysis was carried out in order to confirm the presence of ligand molecules as well as guest molecules in the porous framework of as-synthesized **4**. As shown in Figure 4.6, the IR spectra of as-synthesized **4** consists of a strong peak at around 1658 cm^{-1} , which can be ascribed to the carbonyl group of the occluded DMF molecules. Both **4** and **4'** showed strong absorption peaks at around 1400 and 1595 cm^{-1} in their IR spectra, which can be assigned to the symmetric and asymmetric stretching vibration of the carboxylate group of the organic ligand molecules in the framework of Hf-UiO-66-B(OH)_2 compound.

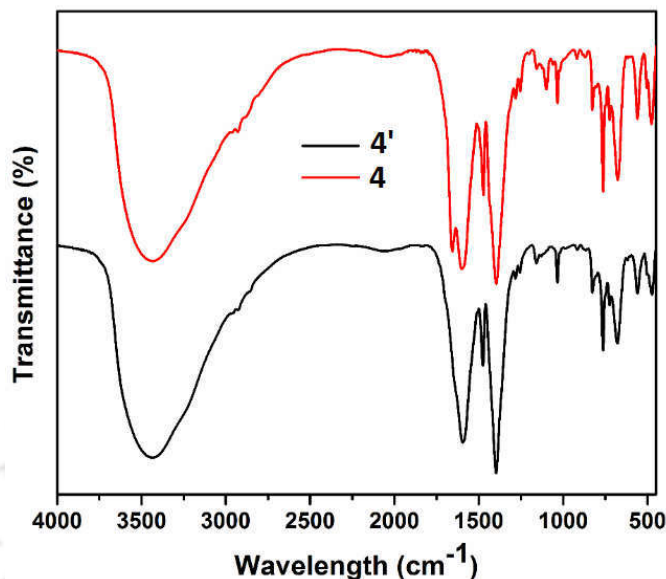


Figure 4.6 FT-IR spectra of as-synthesized **4** (red) and activated **4'** (black).

4.3.3 Thermal and Chemical Stability

The thermal stability of both **4** and **4'** was investigated by TG analysis. The TG analysis revealed that the Hf-UiO-66-B(OH)₂ compound is stable up to 200 °C. In the TG curve (Figure 4.7) of as-synthesized **4**, the first weight loss of 13.9 wt% in the range 30-110 °C can be accountable for the removal of 25 guest H₂O molecules (calcd.: 13.8 wt%). The second weight loss of 11.1 wt% in the range 110-190 °C can be ascribed to the removal of **4** occluded DMF molecules from the pores (calcd.: 10.7 wt%). The decomposition of the BDC-B(OH)₂ ligand start to occur after 200 °C, leading to the collapse of the structural framework.

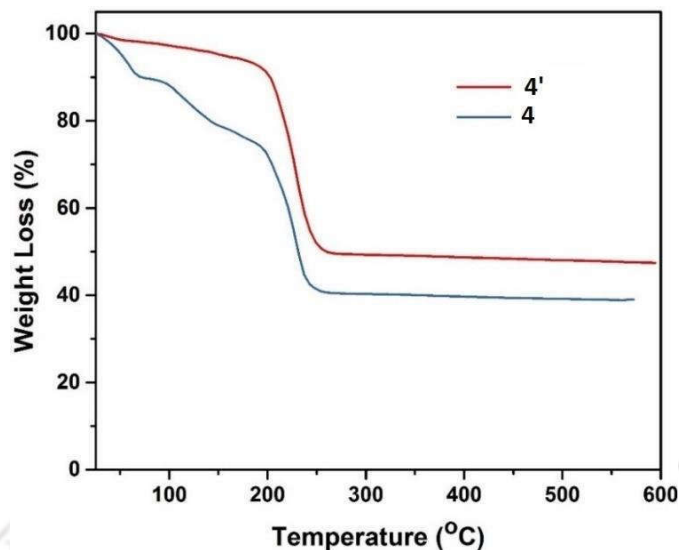


Figure 4.7 TG curves of as-synthesized (blue) and activated (red) forms of **4** measured under air atmosphere with a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

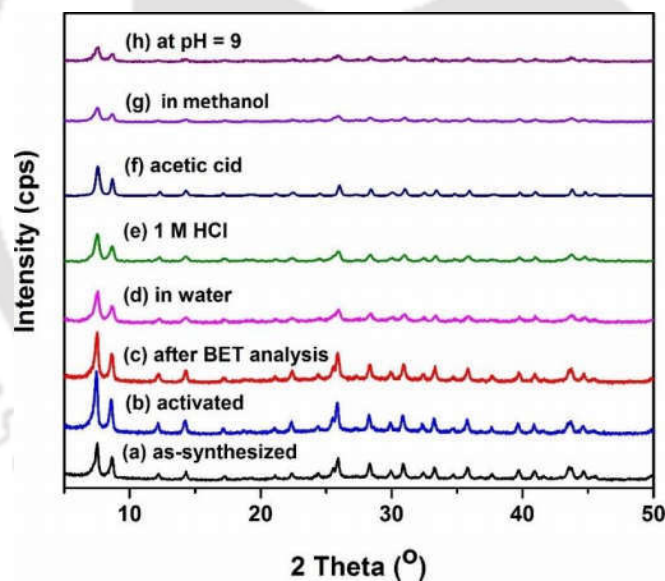


Figure 4.8 XRPD patterns of **4'** in different forms: as-synthesized (a); activated (b); after BET measurement (c); after treatment with water (d); after treatment with 1(M) HCl (e); after treatment with acetic acid (f); after treatment with methanol (g); after treatment with NaOH at pH = 9 (h).

The chemical stability of **4'** was investigated by XRPD experiments. The XRPD pattern of **4'** (20 mg) was collected after stirring for 12 h at ambient temperature in different liquids (acetic acid, water, 1(M) HCl, methanol and NaOH at pH = 9). It can be unambiguously

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inferred from the XRPD patterns (Figure 4.8) that the crystallinity (i.e. structural integrity) of the activated material was not significantly changed upon exposure to acetic acid, water and 1(M) HCl solutions. The treatment with 1(M) NaOH solution having a pH value of 9 led to decrease in the crystallinity of **4'**. These results confirm that the Hf-UiO-66-B(OH)₂ compound displayed high structural robustness. The high chemical stability of the compound is comparable with the formerly reported, functionalized Hf-UiO-66 materials.⁶⁸

4.3.4 Surface Area Measurement

The BET surface area of activated **4'** was determined from the N₂ adsorption isotherm (Figure 4.9) collected at -196 °C. The BET surface area of activated Hf-UiO-66-B(OH)₂ material is 427 m² g⁻¹, which is lower than the un-functionalized Hf-UiO-66 compound.⁶⁹ This lowering of specific BET surface area can be attributed to the incorporation of -B(OH)₂ group in the BDC linker.

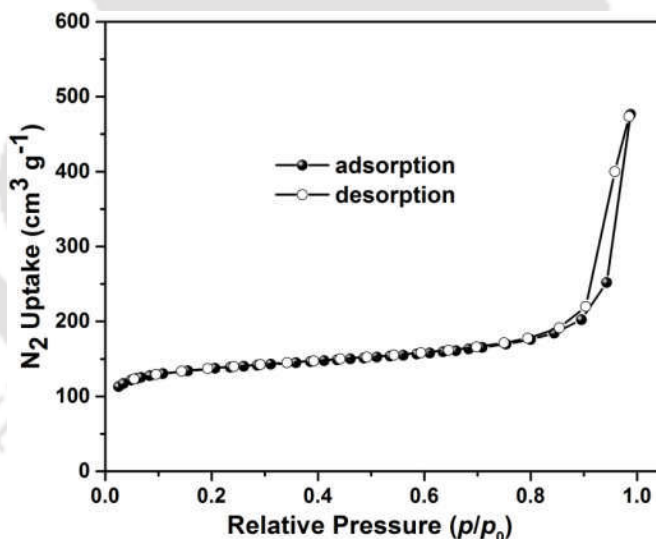


Figure 4.9 N₂ adsorption (filled circles) and desorption (empty circles) isotherms of **4'** measured at -196 °C.

4.3.5 Detection of Peroxynitrite in HEPES Buffer

The Hf-based UiO-66 compound containing the boronic acid groups tagged with the coordinated BDC ligands exhibits weak fluorescence intensity in HEPES buffer at pH =

7.4. Upon treatment with peroxynitrite, the -B(OH)_2 group attached with the BDC ligand is converted to -OH group. The resulting Hf-based UiO-66 MOF incorporating BDC-OH ligand displays stronger fluorescence intensity as compared to the parent Hf-UiO-66- B(OH)_2 compound. Hence, fluorescence increment behavior is observed when peroxynitrite solution is gradually added to the suspension of **4'**. This fluorescence turn-on property of **4'** in presence of peroxynitrite is similar to those of boronic acid or boronate functionalized small organic molecules based fluorescent probes upon treatment with ONOO^- and H_2O_2 .^{70, 71}

The ROS/RNS used in this study comprise peroxynitrite, superoxide anion ($\text{O}_2^{\bullet-}$), nitric oxide radical ($\text{NO}^\bullet$), nitrosonium ion (NO^+), nitrite (NO_2^-), nitrate (NO_3^-), hypochlorite anion (ClO^-), hydroxyl radical ($\text{HO}^\bullet$), *tert*-butoxy radical ($^t\text{BuO}^\bullet$), *tert*-butyl hydroperoxide (TBHP) and singlet oxygen ($^1\text{O}_2$). To verify the fluorescence turn-on response towards peroxynitrite, 0.5 mM solution of each ROS/RNS was added in a stepwise manner to the suspension of **4'** (2 mL) in 10 mM HEPES buffer (pH = 7.4). We have collected the fluorescence spectrum of the suspension of **4'** after each addition step. It is obvious from Figure 4.10 that there was a dramatic increase in the fluorescence intensity of **4'** with the gradual addition of peroxynitrite solution. The addition of 100 μL of 0.5 mM peroxynitrite solution caused $\sim 80\%$ increase (5-fold) in the fluorescence intensity of **4'**. As evident from the Figure 4.11, the other competing ROS/RNS did not result in significant increase in the fluorescence intensity of **4'**. These results can be attributed to the selective reaction of the MOF material with peroxynitrite as compared to the other competing ROS/RNS.

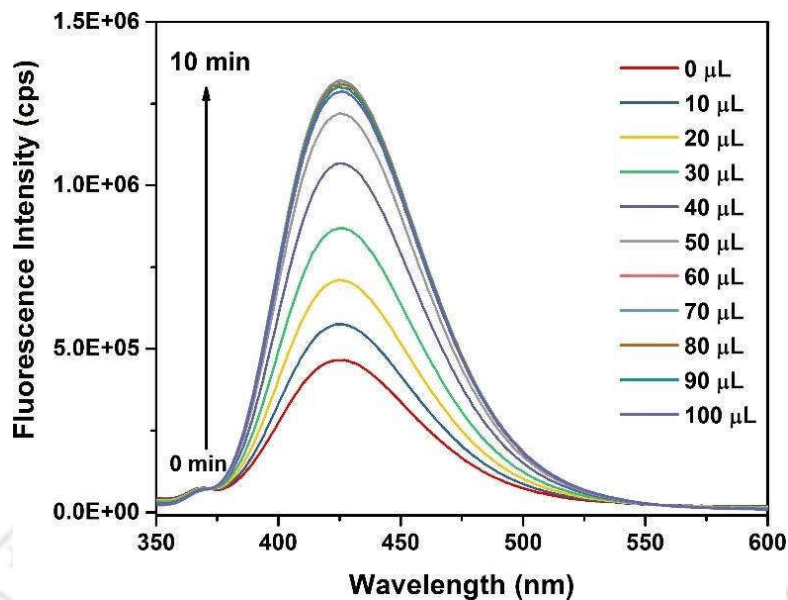


Figure 4.10 Selective turn-on response of **4'** (in 10 mM HEPES buffer at pH = 7.4) upon incremental addition of 0.5 mM ONOO^- solution ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 426$ nm).

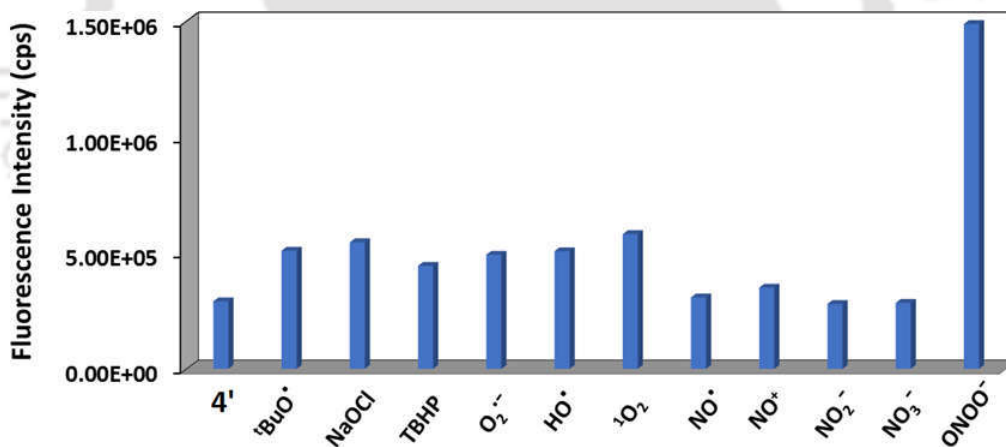


Figure 4.11 Comparative fluorescence enhancement behavior of **4'** in HEPES buffer (10 mM, pH = 7.4) towards different ROS/RNS (**4'**, 0.5 mM of $t\text{BuO}^\bullet$, NaOCl, TBHP, $\text{O}_2^{\bullet-}$, $\text{HO}^\bullet$, $^1\text{O}_2$, $\text{NO}^\bullet$, NO^+ , NO_2^- , NO_3^- and ONOO^-) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 426$ nm).

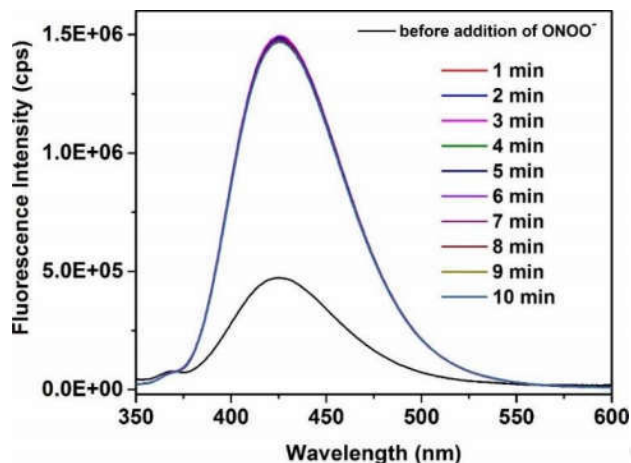


Figure 4.12 Change in the fluorescence spectrum of **4'** in presence of 0.5 mM ONOO^- as a function of time ($\lambda_{\text{ex}} = 330 \text{ nm}$ and $\lambda_{\text{em}} = 426 \text{ nm}$).

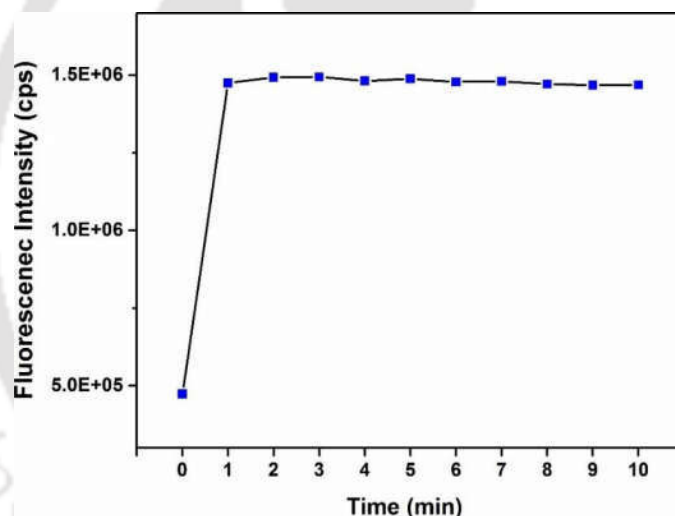


Figure 4.13 Change in the fluorescence spectrum of **4'** in presence of 0.5 mM ONOO^- as a function of time ($\lambda_{\text{ex}} = 330 \text{ nm}$ and $\lambda_{\text{em}} = 426 \text{ nm}$).

Next, we have carried out time-dependent fluorescence experiments for determining the response time of **4'** towards peroxynitrite. For this purpose, 100 μL of 0.5 mM peroxynitrite solution was added to a 2 mL suspension of **4'** in 10 mM HEPES buffer at $\text{pH} = 7.4$. After every 1 min, the fluorescence spectrum of the Hf-UiO-66-B(OH)₂ probe was recorded and the time-dependent study was continued up to 10 min. It is revealed from Figures 4.12 and 4.13, that the fluorescence intensity of the fluorescent probe reached saturation within 1 min. This result demonstrated that material **4'** has ability to detect the

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peroxynitrite with very short response time (1 min) under physiological conditions at room temperature.

The high selectivity of **4'** for peroxynitrite over other intrusive ROS/RNS (Figure 4.11) encouraged us to explore the selectivity of the fluorescent probe in the presence of these competing ROS/RNS. This investigation is highly required for the practical sensing of peroxynitrite in complex biological systems where other interfering ROS/RNS co-exist with peroxynitrite. In this experiment, 100 μL of 0.5 mM solution of different competing ROS/RNS was initially added to the suspension of **4'** in HEPES buffer, followed by the addition of 100 μL of 0.5 mM solution of peroxynitrite. It can be noticed from Figure 4.14 that there was significant increase in the fluorescence intensity of **4'** after the addition of peroxynitrite even in the presence of other interfering ROS/RNS. These results indicate that the Hf-UiO-66-B(OH)₂ probe exhibits high selectivity for peroxynitrite even in the existence of other competitive ROS/RNS.

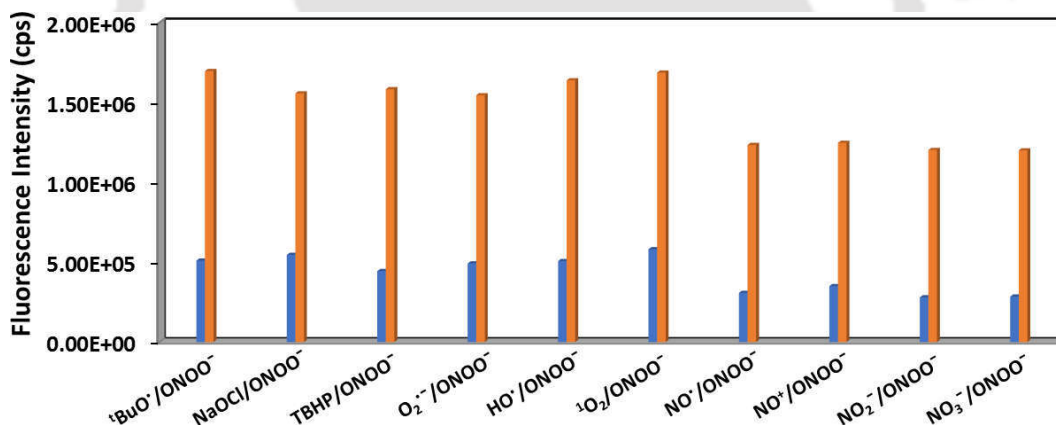


Figure 4.14 Fluorescence responses of **4'** (suspended in 10 mM HEPES buffer, pH = 7.4) towards ONOO⁻ solution (100 μL , 0.5 mM) in the presence of other ROS/RNS solutions (100 μL , 0.5 mM) (λ_{ex} = 330 nm and λ_{em} = 426 nm).

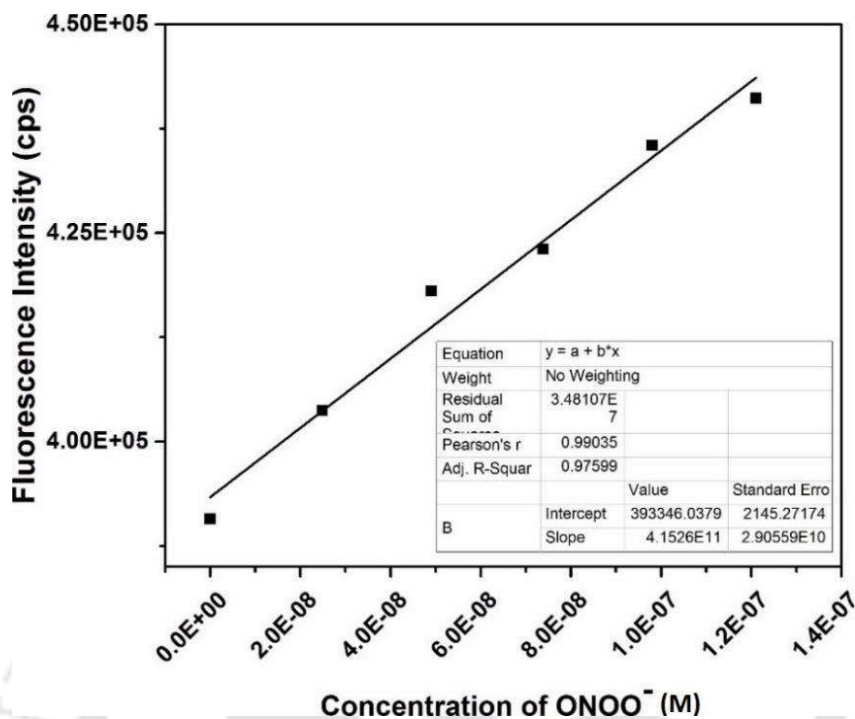


Figure 4.15 Change in the fluorescence intensity of 4' in 10 mM HEPES suspension (pH = 7.4) as a function of ONOO⁻ concentration.

After obtaining short response time and extraordinary selectivity for the probe towards peroxynitrite even in the presence of other competing ROS/RNS, we decided to estimate its limit of detection (LOD) for peroxynitrite in HEPES buffer. The high sensitivity of a fluorescent probe is an important criterion for the real-life sensing of peroxynitrite in biological medium. By following our previously established procedure,⁴⁸ the LOD value was calculated (Figure 4.15). For probe 4', the estimated LOD value for peroxynitrite was found to be 9.0 nM. Hence, the Hf-UiO-66-B(OH)₂ material exhibited outstanding sensitivity towards peroxynitrite in HEPES buffer at physiological pH.

We have also verified the fluorescence response behavior, selectivity and detection limit with the free H₂BDC-B(OH)₂ ligand towards peroxynitrite. We have observed that the probe 4' displayed much better response toward peroxynitrite than free ligand (Figure 4.16) Though the ligand is selective towards but the fluorescence emission enhancement response towards peroxynitrite for 4' is quite high than free ligand (Figure 4.17). Moreover, the limit of detection towards peroxynitrite for 4' is much better (9 nM) (Figure

4.15) than free ligand (21 nM) (Figure 4.18). Hence, it becomes obvious that **4'** is a potential candidate for selective and sensitive peroxynitrite sensing over the free ligand.

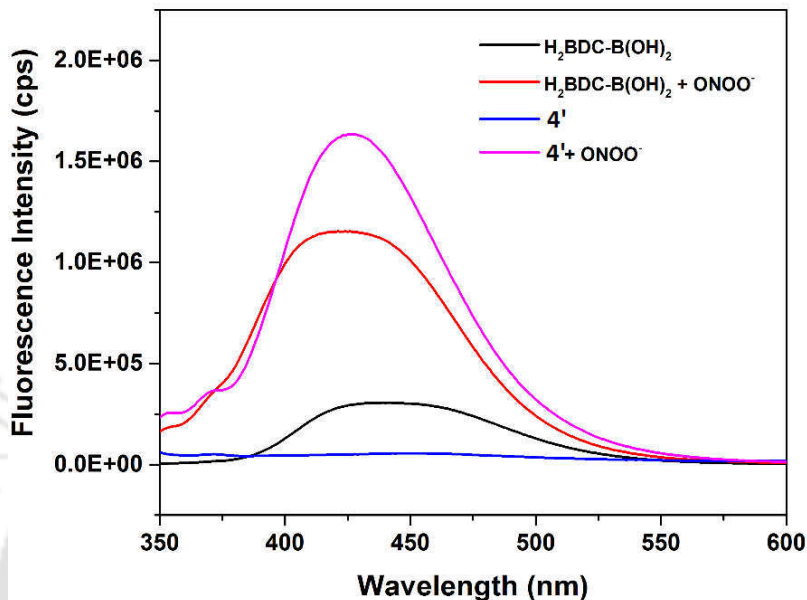


Figure 4.16 Fluorescence response of **4'** and free ligand towards addition of 100 μL peroxynitrite (0.5 mM) in 10 mM HEPES suspension (pH = 7.4) (λ_{ex} = 330 nm and λ_{em} = 426 nm).

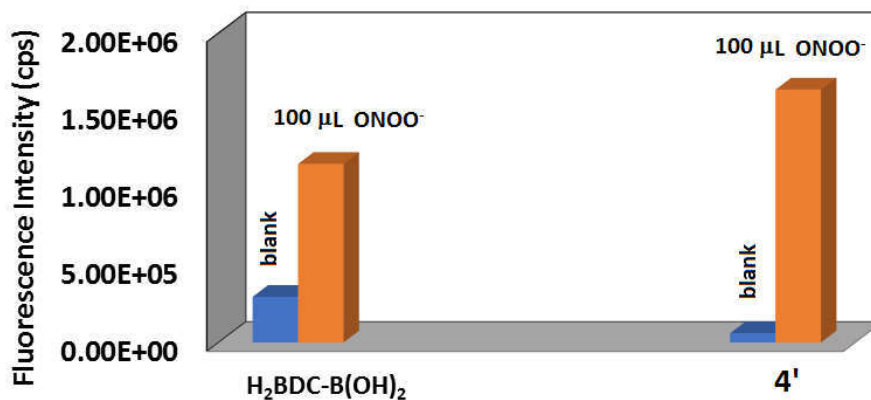


Figure 4.17 Fluorescence response of **4'** and free ligand towards addition of 100 μL peroxynitrite (0.5 mM) in 10 mM HEPES suspension (pH = 7.4).

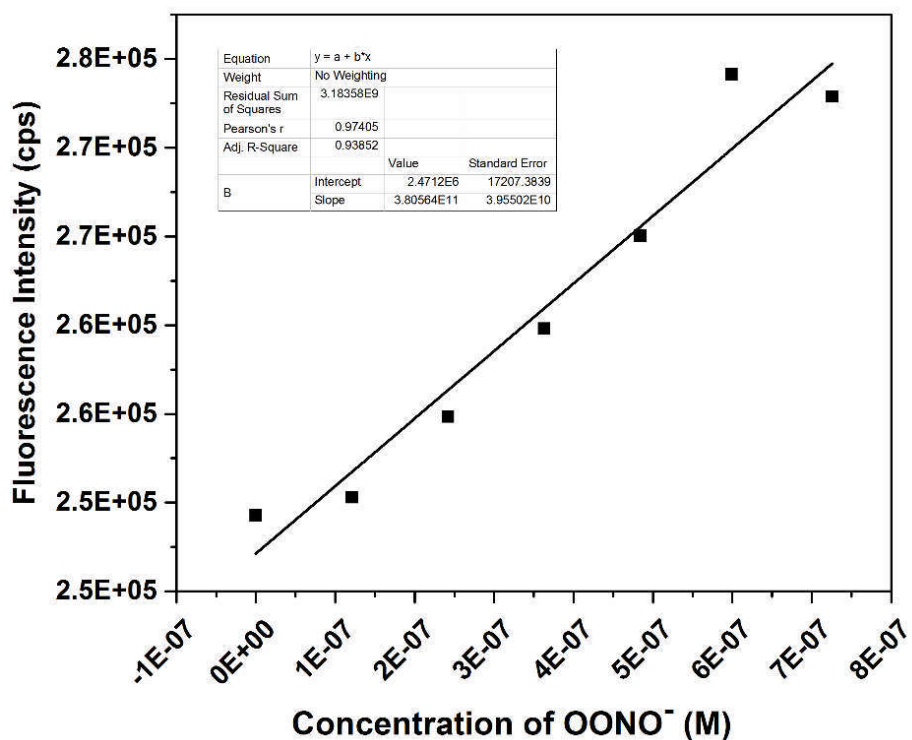


Figure 4.18 Change in the fluorescence intensity of $\text{H}_2\text{BDC-B(OH)}_2$ in 10 mM HEPES suspension (pH = 7.4) as a function of ONOO^- concentration. (b) Recyclability test for $\mathbf{4'}$ in HEPES buffer at pH = 7.4 (λ_{ex} = 330 nm and λ_{em} = 426 nm).

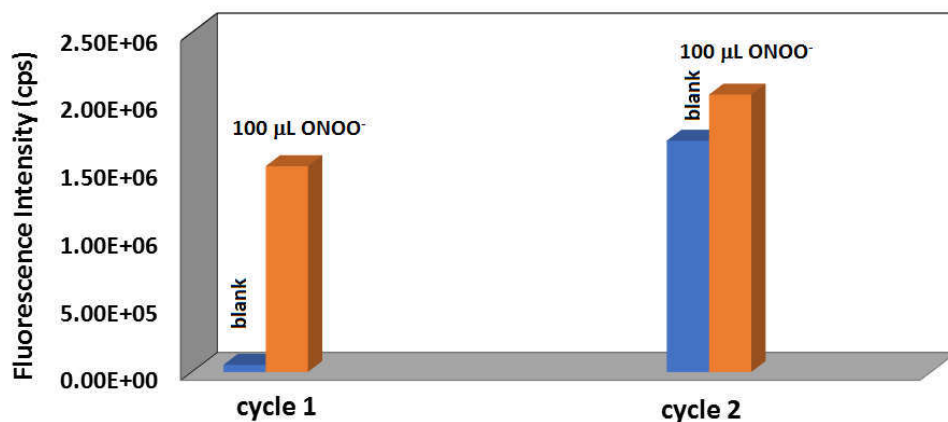


Figure 4.19 Recyclability test for $\mathbf{4'}$ in HEPES buffer at pH = 7.4 (λ_{ex} = 330 nm and λ_{em} = 426 nm).

We have also performed the recyclability test for probe **4'** towards peroxynitrite sensing. After the first cycle of sensing experiment, the boronic acid group in the ligand part was irreversibly converted into the hydroxyl group in the presence of peroxynitrite. Hence, the probe was turned into the fluorescence turn-on state after the first cycle and no further fluorescence turn-on response was observed in the second cycle (Figure 4.19). Therefore, **4'** is a reaction-based fluorescent probe and it is not recyclable.

4.3.6 Detection of Peroxynitrite in Live Cells

Encouraged by its high selectivity and sensitivity as well as short response time for peroxynitrite in HEPES buffer (10 mM, pH 7.4), we decided to carry out fluorescence microscopy experiments to explore the suitability of probe **4'** for imaging peroxynitrite in J774A.1 macrophage cells. Before the cell imaging study, the cellular cytotoxicity of **4'** or peroxynitrite (ONOO^-) toward J774A.1 macrophage cells were performed according to the earlier procedure.⁶⁵ J774A.1 macrophage cells were treated with different concentrations of probe (0-1 mg/mL) or peroxynitrite (0-50 μM) for 12 h in triplicate at 37 °C to verify the morphological change due to toxicity. The concentration-dependent morphology change of the cells is shown in Figure 4.20a. The probe was nontoxic to the macrophage cells and the cells showed ~100% viability after incubation for 12 h. In contrast and as expected, peroxynitrite was extremely toxic to the cells and high concentration caused 100% death of macrophages in 12 h (Figure 4.20b). We treated the J774A.1 cells with peroxynitrite for only 10 min in the cellular imaging experiment. This short period of exposure does not affect the cellular morphology and is nontoxic to the cells (Figures 4.20a-4.20b).

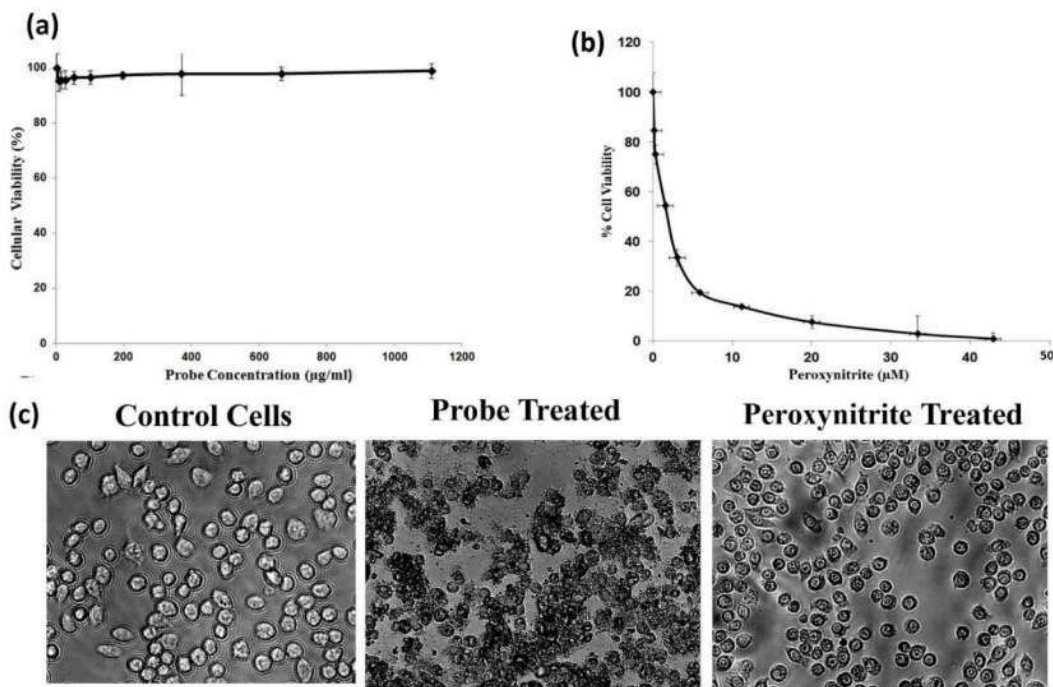


Figure 4.20 (a) MTT assay for probe-treated macrophage J774A.1 cells. (b) MTT assay for peroxynitrite-treated macrophage J774A.1 cells. (c) Morphological analysis of control cells, probe-treated cells and peroxynitrite-treated cells.

The unloaded macrophage cells were healthy (Figure 4.21a, bright-field panel) and did not give any blue fluorescence (Figures 4.21b and 4.21c, fluorescence and superimposed panels). Fluorescent probe **4'** was taken up by the macrophage cells. The bright-field image (Figure 4.21d, bright-field panel) revealed that the mammalian cells did not undergo any morphological change in the presence of the probe. Furthermore, the cellular viability remained unaffected upon consumption of the probe material. It can be observed from the blue channel images (Figures 4.21e and 4.21f, fluorescence and superimposed panels) that the few macrophage cells were giving fluorescent signal. The population of activated macrophage cells produces intracellular peroxynitrite and the fluorescence signal is appearing from these cells.⁷² Next, we have incubated the probe-loaded cells with 5 μM peroxynitrite solution for 10 min. In presence of peroxynitrite, the probe-loaded cells did not change their morphology (Figure 4.21g, bright-field panel). It is remarkable that the probe inside the cells responded toward the peroxynitrite solution to give intense blue fluorescent signal (Figures 4.21h and 4.21i, fluorescence and superimposed panels). This fluorescence microscopy study with J774A.1 macrophage cells unambiguously

demonstrates that the Hf-UiO-66-B(OH)₂ MOF probe is suitable to image peroxynitrite in live cells. Also, probe **4'** is robust in sensing intracellular peroxynitrite generated in biological system and has potential in monitoring these processes for better understanding downstream immune responses.

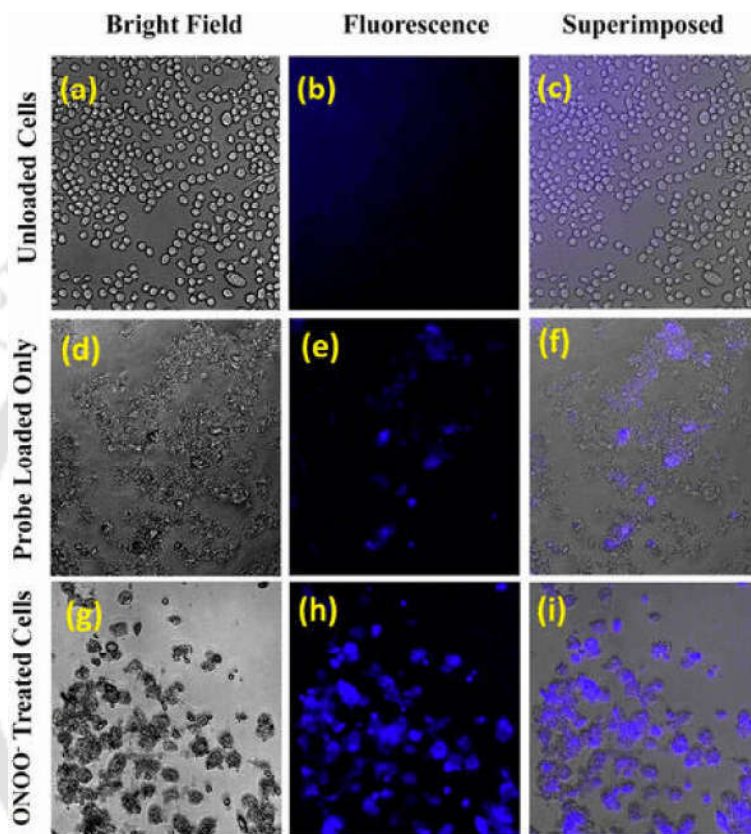
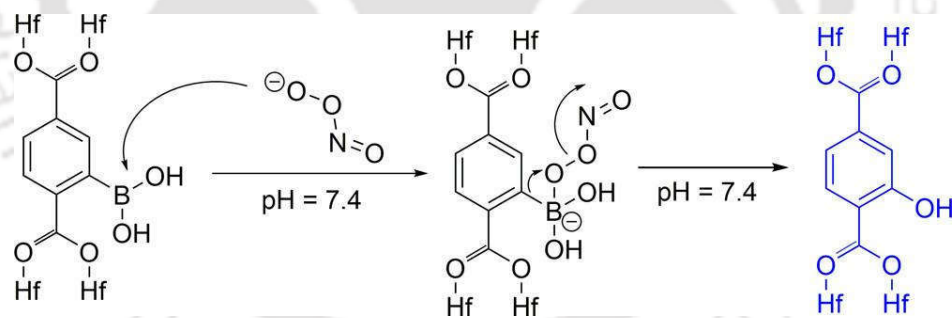


Figure 4.21 Sensing of ONOO^- in J774A.1 macrophage cells using **4'**. Bright-field (a, d, g) and fluorescence channel (b, e, h) images as well as their superposition (c, f, i) are shown for the unloaded cells, probe-loaded cells, and probe-loaded cells after treatment with ONOO^- .

4.3.7 Mechanism for the Detection of Peroxynitrite

Probe **4'** showed excellent selectivity for peroxynitrite over other ROS/RNS (Figure 4.11). The detection of peroxynitrite via fluorescence method is dependent on the oxidative breaking of boronic acid or boronate ester groups, leading to the production of corresponding hydroxyl groups. The probe molecules containing hydroxyl groups show strong fluorescence in presence of peroxynitrite. Based on this strategy, numerous

fluorescent probes based on small organic molecules^{73, 74} and a surface-coated MOF grafted with molecular probe possessing boronic acid group has been reported⁷⁵ till date. Similar to the previously reported probes for peroxynitrite, the presented probe (**4'**) contains the BDC-B(OH)₂ ligand in its structural framework. Upon treatment with peroxynitrite, the framework BDC-B(OH)₂ ligand molecules are expectedly converted to the BDC-OH ligand molecules, giving rise to noticeable fluorescence turn-on response. The occurrence of such organic transformation is not possible with other ROS/RNS. According to the mechanism reported in the literature literature,⁷³⁻⁷⁵ the selective fluorescence turn-on response by material **4'** should be attributed to the chemoselective oxidative breaking of the boronic acid group anchored with the framework ligands by peroxynitrite. This reaction in presence of peroxynitrite under basic conditions (pH = 7.4) is similar to Baeyer-Villiger oxidation (Scheme 4.2).⁷⁶ The treatment of **4'** with peroxynitrite during the sensing event in HEPES buffer (pH = 7.4) did not affect its structural integrity. This fact was verified by the XRPD experiments which revealed that the crystallinity of the material after the sensing experiment was very similar to the untreated compound (Figure 4.22).



Scheme 4.2 Proposed mechanism for the selective response of **4'** towards ONOO^- in 10 mM HEPES buffer at pH = 7.4.

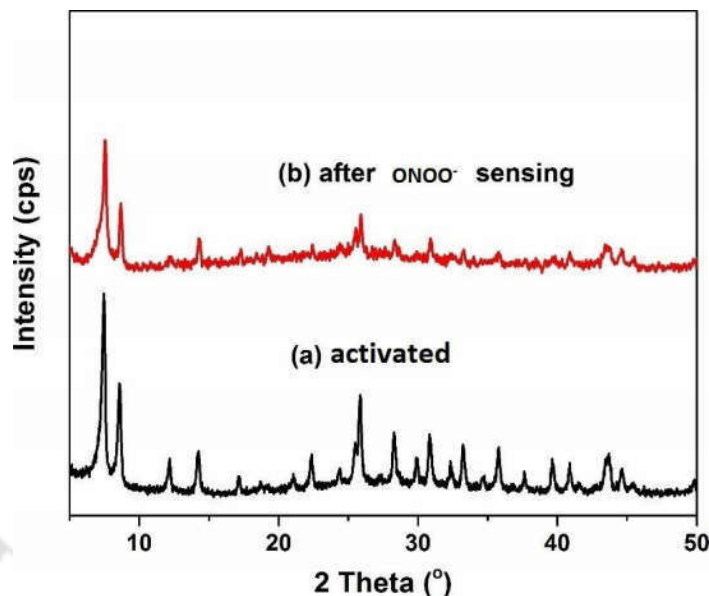


Figure 4.22 XRPD patterns of **4'** in different forms: activated (a); after peroxynitrite sensing (b).

We conducted mass spectrometry and ^1H NMR spectroscopic investigation in order to confirm the anticipated mechanism involving the conversion of framework BDC-B(OH)_2 ligand to BDC-OH . It is disclosed from Figure 4.23 that the mass spectrum of untreated **4'** contains an m/z peak at 181.0088. This peak corresponds to the $[\text{M-H}]^-$ ion, where M represents the mass of $\text{H}_2\text{BDC-OH}$ ligand. A comparison between the ^1H NMR spectra (measured after digestion in $\text{HF/DMSO-}d_6$) of un-treated and peroxynitrite-treated **4'** unveiled the appearance of extra peaks at 7.41, 7.44 and 7.87 ppm in the ^1H NMR spectrum of the latter (Figure 4.24). These new peaks in the aromatic region, which appeared in addition to the peaks of BDC-B(OH)_2 ligand, correspond to the protons of BDC-OH ligand.⁷⁷ The BDC-OH ligand was generated from the BDC-B(OH)_2 ligand incorporated in the framework structure of **4'** upon reaction with peroxynitrite. From the ^1H -NMR spectroscopic investigation, we found that there was $\sim 85\%$ conversion of the BDC-B(OH)_2 ligand into BDC-OH ligand in the structural framework of **4'**.

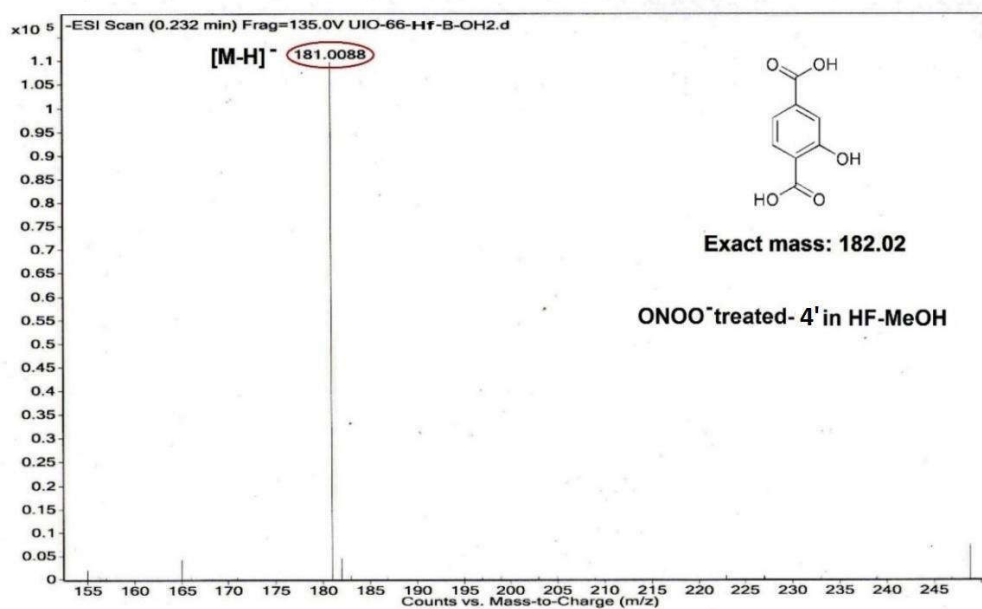


Figure 4.23 Mass spectrum of 4' after treatment with ONOO⁻ in 10 mM HEPES buffer (pH = 7.4).

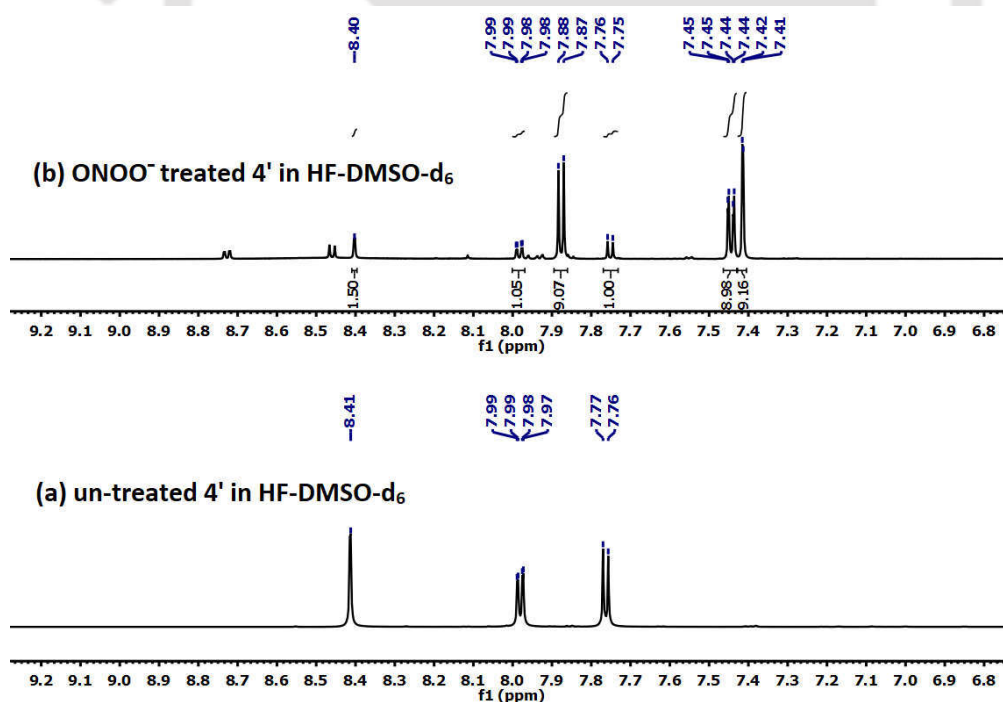


Figure 4.24 ¹H NMR spectra of (a) un-treated 4' with ONOO⁻ in HF/DMSO-d₆ and (b) ONOO⁻-treated 4' after digestion in HF/DMSO-d₆.

4.4 Conclusions

The boronic acid functionalized Hf-based UiO-66 material was prepared under solvothermal conditions and characterized thoroughly. After removal of guest molecules from the pores, the activated Hf-UiO-66-B(OH)₂ material (**4'**) was utilized to detect both extra- and intracellular peroxynitrite. When employed as a fluorescent turn-on probe in HEPES buffer at pH = 7.4, high selectivity with short response time was observed toward peroxynitrite over other potentially interfering ROS/RNS. In addition to its fast response and great selectivity, probe **4'** featured outstanding sensitivity toward peroxynitrite. The estimated detection limit for peroxynitrite falls in the nanomolar level (detection limit = 9.0 nM). The fluorescent turn-on response of the probe toward peroxynitrite can be ascribed to the oxidative cleavage of the boronic acid groups attached with the framework ligands into the corresponding hydroxyl groups. The proposed mechanism for the fluorescent turn-on response of **4'** in the presence of peroxynitrite has been confirmed by mass spectrometry and ¹HNMR spectroscopy. Because of its low cytotoxicity, short response time, and excellent selectivity and sensitivity for peroxynitrite in simulated physiological medium (10 mM HEPES buffer at pH = 7.4), the probe was applied for the imaging of peroxynitrite inside living cells (J774A.1 macrophage cells).

4.5 References

1. D. Gius and D. R. Spitz, *Antioxid. Redox Signal.*, 2006, **8**, 1249-1252.
2. B. Halliwell, *Plant Physiol.*, 2006, **141**, 312–322.
3. V. M. Darley-Usmar, N. Hogg, V. J. O'Leary, M. T. Wilson and S. Moncada, *Free Radical Res. Commun.*, 1992, **17**, 9-20.
4. J. S. Beckman, T. W. Beckman, J. Chen, P. A. Marshall and B. A. Freeman, *Proc. Natl. Acad. Sci. U.S.A.*, 1990, **87**, 1620–1624.
5. G. Ferrer-Sueta and R. Radi, *ACS Chem. Biol.*, 2009, **4**, 161–177.
6. G. L. Squadrito and W. A. Pryor, *Free Radical Biol. Med.*, 1998, **25**, 392-403.
7. R. T. Dean, S. Fu, R. Stocker and M. J. Davies, *Biochem J.*, 1997, **324**, 1-18.
8. J. S. Richman and J. R. Moorman, *Am. J. Physiol.: Heart Circ. Physiol.*, 2000, **278**, H2039-H2049.
9. G. Supinski, D. Stofan, L. A. Callahan, D. Nethery, T. M. Nosek and A. DiMarco, *J. Appl. Physiol.*, 1999, **87**, 783-791.

10. H. Wiseman and B. Halliwell, *Biochem. J.*, 1996, **313**, 17-29.
11. C. R. White, T. A. Brock, L. Y. Chang, J. Crapo, P. Briscoe, D. Ku, W. A. Bradley, S. H. Gianturco, J. Gore and B. A. Freeman, *Proc. Natl. Acad. Sci. U.S.A.*, 1994, **91**, 1044-1048.
12. J. S. Beckman, M. Carson, C. D. Smith and W. H. Koppenol, *Nature*, 1993, **364**, 584-585.
13. B. C. Dickinson and C. J. Chang, *Nat. Chem. Biol.*, 2011, **7**, 504-511.
14. D. Tsikas, *Analyt.*, 2011, **136**, 979-987.
15. W. C. A. Koh, J. I. Son, E. S. Choe and Y.-B. Shim, *Anal. Chem.*, 2010, **82**, 10075-10082.
16. J. Xue, X. Ying, J. Chen, Y. Xian, L. Jin and J. Jin, *Anal. Chem.*, 2000, **72**, 5313-5321.
17. S. L. Chen, I. Jian and H. Q. Lang, *Luminescence*, 2013, **18**, 249-253.
18. A. Daiber, M. Oelze, M. August, M. Wendt, K. Sydow, H. Wieboldt, A. L. Kleschyov and T. Munzel, *Free Radic. Res.*, 2004, **38**, 259-269.
19. A. Sikora, J. Zielonka, M. Lopez, J. Joseph and B. Kalyanaraman, *Free Radic. Biol. Med.*, 2009, **47**, 1401-1407.
20. J. Zielonka, A. Sikora, M. Hardy, J. Joseph, B. P. Dranka and B. Kalyanaraman, *Chem. Res. Toxicol.*, 2012, **25**, 1793-1799.
21. D. Yang, H.-L. Wang, Z.-N. Sun, N.-W. Chung and J.-G. Shen, *J. Am. Chem. Soc.*, 2006, **128**, 6004-6005.
22. F. Yu, P. Li, B. Wang and K. Han, *J. Am. Chem. Soc.*, 2013, **135**, 7674-7680.
23. F. Yu, P. Li, G. Li, G. Zhao, T. Chu and K. Han, *J. Am. Chem. Soc.*, 2011, **113**, 11030-11033.
24. T. Ueno, Y. Urano, H. Kojima and T. Nagano, *J. Am. Chem. Soc.*, 2006, **128**, 10640-10641.
25. Q. Zhang, Z. Zhu, Y. Zheng, J. Cheng, N. Zhang, Y.-T. Long, J. Zheng, X. Qian and Y. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 18479-18482.
26. K.-K. Lin, S.-C. Wu, K.-M. Hsu, C.-H. Hung, W.-F. Liaw and Y.-M. Wang, *Org. Lett.*, 2013, **15**, 4242-4245.
27. Y. L. Pak, K. M. K. Swamy and J. Yoon, *Sensor*, 2015, **15**, 24374-24396.
28. Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815-5840.

Chapter 4

29. S. Cai, H. Shi, D. Tian, H. Ma, Z. Cheng, Q. Wu, W. Gu, L. Huang, Z. An, Q. Peng and W. Huang, *Adv. Funct. Mater.*, 2018, **28**, 1705045-1705052.
30. H. Li, W. Shi, K. Zhao, Z. Niu, H. Li and P. Cheng, *Chem. Eur. J.*, 2013, **19**, 3358–3365.
31. Y. Lin, X. Zhang, W. Chen, W. Shi and P. Cheng, *Inorg. Chem.*, 2017, **56**, 11768–11778.
32. S.-Y. Zhang, W. Shi, P. Cheng and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2015, **137**, 12203–12206.
33. J. Zhou, H. Li, H. Zhang, H. Li, W. Shi and P. Cheng, *Adv. Mater.*, 2015, **27**, 7072–7077.
34. J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.
35. P. Ramaswamy, N. E. Wong and G. K. H. Shimizu, *Chem. Soc. Rev.*, 2014, **43**, 5913-5932.
36. Y. Chen, D. Wang, X. Deng and Z. Li, *Catal. Sci. Technol.*, 2017, **7**, 4893-4904.
37. L. Zhu, X.-Q. Liu, H.-L. Jiang and L.-B. Sun, *Chem. Rev.*, 2017, **117**, 8129-8176.
38. M. C. So, G. P. Wiederrecht, J. E. Mondloch, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2015, **15**, 3501-3510.
39. L. Sun, S. S. Park, D. Sheberla and M. Dincă, *J. Am. Chem. Soc.*, 2016, **138**, 14772-14782.
40. J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869-932.
41. Z. Zou, S. Li, D. He, X. He, K. Wang, L. Li, X. Yang and H. Li, *J. Mater. Chem. B*, 2017, **5**, 2126-2132.
42. S. Nandi, H. Reinsch, S. Banesh, N. Stock, V. Trivedi and S. Biswas, *Dalton Trans.*, 2017, **46**, 12856-12864.
43. R. Dalapati, U. Koekcam-Demir, C. Janiak and S. Biswas, *Dalton Trans.*, 2018, **47**, 1159-1170.
44. A. Das and S. Biswas, *Sens. Actuators, B.*, 2017, **250**, 121-131.
45. R. Dalapati and S. Biswas, *Sens. Actuators, B.*, 2017, **239**, 759-767.
46. S. S. Nagarkar, A. V. Desai and S. K. Ghosh, *Chem. Eur. J.*, 2015, **21**, 9994-9997.
47. R. Dalapati, S. N. Balaji, V. Trivedi, L. Khamari and S. Biswas, *Sens. Actuators, B.*, 2017, **245**, 1039-1049.
48. A. Das, S. Banesh, V. Trivedi and S. Biswas, *Dalton Trans.*, 2018, **47**, 2690-2700.

49. A. V. Desai, P. Samanta, B. Manna and S. K. Ghosh, *Chem. Commun.*, 2015, **51**, 6111-6114.
50. Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126-1162.
51. Y. Cui, F. Zhu, B. Chen and G. Qian, *Chem. Commun.*, 2015, **51**, 7420-7431.
52. Z. Hu, K. Tan, W. P. Lustig, H. Wang, Y. Zhao, C. Zheng, D. Banerjee, T. J. Emge, Y. J. Chabal and J. Li, *Chem. Sci.*, 2014, **5**, 4873-4877.
53. Z. Hu, A. Nalaparaju, Y. Peng, J. Jiang and D. Zhao, *Inorg. Chem.*, 2016, **55**, 1134-1141.
54. M. H. Beyzavi, R. C. Klet, S. Tussupbayev, J. Borycz, N. A. Vermeulen, C. J. Cramer, J. F. Stoddart, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2014, **136**, 15861-15864.
55. V. Benin, S. Durganlal and A. B. Morgan, *J. Mater. Chem.*, 2012, **22**, 1180-1190.
56. A. Boulton and D. J. Louer, *J. Appl. Crystallogr.*, 1991, **24**, 987-993.
57. A. Karmakar, B. Joarder, A. Mallick, P. Samanta, A. V. Desai, S. Basu and S. K. Ghosh, *Chem. Commun.*, 2017, **53**, 1253-1256.
58. D. Srikun, E. W. Miller, D. W. Domaille and C. J. Chang, *J. Am. Chem. Soc.*, 2008, **130**, 4596-4597.
59. M. Kim, S.-K. Ko, H. Kim, I. Shin and J. Tae, *Chem. Commun.*, 2013, **49**, 7959-7961.
60. L. Yuan, W. Lin and J. Song, *Chem. Commun.*, 2010, **46**, 7930-7932.
61. A. Beltrán, M. I. Burguete, D. R. Abánades, D. Pérez-Sala, S. V. Luis and F. Galindo, *Chem. Commun.*, 2014, **50**, 3579-3581.
62. S. Nandi, H. Reinsch, S. Banesh, N. Stock, V. Trivedi and S. Biswas, *Dalton Trans.*, 2017, **46**, 12856-12864.
63. A. Buragohain and S. Biswas, *CrystEngComm*, 2016, **18**, 4374-4381.
64. S. J. Deka, A. Roy, V. Ramakrishnan, D. Manna and V. Trivedi, *Chem. Biol. Drug Des.*, 2017, **89**, 953-963.
65. R. Deshmukh and V. Trivedi, *Toxicol. In Vitro*, 2013, **27**, 16-23.
66. S. Jakobsen, D. Gianolio, D. S. Wragg, M. H. Nilsen, H. Emerich, S. Bordiga, C. Lamberti, U. Olsbye, M. Tilset and K. P. Lillerud, *Phys. Rev. B* 2012, **86**, 125429-125440.

67. S. Jakobsen, D. Gianolio, D. S. Wragg, M. H. Nilsen, H. Emerich, B. Silvia, C. Lamberti, U. Olsbye, M. Tilset and K. P. Lillerud, *Phys. Rev. B*, 2012, **86**, 125429-125429.
68. Z. Hu, A. Nalaparaju, Y. Peng, J. Jiang and D. Zhao, *Inorg. Chem.*, 2016, **55**, 1134–1141.
69. H. Xu, B. Zhai, C.-S. Cao and B. Zhao, *Inorg. Chem.*, 2016, **55**, 9671–9676.
70. H. Zhang, J. Liu, Y.-Q. Sun, Y. Huo, Y. Li, W. Liu, X. Wu, N. Zhu, Y. Shi and W. Guo, *Chem. Commun.*, 2015, **51**, 2721-2724.
71. K.-K. Lin, S.-C. Wu, K.-M. Hsu, C.-H. Hung, W.-F. Liaw and Y.-M. Wang, *Org. Lett.*, 2013, **15**, 4242–4245.
72. C. Prolo, M. N. Álvarez and R. Rafael, *Biofactors*, 2014, **40**, 215–225.
73. X. Sun, Q. Xu, G. Kim, S. E. Flower, J. P. Lowe, J. Yoon, J. S. Fossey, X. Qian, S. D. Bull and T. D. James, *Chem. Sci.*, 2014, **5**, 3368-3373.
74. J. Zhang, Y. Li and W. Guo, *Anal. Methods*, 2015, **7**, 4885-4888.
75. Z. Ding, J. Tan, G. Feng, Z. Yuan, C. Wu and X. Zhang, *Chem. Sci.*, 2017, **8**, 5101-5106.
76. J. Zhang, Y. Li, J. Zhao and W. Guo, *Sens. Actuators, B*, 2016, **237**, 67-74.
77. S. Biswas, D. E. P. Vanpoucke, T. Verstraelen, M. Vandichel, S. Couck, K. Leus, Y.-Y. Liu, M. Waroquier, V. V. Speybroeck, J. F. M. Denayer and P. V. D. Voort, *J. Phys. Chem. C*, 2013, **117**, 22784–22796.

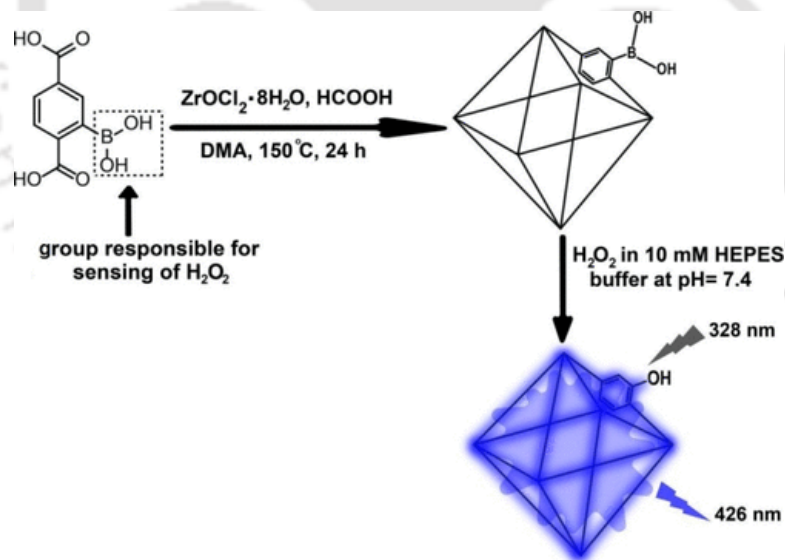


5.1 Introduction

The reactive oxygen species (ROS) play important role in living organisms for causing aging and various diseases is well-known.¹ The ROS family such as hydroperoxy radical ($\text{HO}_2^\bullet$), superoxide anion ($\text{O}_2^{\bullet-}$), hydroxyl radical ($\text{HO}^\bullet$), peroxy radical ($\text{RO}_2^\bullet$), singlet oxygen ($^1\text{O}_2$), hydrogen peroxide (H_2O_2), alkoxy radical ($\text{RO}^\bullet$), nitric oxide (NO), *tert*-butyl hydroperoxide (TBHP), *tert*-butoxy radical ($^t\text{BuO}^\bullet$) and hypochlorite ion (ClO^-). Generally, most of ROS in biological systems are generated from molecular oxygen in living cell.² The high levels of ROS can result in oxidative damage to proteins, lipids or nucleic acids in cells, thereby resulting several abnormalities such as aging,³ cancer,⁴ diabetes,⁵ cardiovascular disorder,⁶ Alzheimer's and related neurodegenerative diseases,⁷ etc.

Among various ROS, H_2O_2 is a major part for oxidative stress in biological system.^{8, 9} The adequate levels of H_2O_2 in the live cells contribute to several cellular processes such as differentiation, migration, growth, proliferation and phagocytosis. On the other hand, excessive levels of H_2O_2 in the live cells results in pathological defects that contribute to aging,³ cancer,^{1, 10} Alzheimer's disease,^{11, 12} diabetes,^{13, 14} nucleic acid damage,¹⁵ mutation¹⁶ and genetic instability.¹⁷ For studying the complex nature of action and behaviour of H_2O_2 in live cells, various analytical methods have been developed so far, which include mass spectrometry, electrochemistry, positron emission tomography, chemiluminescence, absorption spectroscopy, MRI, etc.¹⁸ On the other hand, the utilization of fluorescence spectroscopy for the sensing of H_2O_2 with the help of small organic molecules has attracted growing research interests in recent years.¹⁹ In these cases, fluorescence and in-vivo bioluminescence methods have been demonstrated to provide high selectivity and sensitivity for the sensing of H_2O_2 in animals and living cells. In addition, the fluorescence technique is non-destructive in nature and can be applied for the real-time monitoring of H_2O_2 . For the detection of H_2O_2 by fluorescence technique, several approaches have been reported, which consist of hydrolysis of sulfonate group, Baeyer-Villiger type of reaction, oxidation of triphenylphosphine, oxidative breaking of arylboronate to phenol, etc.²⁰ Among them, the chemoselective reaction of arylboronates to phenols have been vastly exploited for the fluorometric detection of H_2O_2 in living biological media.^{21, 22}

MOFs are potential candidates in both materials and biological science.^{23, 24} The functionalization of the organic ligands make them potential candidates for selective gas adsorption,²⁵ separation,²⁶ magnetic application,²⁷ proton conductivity, electrical conductivity,²⁸ heterogeneous catalysis,²⁹ photo-catalysis,³⁰ medicinal drug delivery,³¹ etc. Furthermore, the aromatic ligands of MOFs can be functionalized with desired substituents for the detection of the target analyte. These functional groups can interact (or react) with the target analytes, leading to measurable changes in fluorescence intensity. By virtue of these benefits, several MOFs have been reported so far for the selective sensing of metal ions,^{32, 33} explosive compounds,^{34, 35} small organic molecules,^{36, 37} biological signalling molecules,³⁸ ROS,³⁹ etc. Among various ROS, the fluorescence method has been used for the sensing of only NO by the Zr-UiO-66-NH₂ MOF.³⁹ Recently, a boronic acid functionalized Eu-MOF has been reported⁴⁰ for the detection of F⁻ ion. Although the detection of H₂O₂ has been accomplished by various MOFs employing different techniques such as electrochemistry,⁴¹ chemiluminescence⁴² and absorption spectroscopy.⁴³ The fluorometric sensing of H₂O₂ using MOFs and its application in live-cell imaging have remained completely unexplored so far.



Scheme 5.1 Preparation scheme for the Zr-UiO-66-B(OH)₂ compound (**5**). Selective fluorescence sensing of H₂O₂ by activated **5'** via turn-on mechanism in HEPES (pH = 7.4, 10 mM) buffer.

In this work, we have synthesized a boronic acid functionalized Zr(IV) MOF with UiO-66 structure (Scheme 5.1). The solvothermal reaction of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ with $\text{H}_2\text{BDC-B(OH)}_2$ in DMA in presence of formic acid led to the formation of Zr-UiO-66-B(OH)₂ MOF (**5**). The activated material (**5'**) has been used to detect H_2O_2 selectively in 10 mM HEPES at pH = 7.4 (simulated biological medium) through fluorescence turn-on mechanism. Moreover, the probe has been utilized for the imaging of H_2O_2 in living cells.

5.2 Experimental Section

5.2.1 Materials and General Methods

All other reagents were received from the commercial suppliers. The FT-IR spectra in the range of 440–4000 cm^{-1} were measured with a Perkin Elmer Spectrum Two FT-IR instrument. The absorption bands were characterized with the following indications: weak (w), medium (m), strong (s), very strong (vs), broad (br) and shoulder. TG measurements were conducted with a SDT Q600 V20.9 Build 20 thermogravimetric instrument in the range of 25–650 °C under air atmosphere at a heating rate of 5 °C min^{-1} . The PXRD measurements at room temperature were performed with a Bruker D2 Phaser X-ray diffractometer (30 kV, 10 mA) utilizing Cu-K α ($\lambda = 1.5406 \text{ \AA}$) radiation. To carry out the EDX experiments, a Zeiss Supra 55VP SEM-EDX (SEM = scanning electron microscope) equipment was utilized. For collecting the mass spectrum, an Agilent 6520 Q-TOF high-resolution mass spectrometer (HR-MS) was used. The mass spectrum of H_2O_2 -treated **5'** (10 mg) was recorded after digestion by adding of 48% HF (60 μL) to methanol (1.0 mL). The ^1H NMR spectra of untreated and H_2O_2 -treated **5'** (30 mg) were collected after digestion by 48% HF (50 μL) in DMSO- d_6 (500 μL). For recording the NMR spectrum, a Bruker AM 600 spectrometer was employed. A Quantachrome Autosorb iQ-MP volumetric gas sorption equipment was utilized for carrying out the N_2 sorption experiments at -196°C . Before conducting the gas adsorption measurement, we degassed the sample under high vacuum for 24 h at 120°C . For collecting the fluorescence emission spectra, a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer was used. For the fluorescence emission experiments, the excitation and emission wavelengths were 328 and 426 nm, respectively.

5.2.2 Synthesis and Activation of the MOF Material

Synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC-B}(\text{OH})_2)_6]\cdot 13.0\text{H}_2\text{O}\cdot 3.5\text{DMA}$ (Zr-UiO-66-B(OH)₂, 5)

For the synthesis of Zr-UiO-66-B(OH)₂, we have followed a similar procedure as reported by Biswas et al. for the preparation of various functionalized Zr-UiO-66-X (X = -F, Cl, -Br, -CH₃, -NO₂, -NH₂, -OH, -CO₂H, -SO₃H, etc.) compounds.⁴⁴ The heating of a mixture consisting of ZrOCl₂·8H₂O (50 mg, 0.15 mmol), H₂BDC-B(OH)₂ ligand (33 mg, 0.15 mmol), formic acid (0.6 mL, 3.18 mmol) and DMA (3 mL) was carried out inside a sealed Pyrex tube (10 mL). The heating was conducted by a dry block heater at 150 °C for 24 h. After that the tube was cooled down to room temperature. The resulting precipitate was filtered off by vacuum filtration technique. It was washed several times with acetone and then dried in an air oven at 80 °C for 6 h. Yield: 26 mg (0.01 mmol, 41%). Elemental analysis calculated for C₆₂H_{91.5}B₆Zr₆N_{3.5}O_{60.5} (2458.40 g mol⁻¹): C 30.24, H 3.74, N 2.00%. Found: C 22.92, H 3.18, N 1.98%. FT-IR (KBr, cm⁻¹): 3414 (br), 1701 (sh), 1583 (vs), 1472 (m), 1388 (vs), 1282 (w), 1259 (w), 1163 (w), 1029 (m), 917 (w), 867 (w), 823 (m), 760 (s), 721 (w), 666 (s), 548 (m), 492 (m).

Activation of the MOF Material

To get the guest-free material, the as-synthesized material (150 mg) was first stirred in methanol (25 mL) for 24 h at ambient temperature. The methanol molecules were removed from the pores by heating the filtered material under high vacuum at 120 °C for 16 h.

5.2.3 Fluorescence Sensing Experiments

The excitation wavelength for all the fluorescence titration experiments was 328 nm. We have collected the fluorescence emission spectra in range of 350-600 nm. Initially, the concentration-dependent fluorescence sensing investigations were accomplished by the stepwise addition (30 µL in each step) of 10 mM aqueous solutions of different ROS to the suspension of **5'** (2 mL) in 10 mM HEPES buffer inside a quartz cuvette. It was found that the fluorescence intensity of **7'** increased upon the gradual addition of H₂O₂ solution and became saturated after the addition of 240 µL of H₂O₂ solution. Afterwards, time-dependent fluorescence sensing studies were carried out after the addition of 240 µL of H₂O₂ solution to the HEPES suspension of **5'** until the saturation in the fluorescence

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intensity was obtained. For evaluating the selectivity of **5'** in presence of other ROS, initially 240 μL of the competing ROS solution was added to the suspension of **5'** in HEPES buffer and then 240 μL of H_2O_2 solution was added to this mixture. The fluorescence spectrum of the resulting mixture was recorded subsequently.

5.2.4 Preparation of 10 mM ROS Solutions

The aqueous solutions (concentration: 10 mM) of various ROS (ClO^- , $\text{O}_2^{\bullet-}$, $^t\text{BuO}^\bullet$, $\text{HO}^\bullet$, TBHP, $^1\text{O}_2$ and H_2O_2) were prepared by following the earlier reported methods.^{22, 45, 46}

Safety note! All ROS are highly oxidizing and they should be handled cautiously.

5.2.5 Preparation of 10 mM HEPES Buffer (pH = 7.4)

In a volumetric flask, HEPES (1.191 g) was placed and 50 mL Milli-Q water was added. After that 0.5 (M) NaOH solution was added drop wise until the pH of the solution becomes 7.4. Finally, the required amount of Milli-Q water was added so that the total volume of the solution turns out to be 250 mL.

5.2.6 Preparation of the Suspension of **5'** in 10 mM HEPES Buffer (pH = 7.4)

Initially, 12.5 mg of **5'** was kept in a 100 mL volumetric flask. Then, 50 mL of 10 mM HEPES buffer having a pH of 7.4 was added. After that the mixture was sonicated for 30 min. In this way, a homogenous suspension was obtained, which was used for the fluorescence sensing measurements.

5.2.7 Cell Viability Assay

The effect of probe **5'** on cell viability was performed using the method reported earlier.⁴⁷ Cells were seeded at 20,000 per well in a 96 well plate in 200 μL complete media. Cells were treated with different concentrations (0-100 μM) of probe for 48 h in triplicate at 37 $^\circ\text{C}$. Post treatment, cells were observed for morphological changes due to toxicity and images were captured using Cytell imaging system (GE healthcare). Finally, MTT assay was performed to measure the cellular viability. The viability of the untreated cells was considered as 100% and used to express the viability of treated cells.

5.2.8 Cell Culture and Imaging Experiments

The MDAMB-231 cells were cultured in DMEM F12 media containing 10% FBS and 1% antibiotic cocktail as described formerly.⁴⁷ The cells were seeded at a density of 25000/well in 96-well plates. The cells were loaded with probe **5'** (5 μ M) for 12 h in serum-containing media. The cells were washed with phosphate-buffered saline (PBS) three times to remove the excess probe and then treated with H₂O₂ (1 μ M) for 5 min to develop oxidative stress induced ROS generation inside cells in PBS medium. The cells were observed in bright field and in blue channel ($\lambda_{\text{ex}} = 381$ nm, $\lambda_{\text{em}} = 435$ nm) using Cytell cell imaging system (GE Healthcare) and images were captured from randomly selected five fields.

5.3 Results and Discussion

5.3.1 Structure Description

The compound **5** was synthesized by the solvothermal reaction between ZrOCl₂·8H₂O and BDC-B(OH)₂ ligand in DMA. The field-emission scanning electron microscopy (FE-SEM) images of as-synthesized **5** show the formation of homogeneous crystalline nano-sized particles (Figure 5.1).

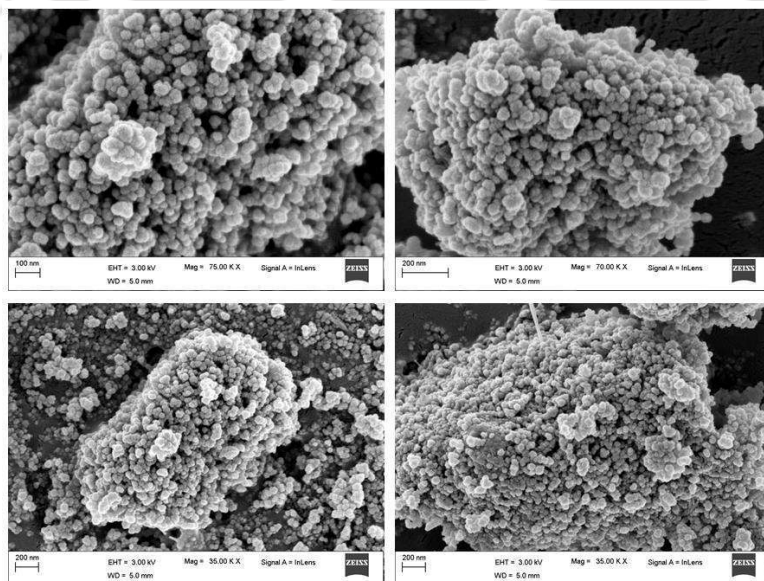


Figure 5.1 FE-SEM images of **5'**.

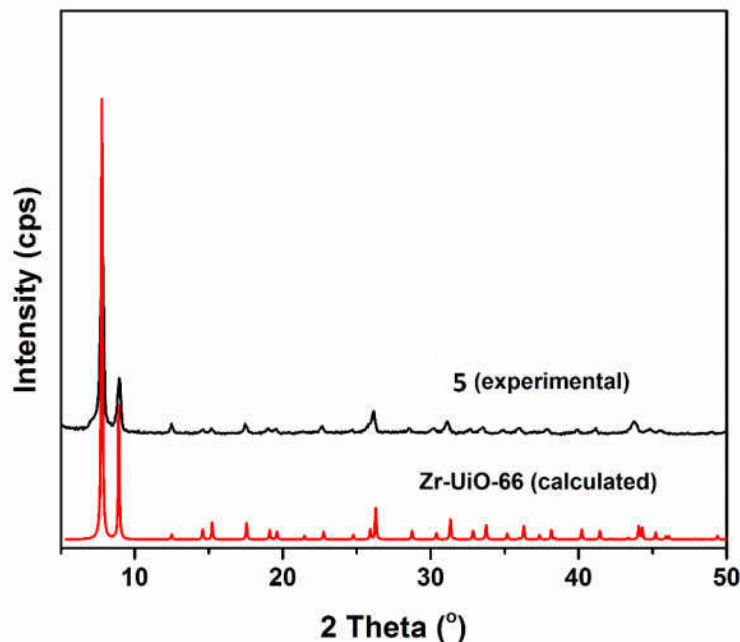


Figure 5.2 Comparison between the experimental XRPD pattern of **5** and calculated XRPD pattern of Zr-UiO-66.

In order to verify the crystal structure of the presented MOF compound, XRPD measurements were conducted. It can be seen from Figure 5.2 that there exists remarkable similarity between the calculated XRPD pattern of Zr-UiO-66 and the observed XRPD pattern of as-synthesized Zr-UiO-66-B(OH)₂ (**5**). Hence, we can conclude that compound **5** has the similar cubic 3D framework structure as the pristine Zr-UiO-66 compound. Like Zr-UiO-66, the title compound possesses smaller tetrahedral and larger octahedral cavities. Unlike un-functionalized UiO-66, the boronic acid functional groups ligands are located in the backbone of the framework structure of compound **5**. Being directed towards the cavities, these functional groups are accessible to externally added analytes in liquid phase.

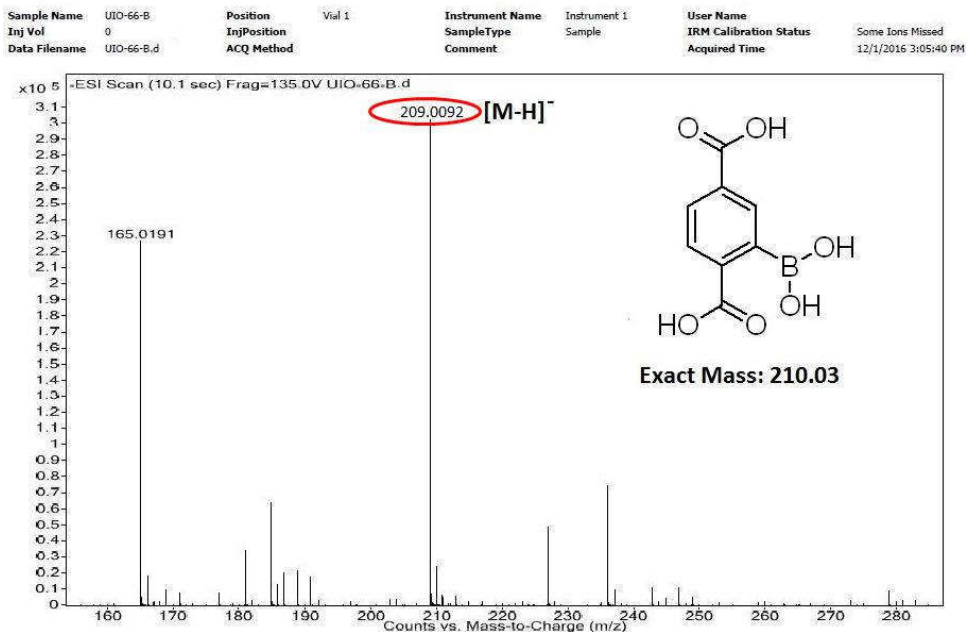


Figure 5.3 ESI-MS spectrum of **5'** after digestion in methanol/HF.

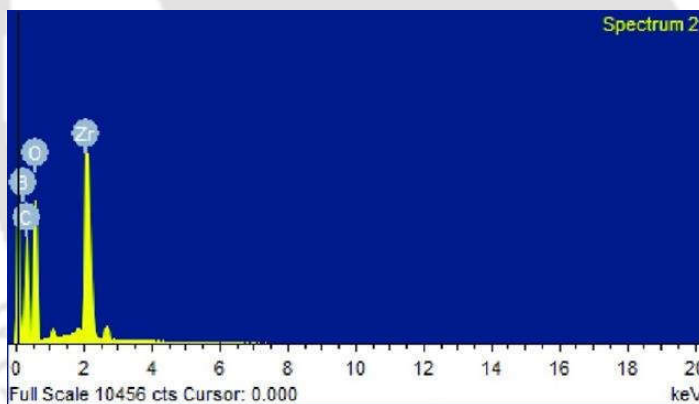


Figure 5.4 EDX spectrum of **5'**.

The C-B bond has low polarity and it can be easily cleaved because of its low bond dissociation energy. To verify the fact that the -B(OH)_2 groups remain attached with the BDC- B(OH)_2 ligand during the synthesis and activation processes, mass spectrometry was performed with material **5'**. In the mass spectrum of **5'** (Figure 5.3) after digestion in HF/MeOH, the signal at $m/z = 209.0092$ corresponds to the $[\text{M-H}]^-$ (M = mass of $\text{H}_2\text{BDC-B(OH)}_2$ ligand) ion. Furthermore, the EDX spectrum of **5'** (Figure 5.4) disclosed that the material contains B atom, which can be assigned to the B atom of the boronic acid

group. These results suggest that the boronic acid group remains intact with the BDC-B(OH)₂ ligand during the preparation and activation of the MOF material.

5.3.2 FT-IR Spectroscopy

As revealed from (Figure 5.5), the FT-IR spectra of both **5** and **5'** consist of very strong absorption peaks at 1590 and 1395 cm⁻¹. These peaks arise from the asymmetric and symmetric carboxylate stretching vibrations of the framework BDC-B(OH)₂ ligands, respectively.^{38, 48-50} A strong absorption peak at ca. 1655 cm⁻¹ is observed in the IR spectrum of as-synthesized **5**. This peak occurs because of the carbonyl stretching vibration of the occluded DMA molecules. Since this peak is absent in the IR spectrum of activated **5'**, it can be concluded that the guest DMA molecules have been completely removed from the cavities of **5**. The FT-IR spectra result of both **5** and **5'** was similar to the reported literature.⁵¹ We could guess that **5'** was in complete activation form.

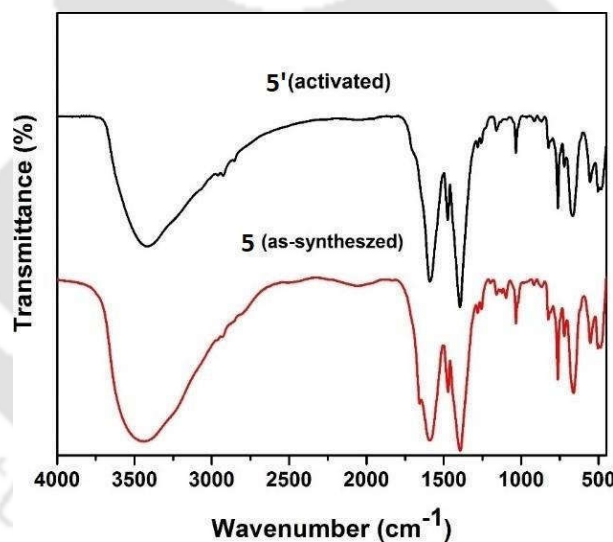


Figure 5.5 FT-IR spectra of as-synthesized **5** (red) and activated **5'** (black).

5.3.3 Thermal and Chemical Stability

As revealed from the thermogravimetric (TG) analysis (Figure 5.6), the compound is stable up to 270 °C under air atmosphere. The TG curve of as-synthesized **5** shows the first weight loss of 9.0 wt% in the range of 30-140 °C, which corresponds to the elimination of 13 H₂O molecules per formula unit (calcd: 9.4 wt%). In the range of 140-

220 °C, the second weight loss of 12.3 wt% occurs, which can be assigned to the removal of 3.5 DMA molecules per formula unit (calcd: 11.9%). The third, steep weight loss step can be accounted for the elimination of BDC-B(OH)₂ ligand molecules from the structural framework. Thus, at 270 °C, the structural decomposition of the material starts to occur.

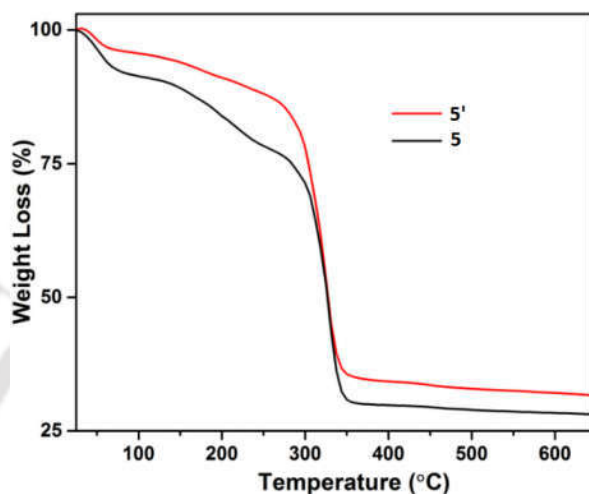


Figure 5.6 TG curve of as-synthesized (red) and activated (black) of **5'** measured under air atmosphere with a heating rate of 5 °C min⁻¹.

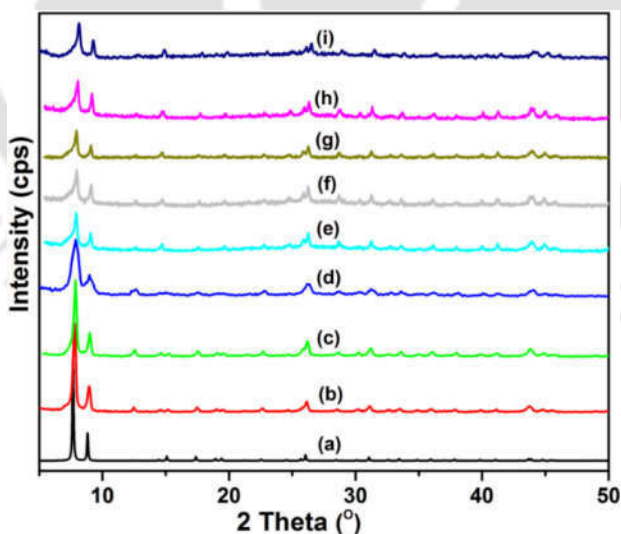


Figure 5.7 XRPD patterns of **5'** in different forms: calculated (a); as-synthesized (b); activated (c); after BET measurement (d); after treatment with water (e); after H₂O₂ sensing experiment (in 10 mM HEPES buffer at pH = 7.4) (f); after treatment with 1(M) HCl (g); after treatment with acetic acid (h); after treatment with NaOH at pH = 10 (i).

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The activated compound was stirred in different liquids (acetic acid, water, 10 mM HEPES buffer at pH = 7.4, NaOH at pH = 10 and 1(M) HCl) for 12 h to verify its chemical stability. After stirring, the XRPD patterns of the filtered materials were recorded. It can be concluded from the XRPD patterns (Figure 5.7) that the exposure of the activated compound in all the above-mentioned liquids does not considerably affect its structural integrity. Hence, the Zr-UiO-66-B(OH)₂ material exhibits high structural robustness, which is in agreement with other functionalized Zr-UiO-66-X compounds.^{44, 52, 53}

5.3.4 Surface Area Analysis

The specific BET surface area of the thermally activated compound was determined by performing N₂ sorption experiments at -196 °C. The N₂ adsorption isotherm (Figure 5.8) revealed that the BET surface area of **5'** is 751 m²g⁻¹. As expected, the BET surface area of **5'** is lower than the pristine⁵⁴ Zr-UiO-66 compound, but it is comparable with other existing functionalized^{44, 53, 55} Zr-UiO-66-X (X = -F, -Cl, -Br, -CH₃, -NO₂, -NH₂, -OH, -CO₂H, -SO₃H, etc.) compounds.

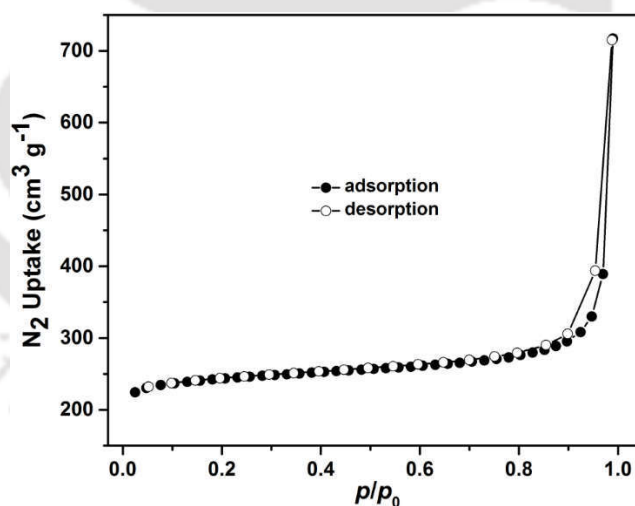


Figure 5.8 N₂ adsorption (filled circles) and desorption (empty circles) isotherms of **5'** measured at -196 °C.

5.3.5 Selective Sensing of H₂O₂ in HEPES Buffer

The Zr-UiO-66-B(OH)₂ compound containing boronic acid groups in its framework structure is weakly fluorescent. After the chemoselective reaction of UiO-66-B(OH)₂ with

H₂O₂, the –B(OH)₂ group attached with the BDC-B(OH)₂ ligand is converted to the –OH group. In this way, the Zr-UiO-66-OH compound is produced, which shows strong fluorescence. Thus, the Zr-UiO-66-B(OH)₂ material is expected to show fluorescence turn-on phenomenon in presence of H₂O₂ solution.^{18, 56}

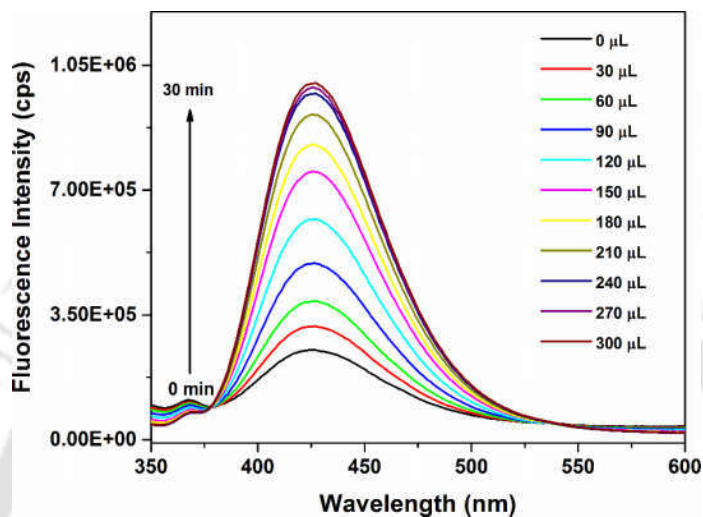


Figure 5.9 Fluorescence turn-on response of **5'** (suspended in 10 mM HEPES buffer, pH = 7.4) upon the stepwise addition of 10 mM H₂O₂ solution at room temperature. The spectra were collected after 3 min of each addition ($\lambda_{\text{ex}} = 328 \text{ nm}$ and $\lambda_{\text{em}} = 426 \text{ nm}$).

Before the H₂O₂ sensing studies, a suspension of **5'** in 10 mM HEPES buffer solution as well as 10 mM aqueous solutions of various ROS and other biologically interfering species (e.g., F[–], glucose, fructose, galactose, xylose and mannose) were prepared. The following ROS were chosen: hypochlorite anion (ClO[–]), superoxide anion (O₂^{•–}), *tert*-butoxy radical (^tBuO[•]), hydroxyl radical (HO[•]), *tert*-butyl hydroperoxide (TBHP), singlet oxygen (¹O₂) and hydrogen peroxide (H₂O₂). To the suspension of **5'** in HEPES buffer, solutions of different ROS and other biologically interfering species were incrementally added. After the addition of various solutions of competing analytes, the fluorescence spectra were collected. It can be seen from Figures 5.9 and 5.10 that the gradual addition of H₂O₂ solution caused dramatic increase in the fluorescence intensity of the MOF compound. There was ~89% increment (4-fold) in the fluorescence intensity of **5'** upon the addition of 240 μL of 10 mM H₂O₂ solution. The subsequent addition of H₂O₂ solution resulted in saturation in the fluorescence intensity of **5'**. The enhancement in the fluorescence intensity of the compound in presence of the other competing analytes (Figure 5.10) was

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very low. From these results, it becomes evident that the MOF material is highly selective for the fluorescence sensing of H_2O_2 over other competing analytes.

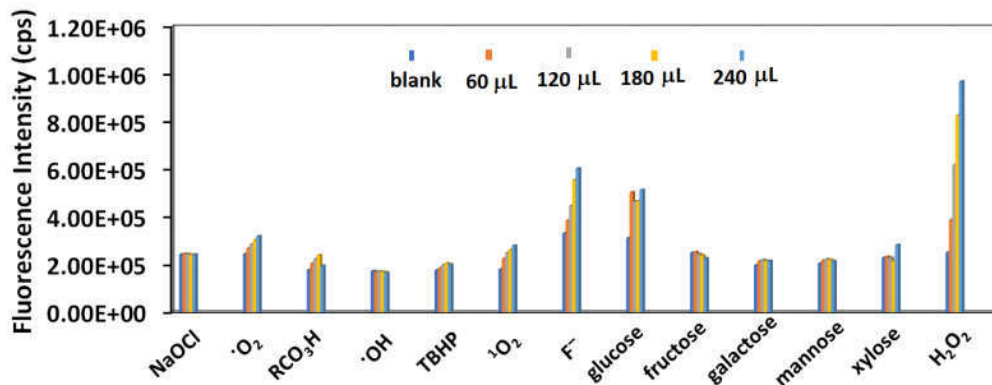


Figure 5.10 Fluorescence responses of **5'** (suspended in 10 mM HEPES buffer, pH = 7.4) upon the addition of solutions of various ROS (10 mM of ClO^- , $\text{O}_2^{\bullet-}$, $^t\text{BuO}^\bullet$, $\text{HO}^\bullet$, TBHP, $^1\text{O}_2$ and H_2O_2) and other biologically relevant species (10 mM of F^- , glucose, fructose, galactose, xylose and mannose) at room temperature. The bars denote fluorescence intensity after the addition of blank, 60, 120, 180 and 240 μL of each ROS. The spectra were collected after 6 min of each addition ($\lambda_{\text{ex}} = 328 \text{ nm}$ and $\lambda_{\text{em}} = 426 \text{ nm}$).

In order to determine the response time for the sensing of H_2O_2 by **5'**, a time-dependent fluorescence study was conducted. In this experiment, 240 μL of 10 mM H_2O_2 was added to the suspension of the Zr-UiO-66-B(OH)_2 compound in HEPES buffer medium. Subsequently, the fluorescence intensity of the probe was monitored at a regular time interval of 1 min. It was found that the fluorescence intensity of the material reached a fixed value (saturation point) after 25 min of the addition of 240 μL of 10 mM H_2O_2 solution (Figures 5.11 and 5.12). Thus, the fluorescent probe exhibited a response time of 25 min for H_2O_2 sensing under the presented experimental conditions.

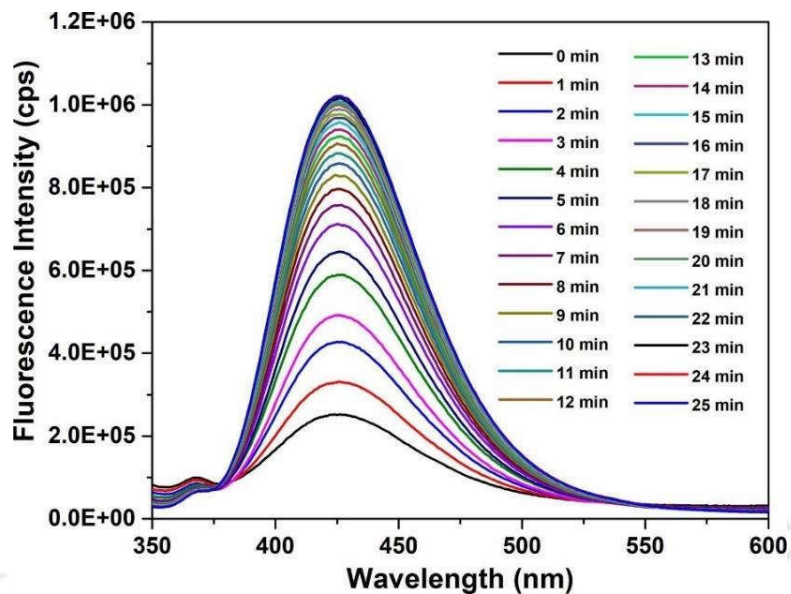


Figure 5.11 Change in the fluorescence spectrum of 5' in presence of 10 mM H₂O₂ as a function of time ($\lambda_{\text{ex}} = 328$ nm and $\lambda_{\text{em}} = 426$ nm).

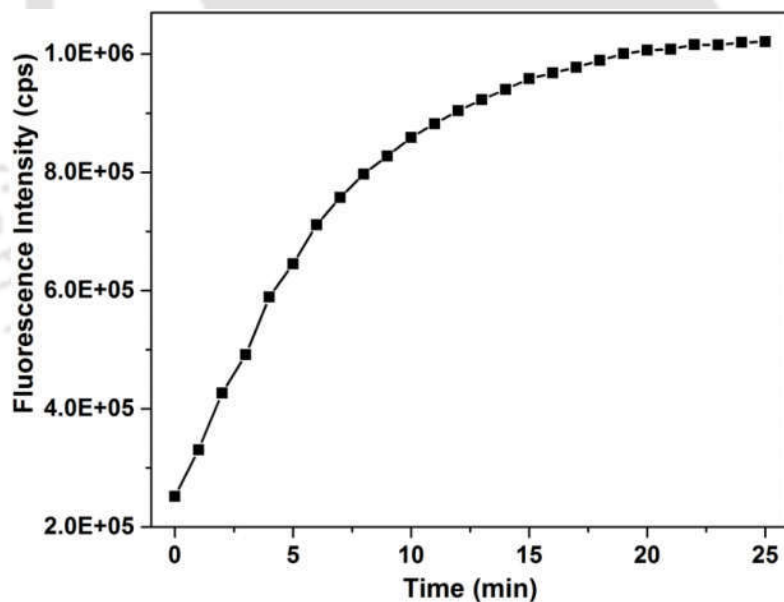


Figure 7.12 Change in the fluorescence intensity of 5' in presence of 10 mM H₂O₂ as a function of time ($\lambda_{\text{ex}} = 328$ nm and $\lambda_{\text{em}} = 426$ nm).

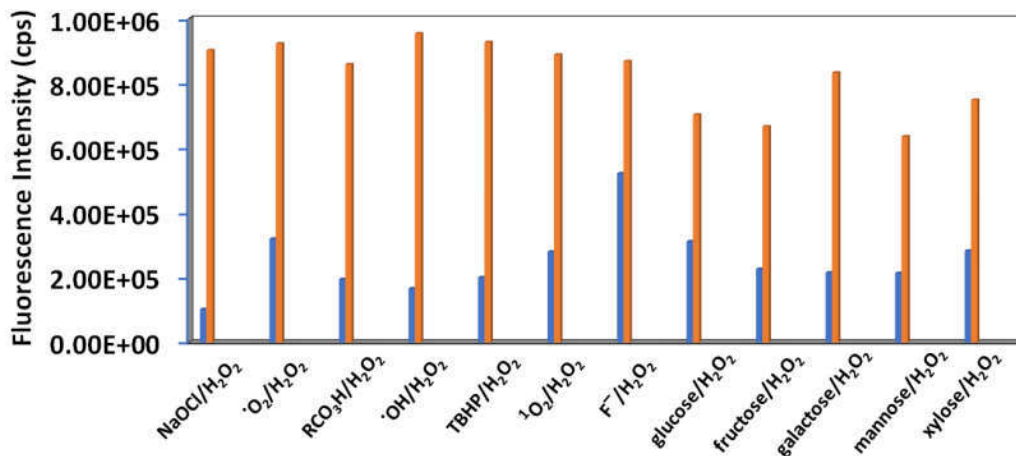


Figure 5.13 Fluorescence responses of **5'** (suspended in 10 mM HEPES buffer, pH = 7.4) upon the addition of H₂O₂ solution (240 μ L, 10 mM) in the presence of interfering ROS (240 μ L, 10 mM) and other biologically relevant species (240 μ L, 10 mM) at room temperature. The spectra were collected after 30 min of each analyte addition. The final concentration of each analyte in the solution was 9.67×10^{-4} M ($\lambda_{\text{ex}} = 328$ nm and $\lambda_{\text{em}} = 426$ nm).

For the practical sensing of H₂O₂ in complicated biological systems, it is highly required that the probe retains its selectivity in the existence of interfering ROS and other biologically relevant species (e.g. F⁻, glucose, fructose, galactose, xylose and mannose). Hence, the selectivity of the Zr-UiO-66-B(OH)₂ probe was assessed towards H₂O₂ even in the presence of interfering ROS and other biologically relevant species. In order to realize this purpose, initially a solution (240 μ L, 10 mM) of the competing analyte was added to the suspension of the compound in HEPES buffer medium and then the solution of H₂O₂ (240 μ L, 10 mM) was added to it. As displayed in Figure 5.13, there was drastic enhancement in the fluorescence intensity of the Zr-UiO-66-B(OH)₂ probe after the addition of H₂O₂ solution, even in the presence of other interfering analytes. Therefore, the material can selectively detect H₂O₂ in the co-existence of other intrusive analytes.

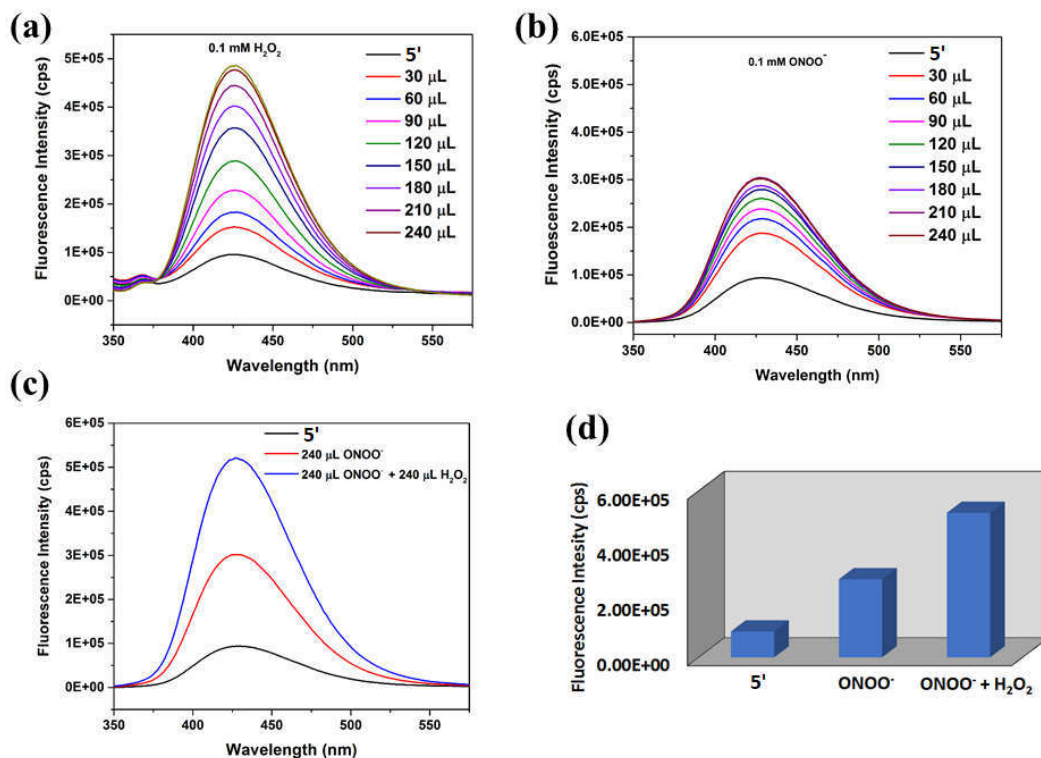


Figure 5.14 (a) Fluorescence turn-on response of **5'** (suspended in 10 mM HEPES buffer, pH = 7.4) upon the stepwise addition of 0.1 mM H_2O_2 solution at room temperature ($\lambda_{\text{ex}} = 328$ nm and $\lambda_{\text{em}} = 426$ nm). (b) Fluorescence turn-on response of **5'** (suspended in 10 mM HEPES buffer, pH = 7.4) upon the stepwise addition of 0.1 mM ONOO^- solution at room temperature ($\lambda_{\text{ex}} = 328$ nm and $\lambda_{\text{em}} = 426$ nm). (c) Fluorescence response of **5'** towards 0.1 mM H_2O_2 in presence of 0.1 mM ONOO^- ($\lambda_{\text{ex}} = 328$ nm and $\lambda_{\text{em}} = 426$ nm). (d) Bar representation of fluorescence response of **5'** towards 0.1 mM H_2O_2 in presence of 0.1 mM ONOO^- ($\lambda_{\text{ex}} = 328$ nm and $\lambda_{\text{em}} = 426$ nm).

It should be noted that probe **5'** also showed selective sensing properties for peroxynitrite (ONOO^-) at 10 mM concentration. However, ONOO^- ion belongs to the RNS (RNS = reactive nitrogen species) family. The present paper focuses on the sensing behavior of **5'** for only the ROS family.

We also investigated the selectivity of H_2O_2 over peroxynitrite at very low concentration (0.1 mM; Figures 5.14a-5.14b). At this lower concentration (0.1 mM, Figures 5.14c-5.14d), good selectivity for H_2O_2 over peroxynitrite was achieved in comparison to the poor selectivity obtained at relatively higher concentration (10 mM, Figure 5.15).

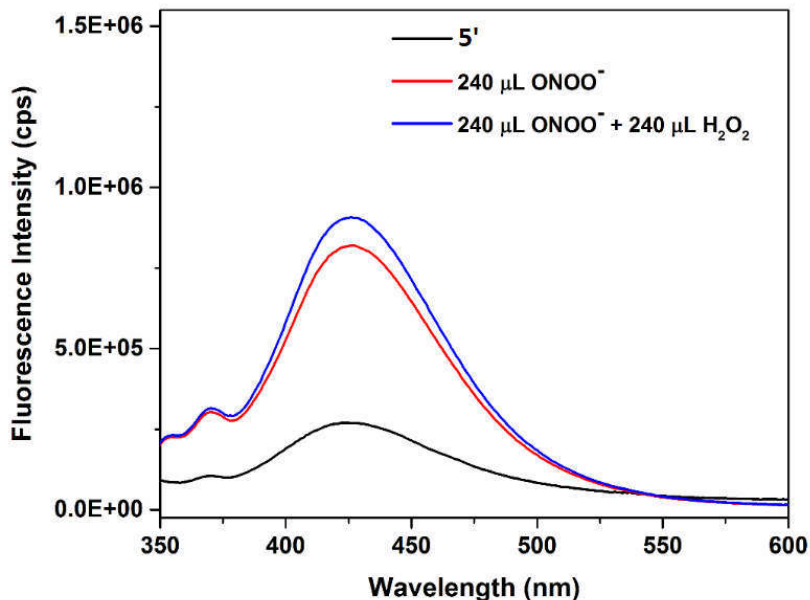


Figure 5.15 Fluorescence response of **5'** towards 10 mM H₂O₂ in presence of 10 mM ONOO⁻ (λ_{ex} = 328 nm and λ_{em} = 426 nm).

In addition to its high selectivity, the Zr-UiO-66-B(OH)₂ probe featured excellent sensitivity for H₂O₂. The limit for detection (LOD) was calculated by using the given formula and carried out similar experiments as described by us in several reports for fluorescence-based sensing of various species by different MOF probes.^{50, 52, 57} It has been found that the LOD value for the detection of H₂O₂ by compound **5'** corresponds to 0.015 μM. This LOD value is significantly lower than those of other MOF materials which have been reported so far for the detection of H₂O₂ by utilizing various other detection procedures (Table 5.1).

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Table 5.1 Comparison of the limit of detection (LOD) values for the H₂O₂ sensing by the MOF materials reported till date using different analytical methods.

Sl. No.	Compounds	Limit of Detection (LOD) (μM)	Analytical Methods	References
1.	hemin@HKUST-1	2.0	chemiluminescence	58
2.	AP-Ni-MOF	0.9	electrochemistry	59
3.	Co/DOBDC	0.5	electrochemistry	60
4.	Cu-MOF	1.0	electrochemistry	61
5.	Co-MOF	3.76	electrochemistry	62
6.	Fe-MIL-53	0.075	electrochemistry	63
7.	Fe-MIL-88	0.562	colorimetry	64
8.	Zr-UiO-66-B(OH) ₂	0.015	fluorescence	this work

5.3.6 Sensing of H₂O₂ in Living Cells

The high selectivity and sensitivity of the Zr-UiO-66-B(OH)₂ probe for H₂O₂ in 10 mM HEPES buffer medium at pH = 7.4 inspired us to evaluate its ability to detect H₂O₂ in MDAMB-231 cells with the help of fluorescence microscopy. Before imaging of H₂O₂ in living cells, cellular cytotoxicity of **5'** towards MDAMB-231 cells was evaluated. The cells were treated with different concentrations (0-100 μM) of probe at 37 °C for 48 h. After treatment for 48 h, the cells were observed under microscope to examine if any morphological change occurred due to the presence of the probe (Figure 5.16a). The cells exhibited ~70% viability in presence of probe **5'** after 48 h of incubation (Figure 5.16b). The results of the cell viability assay suggested that probe **5'** is applicable for the imaging of H₂O₂ in living cells.

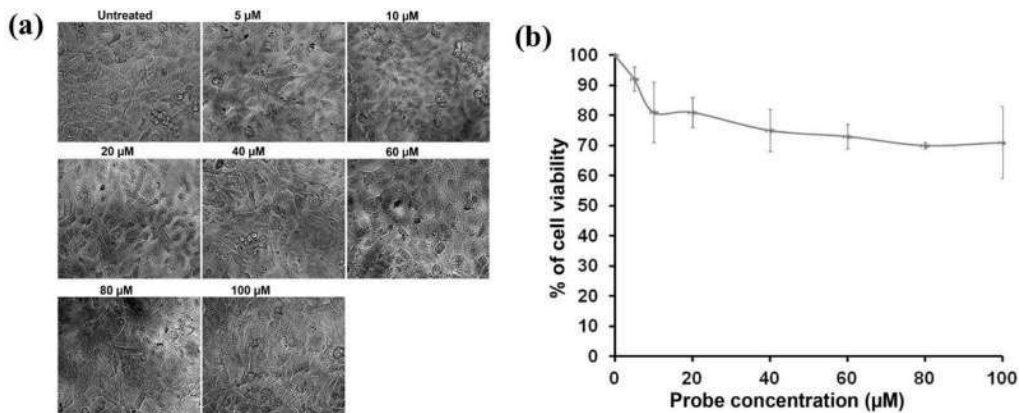


Figure 5.16 (a) Morphological analysis of untreated cells and the cells treated with various concentrations of **5'**. (b) Cell viability assay for **5'**-treated MDAMB-231 cells.

As evident from bright field imaging (Figures 5.17a, 5.17d, 5.17g; Phase Panel), the fluorescent probe **5'** (5 μ M) did not affect the cellular viability. Moreover, it did not cause any morphological change to the mammalian cells. These cells did not exhibit any background fluorescence signal in the blue channel (Figures 5.17b, 5.17e; Fluorescence Panel). The probe-loaded cells were treated with 1 μ M H_2O_2 (in PBS buffer) for 5 min to induce intracellular ROS. Interestingly, the probe responded to the change in the ROS level and gave intense blue fluorescence (Figure 5.17h, Fluorescence Panel). A superposition of the cellular images in bright field and fluorescence channel (Figures 5.17c, 5.17f, 5.17i; Overlay Panel) indicates that the fluorescence signal is more intense on the periphery of the cells and it can be ascribed to the oxidative damage to the membrane proteins. However, the fluorescence is indeed associated with the cells and coming from probe present inside the cells.

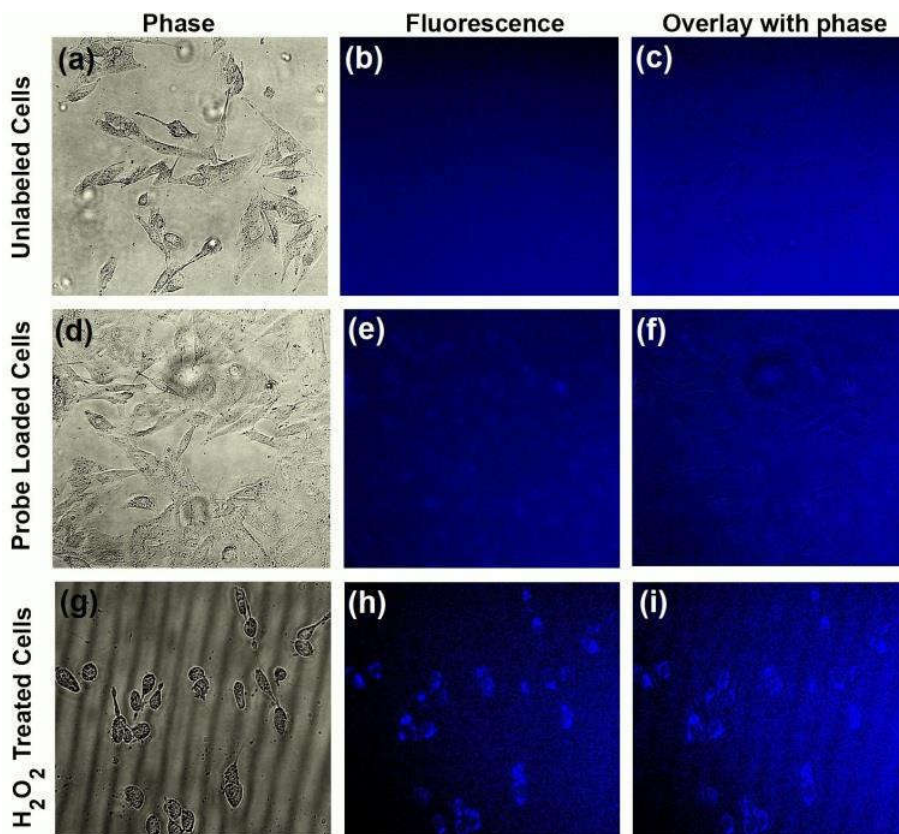
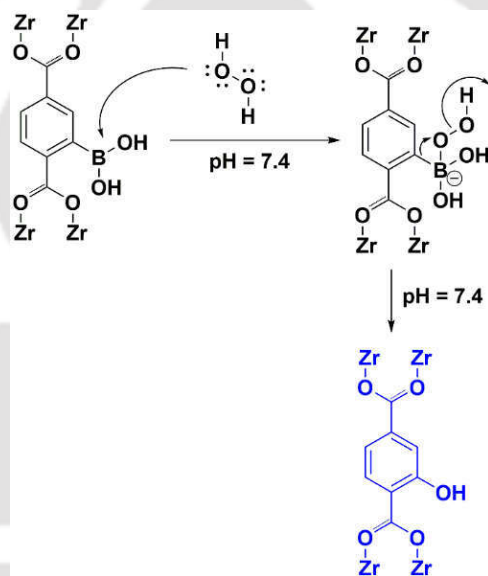


Figure 5.17 Detection of H_2O_2 inside the MDAMB-231 cells loaded with probe **5'**. The panel (a-c) is the unlabeled cells, (d-f) denotes probe-loaded cells and (g-i) represents probe-loaded cells treated with H_2O_2 . The cells either remained unloaded (a-c) or probe ($5\ \mu\text{M}$) loaded cells either remained untreated (d-f) or treated (g-i) with H_2O_2 ($1\ \mu\text{M}$) for 5 min at $37\ ^\circ\text{C}$. The H_2O_2 -treated cells showed bright blue fluorescence as compared to the probe-loaded cells. An overlay of bright field and fluorescence images indicates that the fluorescence is arising from the cell.

5.3.7 Mechanism for the Sensing of H_2O_2

Material **5'** showed remarkable increase in fluorescence intensity in presence of H_2O_2 , whereas the addition of other ROS resulted in negligible enhancement in the fluorescence intensity of the compound (Figure 5.9). For the fluorescence-based sensing of H_2O_2 by small organic molecules, it has been proposed in the literature that the oxidative cleavage of attached boronic acid or boronate ester groups results in the formation of the corresponding hydroxyl-functional molecules showing strong fluorescence.¹⁹ Hence, for our probe, it can be hypothesized that the chemoselective oxidative cleavage in presence

of H_2O_2 leads to the formation of hydroxyl-functionalized ligand (BDC-OH) from the boronic acid functionalized ligand [BDC-B(OH) $_2$] in the structural framework of **5'** and this transformation is similar as the Baeyer-Villiger oxidation reaction^{65, 66} in the presence of H_2O_2 under basic conditions (Scheme 5.2). In case of other ROS, such chemoselective oxidative cleavage of the $-\text{B(OH)}_2$ group does not occur. It is worthy to mention that the structural robustness of material **5'** is preserved during the H_2O_2 sensing experiment in HEPES buffer medium. This fact has been verified by the XRPD measurements (Figure 5.7), in which the XRPD pattern of the material recovered after the H_2O_2 sensing experiment showed close similarity with the un-treated compound.



Scheme 5.2 Proposed mechanism for the fluorescence turn-on behaviour of **5'** in presence of H_2O_2 in 10 mM HEPES buffer at pH = 7.4.

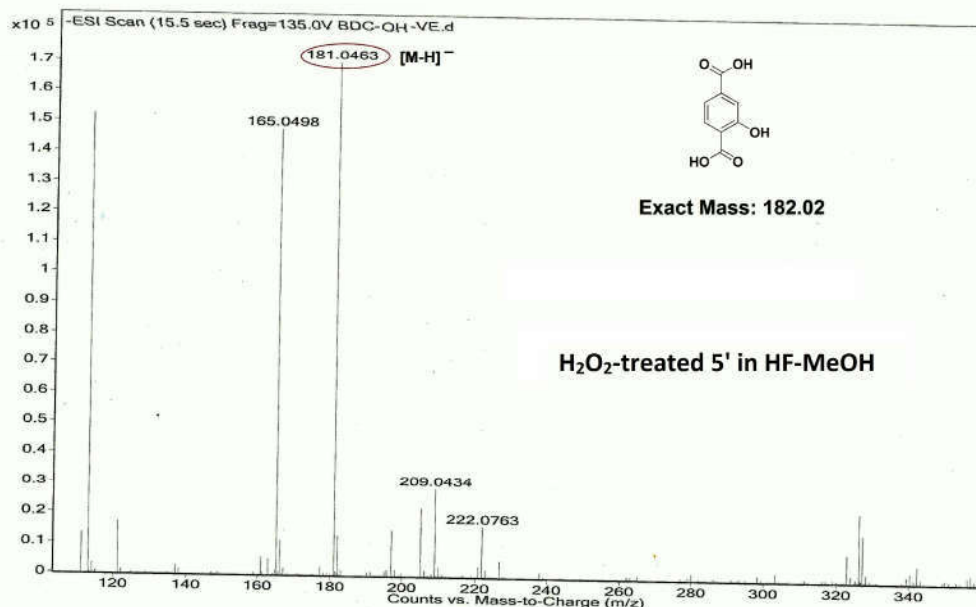


Figure 5.18 ESI-MS spectrum of H₂O₂-treated **5'** after digestion in HF/MeOH. The spectrum shows m/z peak at 181.0463, which corresponds to the $[M-H]^-$ ion (M = mass of H₂BDC-OH ligand).

The proposed mechanism for H₂O₂ sensing by **5'** was verified by ¹H NMR analysis and mass spectrometry. In the mass spectrum (Figure 5.18) of H₂O₂-treated **5'**, there was a peak at m/z = 181.0463, which can be associated with the $[M-H]^-$ ion (M = mass of the H₂BDC-OH ligand). As compared to the un-treated **5'**, the H₂O₂-treated sample of **5'** showed additional peaks at 7.42, 7.45 and 7.88 ppm in its ¹H NMR spectrum (Figure 5.19). These new peaks have emerged in addition to the aromatic signals of the H₂BDC-B(OH)₂ ligand. These additional signals can be assigned to the aromatic protons of the H₂BDC-OH ligand. From the integration of the ¹H NMR peaks, the conversion percentage of the BDC-B(OH)₂ ligand into BDC-OH ligand was found to be 73%. To further verify the sensing mechanism, we have performed EDX elemental mapping analysis with both un-treated and H₂O₂-treated **5'**. It can be observed from Figures 5.20a and 5.20b that the percentage of B atom in H₂O₂-treated **5'** is lower (Figure 5.20b) as compared to untreated **5'** (Figure 5.20a). This result is in accordance with the NMR analysis.

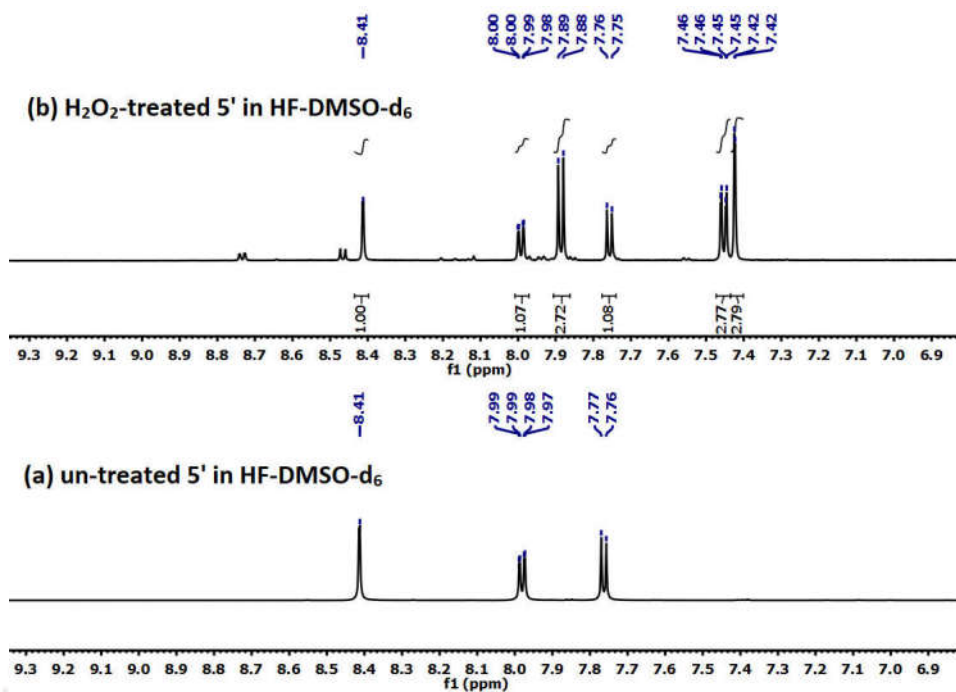


Figure 5.19 ^1H NMR spectra of (a) un-treated **5'** and (b) H_2O_2 -treated **5'** after digestion in HF/DMSO-d_6 . In the spectrum of H_2O_2 -treated **5'**, new peaks appear at 7.42, 7.45 and 7.88 ppm, which can be assigned to the aromatic protons of the $\text{H}_2\text{BDC-OH}$ ligand.

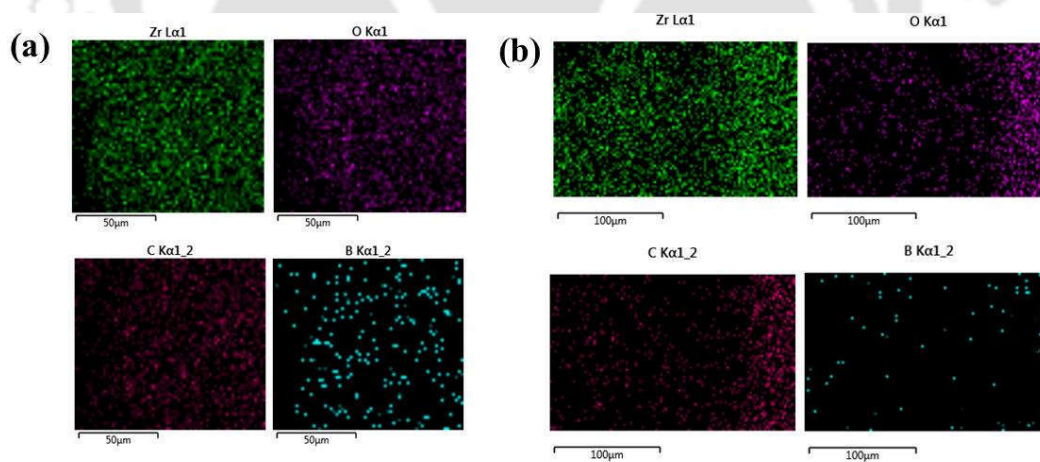


Figure 5.20 (a) EDX elemental mapping of untreated **5'**. (b) EDX elemental mapping of H_2O_2 -treated **5'**.

5.4 Conclusions

A new boronic acid functionalized Zr(IV) MOF namely Zr-UiO-66-B(OH)₂ (**5**) was synthesized under solvothermal conditions. Its activated form (**5'**) was utilized for the fluorometric detection of H₂O₂ in simulated physiological medium. The MOF material displayed high selectivity towards the detection of H₂O₂ over potentially intrusive ROS and other biologically relevant species in 10 mM HEPES buffer having a pH of 7.4. The probe exhibited outstanding sensitivity for H₂O₂ with a detection limit of 0.015 μM. This detection limit value is lower as compared to other MOF based H₂O₂ sensors employing other analytical techniques than fluorescence spectroscopy. The fluorescence increment properties of **5'** can be ascribed to the oxidative breaking of the –B(OH)₂ functional group into –OH functionality in presence of H₂O₂. In addition to its extraordinary selectivity and sensitivity, probe **5'** was effectively utilized for the bioimaging of H₂O₂ inside living cells.

5.5 References

1. T. Finkel, M. Serrano and M. A. Blasco, *Nature.*, 2007, **448**, 767-774.
2. B. Chance, H. Sies and A. Boveris, *Physiol. Rev.*, 1979, **59**, 527–605.
3. M. Giorgio, M. Trinei, E. Migliaccio and P. G. Pelicci, *Nat. Rev. Mol. Cell Biol.*, 2007, **8**, 722-728.
4. H. Ohshima, M. Tatemichi and T. Sawa, *Arch. Biochem. Biophys.*, 2003, **417**, 3-11.
5. R. Pop-Busui, A. Sima and M. Stevens, *Diabetes Metab. Res. Rev.*, 2006, **22**, 257-273.
6. A. M. Shah and K. M. Channon, *Heart.*, 2004, **90**, 486-487.
7. K. J. Barnham, C. L. Masters and A. I. Bush, *Nat. Rev. Drug Discovery.*, 2004, **3**, 205-214.
8. R. S. Balaban, S. Nemoto and T. Finkel, *Cell.*, 2005, **120**, 483–495.
9. K. B. Beckman and B. N. Ames, *Physiol. Rev.*, 1998, **78**, 547-581.
10. J. P. Fruehauf and J. F. L. Meyskens, *Clin. Cancer Res.*, 2007, **13**, 789-794.
11. M. P. Mattson, *Nature*, , 2004, **430**, 631-639.
12. M. T. Lin and M. F. Beal, *Nature.*, 2006, **443**, 787-795.
13. N. Houstis, E. D. Rosen and E. S. Lander, *Nature.*, 2006, **440**, 944-948.

Chapter 5

14. D. Jay, H. Hitomi and K. K. Griendling, *Free Radicals Biol. Med.*, 2006, **40**, 183-192.
15. B. Balasubramanian, W. K. Pogozeidki and T. D. Tullius, *Proc. Natl. Acad. Sci. USA.*, 1998, **95**, 9738-9743.
16. A. Sakai, M. Nakanishi, K. Yoshiyama and H. Maki, *Genes Cells.*, 2006, **11**, 767-778.
17. Y. Wang, *Chem. Res. Toxicol.*, 2008, **20**, 276-281.
18. V. Carroll, B. W. Michel, J. Blecha, H. VanBrocklin, K. Keshari, D. Wilson and C. J. Chang, *J. Am. Chem. Soc.*, 2014, **136**, 14742-14745.
19. A. R. Lippert, G. C. V. D. Bittner and C. J. Chnag, *Acc. Chem. Res.*, 2011, **44**, 793-804.
20. K. Zhang, W. Wu, Y. Li, M. Sun, H. Yu and M. S. Wong, *RSC Adv.*, 2016, **6**, 115298-115302.
21. H. G. Kuivila and A. G. Armour, *J. Am. Chem. Soc.*, 1957, **79**, 5659-5662.
22. D. Srikun, E. W. Miller, D. W. Domaille and C. J. Chang, *J. Am. Chem. Soc.*, 2008, **130**, 4596-4597.
23. S. Keskin and S. Kızılel, *Ind. Eng. Chem. Res.*, 2011, **50**, 1799-1812.
24. P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Ferey, R. E. Morris and C. Serre, *chem. Rev.*, 2012, **112**, 1232-1268.
25. J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.
26. T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F. X. L. Xamena and J. Gascon, *Nat. Mater.*, 2015, **14**, 48-55.
27. W. Zhang and R. G. Xiong, *Chem. Rev.*, 2012, **112**, 1163-1195.
28. Y. Hu, M. Ding, X.-Q. Liu, L.-B. Sunb and H.-L. Jiang, *Chem. Commun.*, 2016, **52**, 5734-5737.
29. J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C. Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011-6061.
30. T. Zhang and W. Lin, *Chem. Soc. Rev.*, 2014, **43**, 5982-5993.
31. S. Rojas, F. J. Carmona, C. R. Maldonado, P. Horcajada, T. Hidalgo, C. Serre, J. A. R. Navarro and E. Barea, *Inorg. Chem.*, 2016, **55**, 2650-2663.
32. L. Li, S. Shen, R. Lin, Y. Bai and H. Liu, *Chem. Commun.*, 2017, **53**, 9986-9989
33. S. Bhattacharyya, A. Chakraborty, K. Jayaramulu, A. Hazraa and T. K. Maji, *Chem. Commun.*, 2014, **50**, 13567-13570.

Chapter 5

34. A. Buragohain, M. Yousufuddin, M. Sarma and S. Biswas, *Cryst. Growth Des.*, 2016, **16**, 842–851.
35. S. S. Nagarkar, A. V. Desai and S. K. Ghosh, *Chem. Commun.*, 2014, **50**, 8915–8918.
36. Z. Hao, X. Song, M. Zhu, X. Meng, S. Zhao, S. Su, W. Yang, S. Song and H. Zhang, *J. Mater. Chem. A*, 2013, **1**, 11043–11050.
37. W. Yan, C. Zhang, S. Chen, L. Han and H. Zheng, *ACS Appl. Mater. Interfaces*, 2017, **9**, 1629–1634.
38. S. Nandi, H. Reinsch, S. Banesh, N. Stock, V. Trivedi and S. Biswas, *Dalton Trans.*, 2017, **46**, 12856–12864.
39. A. V. Desai, P. Samanta, B. Manna and S. K. Ghosh, *Chem. Commun.*, 2015, **51**, 6111–6114.
40. Z.-R. Yang, M.-M. Wang, X.-S. Wang and X.-B. Yin, *Anal. Chem.*, 2017, **89**, 930–1936.
41. L. Yang, C. Xu, W. Ye and W. Liu, *Sens. Actuators, B.*, 2015, **215**, 489–496.
42. F. Luo, Y. Lin, L. Zheng, X. Lin and Y. Chi, *ACS Appl. Mater. Interfaces*, 2015, **7**, 11322–11329.
43. C. Gao, H. Zhu, J. Chen and H. Qiu, *Chin. Chem. Lett.*, 2017, **28**, 1006–1012.
44. S. Biswas and P. V. D. Voort, *Eur. J. Inorg. Chem.*, 2013, **2013**, 2154–2160.
45. M. Kim, S.-K. Ko, H. Kim, I. Shin and J. Tae, *Chem. Commun.*, 2013, **49**, 7959–7961.
46. L. Yuan, W. Lin and J. Song, *Chem. Commun.*, 2010, **46**, 7930–7932.
47. S. J. Deka, A. Roy, V. Ramakrishnan, D. Manna and V. Trivedi, *Chem Biol Drug Des.*, 2017, **89**, 953–963.
48. M. SK, M. Grzywa, D. Volkmer and S. Biswas, *Microporous Mesoporous Mater.*, 2017, **237**, 275–281.
49. R. Dalapati, B. Sakthivel, A. Dhakshinamoorthy and S. Biswas, *CrystEngComm*, 2017, **19**, 5915–5925.
50. A. Das and S. Biswas, *Sens. Actuators, B.*, 2017, **250**, 121–131.
51. M. SK, S. Bhowal and S. Biswas, *Eur. J. Inorg. Chem.*, 2015, **2015**, 3317–3322.
52. R. Dalapati, S. N. Balaji, V. Trivedi, L. Khamari and S. Biswas, *Sens. Actuators, B.*, 2017, **245**, 1039–1049.

53. S. Biswas, J. Zhang, Z. Li, Y.-Y. Liu, M. Grzywa, L. Sun, D. Volkmer and P. V. D. Voort, *Dalton Trans.*, 2013, **42**, 4730-4737
54. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850-13851.
55. M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, *Chem. Mater.*, 2010, **22**, 6632–6640.
56. V. S. Lin, B. C. Dickinson and C. J. Chang, *Meth. Enzymol.*, 2013, **526**, 19-43.
57. A. Buragohain and S. Biswas, *CrystEngComm*, 2016, **18**, 4374-4381
58. F. Luo, Y. Lin, L. Zheng, X. Lin and Y. Chi, *ACS Appl. Mater. Interfaces*, 2015, **7**, 11322–11329.
59. B. Sherino, S. Mohamada, S. N. H. Halima and N. S. A. Manan, *Sens. Actuators, B*, 2018, **254**, 1148–1156.
60. D. Zhang, J. Zhang, H. Shi, X. Guo, Y. Guo, R. Zhang and B. Yuan, *Sens. Actuators, B*, 2015, **221**, 224–229.
61. D. Zhang, J. Zhang, R. Zhang, H. Shi, Y. Guo, X. Guo, S. Li and B. Yuan, *Talanta*, 2015, **144**, 1176–1181.
62. L. Yang, C. Xu, W. Ye and W. Liu, *Sens. Actuators, B*, 2015, **215**, 489–496.
63. D. Cheng, X. Li, Y. Qiu, Q. Chen, J. Zhou, Y. Yang, Z. Xie, P. Liu, W. Cai and C. Zhang, *Anal. Methods*, 2017, **9**, 2082-2088
64. C. Gao, H. Zhu, J. Chen and H. Qiu, *Chin. Chim. Lett.*, 2017, **28**, 1006-1012.
65. A. J. Kotlewska, F. V. Rantwijk, R. A. Sheldon and I. W. C. E. Arends, *Green Chem.*, 2011, **13**, 2154–2160.
66. M. Uyanik and K. Ishihara, *ACS Catal.*, 2013, **3**, 513–520.



Conclusions

The work presented in this thesis demonstrates the synthesis of MOFs with various functionalized organic ligands which show a variety of framework structures. The MOF materials can be utilized for gas storage, gas separation and chemical sensing. Due to the lability of metal-ligand bonds, most of the reported MOFs are unstable in water. A water-stable MOF must be strong enough to defend the intrusion of water molecules in the framework. With careful understanding towards the stability MOF materials in aqueous system, here the MOF materials have been synthesized with high valent metal ions (such as Zr^{4+} , Hf^{4+} and Ce^{4+}) and polycarboxylate based organic ligands. High valent metal ions have been utilized for the construction of MOF materials for making the water-stable framework structures. The water-stable MOF materials have been applied here for the applications in selective gas storage, gas separation, chemical sensing and cell imaging. The functionalized organic ligands have been used here for the construction of functionalized MOF materials for the above-mentioned applications. The attached functional groups of ligands in the MOF frameworks can act as an active site for specific gas molecules (during gas adsorption) or analytes (during fluorescence sensing). Thus, the resulting MOFs enhance their selectivity towards the target gas molecule or analyte. Therefore, the functionalized MOFs can be applied for the selective separation of gas molecules from the gas mixtures. Furthermore, they can be utilized for the fluorogenic detection of targeted analyte in the presence of interfering analytes.

In Chapter 2, the facile synthesis, characterization and gas adsorption properties of two new Zr(IV) and Ce(IV) based MOF materials are presented. The Zr(IV) and Ce(IV)-based MOF materials were successfully synthesized under solvothermal conditions by using H_2CCA ligand in DMF (150 °C, 24 h for Zr(IV); 100 °C, 20 min for Ce(IV)). The crystallinity and phase purity of both materials were confirmed by the XRPD analysis. The XRPD experiments disclosed that both materials are structurally analogous to the DUT-52 framework material. TG analysis revealed that the Zr(IV) and Ce(IV)-based MOF materials are stable up to 390 and 300 °C in air atmosphere, respectively. The chemical stability of both materials was checked by the XRPD experiments. Both materials are moderately stable in water and methanol. However, they lose their crystallinities when exposed to 1M HCl. The N_2 sorption analysis with the Zr(IV) and Ce(IV)-based MOFs revealed that the specific BET surface areas are 870 and 1210 $\text{m}^2 \text{g}^{-1}$, respectively. The

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CO₂ uptake values of the Zr(IV) and Ce(IV)-based MOFs at 0 °C at 1 bar are 2.0 and 1.6 mmol g⁻¹, respectively.

The successful synthesis, complete characterization, thermal and chemical stability as well as fluorescence sensing properties of a new, highly luminescent, thiadiazole-functionalized Zr(IV)-based MOF material having UiO-68 framework topology is presented in Chapter 3. The material was synthesized by using a mixture of ZrCl₄, H₂BTDB ligand and trifluoroacetic acid in DMF under solvothermal conditions. As confirmed by the steady-state fluorescence titration experiments, the activated MOF material showed high selectivity towards 2,4,6-trinitrophenol (TNP). The selectivity towards TNP was also observed in the presence of other potentially interfering nitroaromatic explosives. The limit of detection of the activated material for TNP sensing was found to be 1.63×10^{-6} M, which is comparable with the previously reported MOF-based probes for TNP sensing. The recyclability experiments revealed that the MOF compound is highly photo-stable and reusable. Thus, it can be used for long-term in-field detection of nitroaromatic explosive compounds. Both energy and electron transfer mechanisms could be the cause for the highest fluorescence quenching efficiency of TNP. Moreover, the strong electrostatic interactions between the Lewis basic N-donor sites of the anchored BTDB ligand of the framework and the acidic –OH group of TNP might be ascribed for the high selectivity of TNP. Due to high sensitivity and selectivity towards TNP, the fluorescent MOF-based probe is a potential candidate for the real time detection of TNP.

The first boronic acid functionalized Hf-based UiO-66 MOF having the ability to detect both extracellular and intracellular peroxynitrite is presented in Chapter 4. The MOF material was synthesized under solvothermal conditions by using an equimolar mixture of HfCl₄ and H₂BDC-B(OH)₂ ligand in DMF in presence of formic acid. The XRPD experiments revealed that the MOF compound is isostructural with the Hf-UiO-66 framework. The activated compound was utilized as a fluorescent turn-on probe for the rapid sensing of extracellular peroxynitrite (ONOO⁻) under simulated biological conditions (10 mM HEPES buffer, pH = 7.4). Moreover, it selectively senses the peroxynitrite even in the presence of other reactive oxygen/nitrogen species (ROS/RNS). The oxidative cleavage of attached boronic acid groups forming corresponding hydroxy-functionalized ligands can be accounted for the fluorescent increment phenomenon in the

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presence of ONOO^- . The probe showed extraordinary sensitivity (detection limit = 9.0 nM) toward ONOO^- in 10 mM HEPES buffer at pH = 7.4. The probe-loaded cells did not display cytotoxicity and morphological deformities. It is remarkable that the probe inside the cells responded toward the peroxynitrite solution to give an intense blue fluorescent signal. The fluorescence microscopy investigation with J774A.1 macrophage cells clearly demonstrated that the MOF probe is suitable to image peroxynitrite in living cells.

In Chapter 5, a new boronic acid functionalized Zr(IV) MOF having the capability of sensing H_2O_2 in live cells is presented. The Zr-MOF bears UiO-66 structure. It was synthesized under solvothermal conditions by using a mixture of ZrCl_4 , $\text{H}_2\text{BDC-B(OH)}_2$ ligand and formic acid in DMA. The activated MOF material was employed for the fluorometric detection of H_2O_2 in 10 mM HEPES buffer at pH = 7.4. It showed high selectivity towards H_2O_2 even in the presence of interfering ROS and other biologically relevant analytes. The fluorescent probe was found to display extraordinary sensitivity for H_2O_2 (detection limit = 0.015 μM) in HEPES buffer, which represents a lower value in comparison to those of the MOF probes documented so far for sensing H_2O_2 using other analytical methods than fluorescence spectroscopy. The fluorescence increment properties of the probe can be ascribed to the oxidative cleavage of the $-\text{B(OH)}_2$ functional group into an $-\text{OH}$ functionality in the presence of H_2O_2 . Taking advantage of its high selectivity and sensitivity for H_2O_2 in HEPES buffer, the MOF probe was successfully applied for the imaging of intracellular H_2O_2 . Imaging studies with MDAMB-231 cells disclosed the emergence of bright blue fluorescence after loading with the MOF probe and subsequent treatment with H_2O_2 solution.

Conclusions



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Publications and Conference attended

List of Publications

- 1) **Mostakim SK**, Maciej Grzywa, Dirk Volkmer and Shyam Biswas,* “Gas sorption and transition-metal cation separation with a thienothiophene based zirconium metal–organic framework” *J. Solid State Chem.*, 2015, 232, 221-227.
- 2) **Mostakim SK**, Soumya Bhowal and Shyam Biswas,* “Synthesis, Characterization, Stability, and Gas Adsorption Characteristics of a Highly Stable Zirconium Mesaconate Framework Material” *Eur. J. Inorg. Chem.* 2015, 2015, 3317–3322.
- 3) **Mostakim SK** and Shyam Biswas,* “A thiadiazole-functionalized Zr(IV)-based metal–organic framework as a highly fluorescent probe for the selective detection of picric acid” *CrystEngComm*, 2016, 18, 3104–3113.
- 4) **Mostakim SK**, Maciej Grzywa, Dirk Volkmer and Shyam Biswas,* “Zr(IV) and Ce(IV)-based metal-organic frameworks incorporating 4-carboxycinnamic acid as ligand: Synthesis and properties” *Microporous Mesoporous Mater.* 2017, 237, 275-281.
- 5) **Mostakim SK**, Soutick Nandi, Rakesh Kumar Singh, Vishal Trivedi and Shyam Biswas,* “Selective Sensing of Peroxynitrite by Hf-Based UiO-66-B(OH)₂ Metal-Organic Framework: Applicability to Cell Imaging” *Inorg. Chem.* 2018, 57, 10128–10136.
- 6) **Mostakim SK**, Sooram Banesh, Vishal Trivedi and Shyam Biswas,* “Selective and Sensitive Sensing of Hydrogen Peroxide by a Boronic Acid Functionalized Metal-Organic Framework and its Application in Live-Cell Imaging” *Inorg. Chem.* 2018, 57, 14574–14581.

Publications and Conference attended

- 7) Aniruddha Das, Nagaraj Anbu, **Mostakim SK**, Amarajothi Dhakshinamoorthy* and Shyam Biswas,* “A Highly Active Urea Functionalized Zr(IV)-UiO-67 Metal-Organic Framework as Hydrogen Bonding Heterogeneous Catalyst for Friedel-Crafts Alkylation” *Inorg. Chem.* 2019, 58, 5163–5172.
- 8) **Mostakim SK**, Mohammed Rafi Uz Zama Khan, Aniruddha Das, Soutick Nandi, Vishal Trivedi and Shyam Biswas* “A phthalimide functionalized UiO-66 metal-organic framework for the fluorogenic detection of hydrazine in live-cells” *Dalton Trans.*, 2019, 48, 12615-12621
- 9) **Mostakim SK**, Soumitra Barman, Shounik Paul, Ratnadip De, Sreejith S. S., Helge Reinsch, Maciej Grzywa, Norbert Stock, Dirk Volkmer, Shyam Biswas* and Soumyajit Roy* “An Anthracene-Based Metal-Organic Framework for Selective Photo-Reduction of Carbon Dioxide to Formic Acid Coupled with Water Oxidation” *ACS Catalysis*. (Resubmitted, 2019).
- 10) Aniruddha Das, Nagaraj Anbu, **Mostakim SK**, Amarajothi Dhakshinamoorthy* and Shyam Biswas,* “A Functionalized UiO-66 MOF for Turn-On Fluorescent Sensing of Superoxide in Water and Efficient Catalysis of Knoevenagel Condensation” *Dalton Trans.*, 2019 (Submitted, 2019)

Publications and Conference attended

List of Conferences and Symposia Attended

- 1) Poster entitled “**Gas sorption and transition-metal cation separation with a thienothiophene presented based zirconium metal–organic framework**” was presented in the symposium *Chemconvene, 2015*, arranged at Indian Institute of Technology Guwahati.
- 2) Poster entitled “**Selective Turn-On Sensing of Gaseous SO₂ by the Redox Tuning of UiO-66-(OH)₂ Metal-Organic Framework**” was presented in the *International Conference on Advanced Nanomaterials and Nanotechnology, ICANN-2017*, Centre for Nanotechnology, Indian Institute of Technology Guwahati.
- 3) Poster entitled “**A thiadiazole-functionalized Zr (IV)-based metal–organic framework as a highly fluorescent probe for the selective detection of picric acid**” was presented in the *International Conference on Emerging Trends in Chemical Sciences, 2018*, arranged at Department of Chemistry, Dibrugarh University.
- 4) Poster entitled “**Selective Sensing of Peroxynitrite by Hf-Based UiO-66-B(OH)₂ Metal– Organic Framework: Applicability to Cell Imaging**” was presented in the *International Conference on Frontiers in Chemical Sciences, 2018*, arranged at Department of Chemistry, Indian Institute of Technology Guwahati.