In situ encapsulation of ZrQ in UiO-66 (Zr-BDC) for pore size control to enhance detection of a nerve agent simulant dimethyl methyl phosphonate (DMMP)

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<u>Abstract</u>

Chemical warfare agents are toxic chemicals that require rapid, easy-to-use, sensitive, and selective sensors to countermeasure. Simulants, such as dimethyl methyl phosphonate (DMMP), are used to test the effectiveness of sensors towards nerve agents. Metal organic frameworks (MOFs) offer large surface area and selective accessibility to active sites making them appealing for chemical sensing applications. In this work, we propose a fast, facile, direct synthesis method for manufacturing fluorescent MOFs with high sensitivity and selectivity. Zr-BDC is synthesized with 1, 4-benzenedicarboxylic acid (BDC) as an organic ligand and zirconium (Zr) metal. Fluorescent materials are then encapsulated in a novel and rapid in-situ approach with strong solvents. X-ray diffraction, UV-visible spectroscopy, Fourier-transform infrared spectroscopy and Raman spectroscopy are used to verify the successful formation of fluorescent MOFs. Compared to other methods, the gel synthesis method helps to control crystal growth leading to higher BET surface areas of ~ 1150 m²/g for Zr-BDC and 850 m²/g for ZrQ@Zr-BDC. Titration experiments show the sensitivity of the material to DMMP down to 8.3 nM with a highly linear response. Enhanced fluorescence and occupation of mesopores by ZrQ enable lower limit of detection than those of comparable works in literature. The encapsulation mechanism also prevents substantial defects that would otherwise lead to water adsorption.

<u>Keywords</u>

Metal organic framework; fluorescent sensing; DMMP detection; in situ encapsulation

<u>1. Introduction</u>

Chemical warfare agents (CWAs), such as sarin, are extremely toxic and often lethal chemicals that pose substantial health and safety risks. These colorless and odorless chemicals disrupt the transfer of signals from nerve cells to organs. Dimethyl methyl phosphonate (DMMP) has comparable structure to sarin and is thus commonly used as a CWA simulant. DMMP is also commonly used as a flame retardant. Threat of military use and terrorist attacks have prompted the need for rapid, easy-to-use, sensitive, and selective sensors. Many sensors have been developed to detect DMMP including electrochemical sensor,^[1] chemomechanical sensor,^[2] chemiresistive sensor arrays,^[3] and microelectromechanical sensor system.^[4] However, the critical limitation of these is the requirement of complex equipment and instrumentation.

Fluorescent sensors offer high sensitivity, rapid detection and ease of fabrication.^[5] The most common mechanism involves photo-induced electron transfer from the excited fluorescent sensor to the target analyte resulting in quenching.^[6] The primary detection mechanism is a covalent, irreversible reaction between the sensing material and the analyte.^[7] As a result, the materials are often not reusable. Many sensing materials proposed in literature require complex synthesis methods that drive up the sensor cost and reduce the economic feasibility. Similarly, the synthesis process often takes long periods of time. One study took approximately 5 days to synthesize pyrene hexafluoro isopropanol-decorated single-walled carbon nanotubes for fluorescent DMMP detection.^[8]

Metal organic frameworks (MOFs) have shown promise for numerous sensing applications.^{[9–} ^{11]} Fluorescent sensors have been synthesized using Zr, 4,4'-stilbenedicarboxylic acid and Eosin Y for nitroaromatics sensing.^[12] Zr-BDC, also known as UiO-66, have been used for DMMP detection and even degradation.^[13] Degradation of such CWAs is primarily achieved by adsorbing the DMMP molecules and breaking P-X bonds to form less toxic by-products by forming hydrogen bonds with free hydroxyl groups.^[14] MOFs provide an abundance of active sites for detection and ultra-high surface area for both chemisorption and physisorption. Zr-based MOFs show good thermal and chemical stability when linked to carboxylates of 1,4-benzene dicarboxylate (BDC) ligands.^[15] Zr-BDC, commonly known as UiO-66, also has the benefit of good water stability and good sensing performance.^[16,17] However, Zr-BDC typically requires functionalization to achieve fluorescent and selective sensing.

In this work, we propose a facile approach to synthesize Zr-BDC gel materials. Subsequently, we use a novel in-situ encapsulation technique to functionalize the framework with fluorescent ZrQ (zirconium 8-hydroxyquinoline). 8-hydroxyquinoline is chosen as the fluorescent material due to

inherent ability to form complexes even at low Zr concentrations.^[18] The gel can be noted instantly with no external treatment or energy sources. The encapsulation process also causes negligible morphological and chemical changes that can be observed through scanning electron microscopy (SEM), x-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR) and Raman spectroscopy. This validates the successful encapsulation and formation of the fluorescent complex ZrQ@Zr-BDC. A lack of defects can also be observed from the hydrophobicity of the nanocomposite and poor water sensitivity. The resulting nanocomposite has mesopores filled with ZrQ resulting in enhanced detection of DMMP. The variation of fluorescence before and after encapsulation, including shifts in the fluorescence wavelengths and intensity, are discussed. The selectivity of the material to common volatile organic compounds and even other CWAs such as 2-chloroethyl ethyl sulfide (CEES) has also been tested.

2. Materials and methods

2.1. Materials

All chemicals are of analytical grade and used without further purification. 1,4benzenedicarboxylic acid (99% BDC, VWR), *N*,*N*-dimethylformamide (DMF, 99.8%, VWR), glacial acetic acid (98%, VWR), zirconium tetrachloride (ZrCl₄, 98 %, VWR), 8-hydroxyquinoline (8-Q, 99%, VWR), hydrochloric acid (HCl, 37%, VWR), acetone (98%, VWR) and deionized water (DIW) are used for the synthesis of fluorescent ZrQ@Zr-BDC. 2-cholroethyl ethyl sulfide (CEES, 97%, Sigma Aldrich), dimethyl methyl phosphonate (DMMP, 98%, VWR), methanol (99%, VWR), and hexane (SigmaAldrich) are used for selectivity testing.

2.2. Synthesis of Zr-BDC and ZrQ@Zr-BDC MOF

A 5 mL clear solution of ZrCl₄ (0.54 mmol, termed solution A) and 0.5 ml HCl (37%) were combined with 5 mL clear solution of BDC (0.75 mmol, termed as solution B). The solvent for every solution is DMF unless otherwise specified. After addition of solution A to solution B and allowing to react in oven at 70 °C for 30 min, a gel like material, Zr-BDC, is formed immediately. For the synthesis of a functionalized MOF, ZrQ@Zr-BDC, a clear solution containing Zr ions and 8-Q (0.8 mmol Zr⁺⁴:0.05 mmol 8-Q) is mixed with solution B (0.75 mmol BDC). After mixing both together, the material is activated in a Teflon-lined autoclave at 150 °C for 3 hours. A gel-like material, ZrQ@Zr-BDC, is noticed after. The final product of Zr-BDC and ZrQ@Zr-BDC are separated by centrifuge at 8,000 rpm. To ensure that the guest species are not left adhered to the ZrQ@Zr-BDC surface, the product is washed thoroughly twice using solvents that solubilize the

guest species. Washing is first done with DMF followed by a 1:1 methanol: acetone mixture. The separated samples are vacuum dried at 70°C for 12 h. This process converts the gel to a powder form that can be characterized.

2.3 Material characterization techniques

A field emission scanning electron microscope (FE-SEM, QuantaTM 250) is utilized to analyze the morphologies of the Zr-BDC and ZrQ@Zr-BDC crystals. Transmission electron microscopy (TEM, Hitachi H7650) is conducted at 80 kV to verify crystal size and morphology. An X-ray diffractometer (Rigaku Multiflex) is used to characterize the crystalline structure of the Zr-BDC and ZrQ@Zr-BDC. Raman spectroscopy (Bruker Raman II, Laser (1064 nm) Power 300 mW, USA) is used to measure the Raman spectra of both Zr-BDC and ZrQ@Zr-BDC. Thermogravimetric analysis and differential scanning calorimetry (Mettler Toledo TGA / DSC 3+) is conducted with 6-8 mg of sample in a 70 µL alumina crucible from 25 to 800 °C at a rate of 20 °C/min in 25 mL/min of air. The Brunauer-Emmett-Teller (BET) measurements (NOVA Station A) are performed for surface area determination by N₂ adsorption at 77 K. The Barrett-Joyner-Halenda model (BJH, Micromeritics TriStar II Plus) is used to determine the pore size distribution at 77 K. Fluorescence spectra of ZrQ, Zr-BDC, and ZrQ@Zr-BDC are measured with a UV-Vis spectrometer (Ocean Optics, Flame-S, USA). 0.5 g of the synthesized, dried powder is compressed into a pellet. FT-IR (Nicolet Nexus 470, USA) is used measure the transmittance spectra in the range of 4000-500 cm⁻¹ with a spectral resolution of 4 cm⁻¹. The contact angle (FemtoLab SmartDrop) of the material is also measured in a pellet form.

2.4 DMMP fluorescence quenching experiments

Fluorescence titration is carried out by adding 10 mg of the dried ZrQ@Zr-BDC into a 120 mL solution of ethanol. The solution is sonicated in ambient conditions for 60 minutes. 4.5 mL of the sample is extracted into a volumetric flask by pipette. Diluted aqueous DMMP with a concentration of 20 ppm is added dropwise into the cuvette to attain different concentrations. The volumetric flask is then topped up to a final volume of 5 mL with ethanol due to known solubility.^[19] The samples are transferred to a quartz cuvette and excited by 365 nm UV light. The fluorescence intensity is measured by the UV-Vis spectrometer. All sensing experiments are conducted at ambient conditions to reduce energy consumption.

3. Results & Discussion

3.1 Structural and morphological characterization of Zr-BDC and ZrQ@Zr-BDC

The crystalline structure of both Zr-BDC and ZrQ@Zr-BDC are confirmed by XRD analysis, as shown in Figure 1(a). The primary peaks for Zr-BDC occur at 8.1°, 9.3°, 12.9°, 17.8° and 26.4° corresponding to (111), (200), (222), (400) and (442) planes, respectively.^[20] Overall, the XRD pattern matches well with other Zr-BDC samples synthesized in literature.^[15] ZrQ@Zr-BDC exhibits the same peaks with no new peaks, but the intensity increases. In particular, the peaks for Zr become more pronounced at 38.2°, 40.1°, 41.3° corresponding to (100), (002) and (101) planes, respectively.^[21] A lack of peaks between 2 to 6° verifies a lack of defects which would arise if encapsulation is not the primary nanocomposite formation mechanism.^[22] The average particle size from the Scherrer equation has been calculated as 117.5 nm for Zr-BDC and 117.9 nm for ZrQ@Zr-BDC, respectively.

Raman spectra, shown in Figure 1(b), agree well with literature for synthesized UiO-66.^[23] Peaks above 800 cm⁻¹ are attributed to the vibrational modes of the BDC organic ligand. Bands below 800 cm⁻¹ may be attributed to Zr atoms, but literature is more limited for these peaks. The in-phase and out-of-phase vibrations of the organic linkers contribute to the high intensity peak at 1612 cm⁻¹. This verifies the structure of the synthesized MOF and shows that the 12 linkers in a unit cell are distant enough to have negligible interaction.^[24] Peaks at 2937 and 3073 cm⁻¹ correspond to C-H bonds within the organic ligand. Minor peaks at 3303 cm⁻¹ are more evident on ZrQ@Zr-BDC corresponding to vibrations from O-H groups.

FT-IR is subsequently used to characterize the functional groups, as shown in Figure 1(c). A broad band with peak at 3395 cm⁻¹ represents the abundance of hydroxyl functional groups on the surface of both materials. The hydroxyl groups arise from the use of BDC as an organic ligand. Carboxylate C=O asymmetric stretching and C=C aromatic bonds can be observed by peaks at 1666 and 1582 cm⁻¹, respectively.^[25] 8-Q typically exhibits a strong C-N band at approximately 1500 cm⁻¹, but no new peaks or changes in the intensity are noted for ZrQ@Zr-BDC. Carboxylic acid, C-O and C-OH, bonds can be observed by the peaks at 1396 and 1248 cm⁻¹. The characteristic vibration at 759 cm⁻¹ was assigned as a stretching vibration of Zr-O, in which the carboxylic oxygen is coordinated with Zr. Both Raman and FTIR spectra are highly comparable between Zr-BDC and ZrQ@Zr-BDC suggesting the successful encapsulation and functionalization.

Structural changes in the synthesized materials after sensing tests are examined by FT-IR, as shown in Figure 1(d). It has previously been shown that FT-IR is more effective at indicating the presence of guest molecules compared to PXRD and other characterization techniques.^[26] Small

changes in Zr-BDC spectra are observed. Both Zr-BDC and ZrQ@Zr-BDC exhibit new peaks at 2998 cm⁻¹ which may be attributed to P-CH₃ asymmetric stretching ($v_a(CH_3)P$).^[27] ZrQ@Zr-BDC also exhibits a small peak at 2924 cm⁻¹ which may be attributed to symmetric stretching of P-CH₃.^[28] A new, strong peak at 1275 cm⁻¹ may be attributed to P=O stretching. In-plane bending of P-CH₃ bonds also causes a strong peaks between 960 and 880 cm⁻¹. PO₂ stretching bonds may also observed at 780 cm⁻¹. These peaks are more evident in ZrQ@Zr-BDC than Zr-BDC verifying the improved sensing performance that can be observed.

PXRD and Raman of the material after sensing is shown in supporting information Figure S1. The PXRD shows a substantial increase in the (400) peak at 17.8° and a decrease in the (111) peak at 8.1° for both Zr-BDC and ZrQ@Zr-BDC. We also observe peak broadening which is predominantly seen at higher angles. This could suggest reductions in the crystallite size and microstrain because of chemical interactions between DMMP and the crystal lattice. The primary change in the Raman spectra is the loss of the peak 3303 cm⁻¹. This verifies that hydrogen bonding at hydroxyl sites is the most likely chemical mechanism.

The BET measurements suggest a loss in the surface area of the pristine Zr-BDC upon the encapsulation process as shown in Figure 1(e). The pristine Zr-BDC has a surface area of 1150 m²/g with a maximum N₂ uptake of 415.8 cm³/g. These values are higher than some previously reported BET surface areas of UiO-66, using comparable Zr metal nodes and BDC coordination ligands, that start at 838 m²/g.^[29,30] Typically, nitrogen saturation also occurs at lower values of 300 cm³/g.^[31] The increase in adsorption capabilities is attributed to small numbers of defects. The addition of ZrQ reduces the BET surface area to 850 m²/g which represents 26 % loss in surface area from Zr-BDC. This further confirms that encapsulation of ZrQ within the pores of Zr-BDC is the primary composite formation mechanism. Surface decoration or other mechanisms would increase surface area rather than the substantial decreases observed when introducing more and more ZrQ. One way to study the formation of missing-cluster defects, as a result of partially deprotonated ligands, in Zr-BDC is to analyze pore size and pore size distributions.^[32]



Figure 1: Structural characterization of Zr-BDC (black) and ZrQ@Zr-BDC (red): (a) Powder XRD patterns; (b) Raman vibrational spectra; (c) FTIR spectra in transmission mode on synthesized, dried powders; (d) FTIR spectra in transmission mode after DMMP sensing tests; (e) N₂ adsorption isotherms for Zr-BDC and ZrQ@Zr-BDC at 77 K; (f) water contact angle of Zr-BDC versus ZrQ@Zr-BDC.

Table 1 shows the change in mean pore diameter and pore volume for Zr-BDC versus ZrQ@Zr-BDC. The encapsulation results in a substantial decrease in the mean pore diameter from 7.64 to 2.02 Å. The 7.64 Å is comparable to reports of 6 Å in literature.^[33] The average pore volume

only decreased slightly from 0.688 cm³/g to 0.638 cm³/g. The pore size distribution is shown in supporting information Figure S2. It can be seen that larger pores > 10 Å are limited upon the introduction of ZrQ. The comparable gravimetric yield is also reported for both materials. After drying, a crystal yield of 90.7% for the batch process Zr-BDC is comparable to previous works.^[34] The increased yield after encapsulating ZrQ is noteworthy, as it suggests that there is no release of excess Zr or 8-Q ions. Visually, the ZrQ is a green-gel like material even after drying which is not observed in the dried ZrQ@Zr-BDC samples visually, or through SEM and TEM images.

Another method to characterize the presence of defects is through water contact angle measurements, as shown in Figure 1(f). Missing linkers have been shown to enhance water adsorption and make Zr-BDC more hydrophilic.^[31] As a result, different synthesis methods have shown wide variations in contact angle. Ultrasonic coating of Zr-BDC on stainless steel meshes yield a hydrophilic contact angle of 25° .^[35] Layer-by-layer synthesis of Zr-BDC on polymer films yields a hydrophobic contact angle between 95 and 138.7°.^[36] 8-Q is a hydrophobic material that is insoluble in water, but ZrQ has a contact angle of 17.7° , as shown in supporting information Figure S3. However, after incorporating the ZrQ into the Zr-BDC, the nanocomposite exhibited a lower contact angle suggesting a more hydrophilic material. The decrease from $69.6 \pm 1.5^{\circ}$ to $62.4 \pm 1.1^{\circ}$ suggests the introduction of missing-cluster defects is compensating for the introduction of ZrQ. The pellet form measurements may contribute to lower contact angles than normal due to the porous nature of the pellet even after compression of the synthesized powder.

| | Yield | Mean Pore Diameter | Pore Volume |
|------------|-------|--------------------|----------------------|
| | (%) | (Å) | (cm ³ /g) |
| Zr-BDC | 90.7 | 7.64 | 0.688 |
| ZrQ@Zr-BDC | 93.2 | 2.02 | 0.638 |

Table 1: Yield, mean pore diameter, micropore and mesopore volume for Zr-BDC versus ZrQ@Zr-BDC.

The synthesized Zr-BDC and ZrQ@Zr-BDC are also characterized using SEM to determine morphological structure and verify encapsulation, as shown in Figure 2(a) and (b). The crystals for both Zr-BDC and ZrQ@Zr-BDC show variations in size ranging from 82 nm to 274 nm. The estimation of crystal size from XRD using the Scherrer equation falls within this range. No surface decoration could be observed from SEM or TEM. The comparable particle size and morphology confirms the successful encapsulation of the fluorescent material. TEM is conducted to attain clear images and to estimate the crystal size, as shown in Figure 2(c) and (d). From the images, the average particle size is roughly estimated to be 173.3 nm and 239.7 nm. The particle size of UiO-66 in literature can range anywhere from 10 nm to 2000 nm.^[37] The relatively low particle sizes may be attributed to the gel-route synthesis method taken which can produce sub-5 nm nanoscale MOFs.^[38] Careful control of the gelation process through gradual addition of ligand may have helped to form the gel illustrated in Figure 1(a). Diameters between 500 and 2000 nm are perhaps most commonly reported corresponding to BET surface areas between 1250 and 1350 m²/g.^[39] Typically, BET surface area is linearly related to the inverse of particle size.^[40] In addition to crystal growth, a reduction in the porosity can also be observed in the ZrQ@Zr-BDC sample from TEM.



Figure 2: SEM images of (a) Zr-BDC, (b) ZrQ@Zr-BDC showing overall crystal morphology. TEM images of (c) Zr-BDC, (d) ZrQ@Zr-BDC showing aggregated crystal structure.

The thermal properties of Zr-BDC, ZrQ and ZrQ@Zr-BDC are analyzed by TGA and DSC, as shown in supporting information Figure S4. Initial solvent losses can be observed beginning at approximately 75 °C. Dehydration of zirconium clusters to Zr₆O₆ may explain the derivative weight change peak at 240 °C. A weight loss and exothermic peak between 550 and 600 °C can be attributed to degradation of organic linkers.^[41] A decrease in the decomposition temperature from Zr-BDC to ZrQ@Zr-BDC by approximately 8 °C may suggest slight weakening in bonds between the organic linker and the metal clusters. As ZrQ is introduced, the exothermic peak temperature decreases

slightly which may suggest an increase in the segmental mobility that may help explain the increased sensitivity.^[42]

3.2 Application of ZrQ@Zr-BDC for DMMP sensing

The fluorescence emission spectra under 365 nm excitation are shown in Figure 3(a). The ZrQ samples show a slight red shift in the fluorescence emission peak. Previous reports have shown that excitation of Zr-BDC at 365 nm results in a singular emission peak centered at 408 nm.^[43] This peak can be clearly observed in the ZrQ@Zr-BDC spectra, but not from the ZrQ spectra. The ZrQ spectra shows a peak emission wavelength of 512 nm with other peaks at 485 nm, 560 nm and 646 nm. The spectral overlap helps to explain the observed new peaks observed at lower wavelengths. The resulting blue shift of the nanocomposite compared to ZrQ can be explained by an energy transfer from the host Zr-BDC to the guest ZrQ. This blue shift can be observed by the shift in max emission wavelength from 512 nm for ZrQ to 496 nm for ZrQ@Zr-BDC, as well as the shift in the peak from 646 nm for ZrQ to 599 nm for ZrQ@Zr-BDC. Previous studies have also observed a blue shift in the fluorescence after encapsulation inside a MOF.^[44] The fluorescence spectra of ZrQ@Zr-BDC shows peaks at 380 nm, 408 nm, 425 nm, 456 nm, 496 nm and 599 nm. The peaks at higher wavelengths, namely 599 nm, match well with ZrQ peaks. This suggests that the fluorescence originates from the organic ligand and does not occur from charge transfer with the metal. The change in the fluorescence intensity is small ($\sim 7\%$) compared to previously reported quenching observed when encapsulating fluorescent material inside a non-MOF host.^[45] Encapsulation and immobilization of the fluorescent material in the MOF channels may help to reduce the aggregation caused quenching effect by limiting the agglomeration of 8-Q.

First, pure Zr-BDC is tested to determine the sensing performance towards DMMP, as shown in Figure 3(b). The changes at 1 and 2 ppm are negligible. At 3 ppm, changes beyond the 3 times the noise could be noticed which can be attributed to a sensor response. Upon increasing to 10 ppm, the change in the sensor response becomes substantial. The variations can arise from numerous factors including crystal size differences and the introduction of defects into the framework. The poor selectivity of pure Zr-BDC can be observed from Figure 3(c). DMMP is the primary compound studied with Zr-BDC. However, the adsorption of CEES and hexane into Zr-BDC (UiO-66) have also been shown in literature.^[46,47] This helps to explain the comparable signals observed between CEES, DMMP and hexane.



Figure 3: (a) A comparison of the fluorescence emission spectra under 365 nm excitation for ZrQ@Zr-BDC, Zr-BDC and ZrQ. (b) Fluorescence intensity at varying concentrations of DMMP showing fluorescence quenching of pure Zr-BDC. (c) Selectivity of pure Zr-BDC to DMMP compared to hexane, methanol, water and CEES. (d) Fluorescence quenching of ZrQ@Zr-BDC at different concentrations of DMMP down to 50 ppn. (e) The Stern-Volmer plot showing the linearity of the fluorescence quenching and for determining K_{sv} of ZrQ@Zr-BDC. (f) Selectivity of ZrQ@Zr-BDC to common VOCs and one other CWA.

Fluorescent sensing is then conducted in liquid state to quantify the DMMP sensing capabilities of ZrQ@Zr-BDC. Fluorescence spectra from 1.2 ppm down to 50 ppb are shown in

Figure 3(d). The gradual reduction in the fluorescence intensity (*F*) from initial levels (*F*₀) shows the fluorescence quenching as higher concentrations of DMMP are added. The quenching results are highly repeatable. The linearity of the sensor with standard deviation from 3 separate experiments are shown in Figure 3(e) as a Stern-Volmer plot. The limit of detection (LOD) can be calculated from the slope of the Stern-Volmer plot (*K*_{sv}) and standard deviation (σ) of 10 blank sensors using equation (1). The resulting LOD is determined to be 1.04 ppb or 8.3 nM. This value is substantially lower than 3 ppm or 32,238 nM observed in pure Zr-BDC samples.

$$LOD = 3\frac{\sigma}{K_{sv}} \tag{1}$$

The selectivity of the sensor is shown in Figure 3(f). Previously, we reported the use of fluorescein encapsulated Zr-BTC for the detection of 2-chloroethyl ethyl sulfide (CEES), also known as half mustard gas.^[48] The alteration of the fluorescent material and the organic ligand substantially reduces the fluorescence quenching from CEES and instead yields substantial fluorescence quenching in the presence of DMMP. The material is also not affected by common VOCs such as hexane. As can be seen, the addition of hexane, water, and methanol causes negligible changes in the fluorescence. Zr-BDC has previously been studied for the adsorption of hexane isomers,^[46] CEES,^[47] as well as sensing of methanol vapor.^[39] However, the functionalization allows for enhanced selectivity. The water stability of Zr-BDC may help to explain the lack of response to pure water in both ZrQ@Zr-BDC and Zr-BDC.

3.3 Encapsulation and Sensing Mechanism

Zr-BDC, or UiO-66, is one of the most common MOFs reported in literature with a wellestablished synthesis process.^[30] To encapsulate fluorescent material in Zr-BDC, ZrQ is synthesized in-situ inside the Zr solution without the need for external energy or heating. The formation of ZrQ in DMF is highly favorable and near instantaneous. The solution is subsequently blended with the BDC ligand. The limited concentration of 8-Q limits the formation of ZrQ and ensures that the fluorescent material is encapsulated. Zr-BDC often requires external energy, typically thermal, to form the organic framework. The activation energy of nucleation has been estimated as 64.5 kJ/mol which is higher than many common MOFs.^[49] Therefore, it is hypothesized that the Zr-BDC assembles around the fluorescent ZrQ as external heating is applied. The assembly of the MOF around the fluorescent ZrQ results in a substantial increase in the crystal size, as shown in Figure 2. Despite the increase in crystal size and reduction in surface area, the ZrQ@Zr-BDC still exhibits higher sensitivity than most works in literature, as shown in Table 2. As can be seen, the 1.04 ppb LOD is lower than previous works using similar MOF materials (UiO-66). Therefore, the sensitivity may be attributed to chemical mechanisms.

| Material | LOD (ppb) | Ref |
|--|-----------|-----------|
| PVDF film on quartz crystal microbalance | 940 | [2] |
| Capacitive micromachined ultrasonic transducer | 56 | [50] |
| UiO-66-NH ₂ coated electrodes | 3 | [51] |
| UiO-66 film on Parylene-patterned resonant | 5 | [52] |
| microcantilever | C C | |
| Au@Ag@ZIF-8 | 2500 | [53] |
| ZrQ@Zr-BDC | 1.04 | This work |

Table 2: Comparison table for DMMP sensing materials in literature.

The diameter of DMMP is estimated to be 5.71 Å.^[54] As a result, physisorption into the remaining larger pores of Zr-BDC can also be occurring. This is supported in literature where it has been reported that physisorption onto surface sites can also occur.^[13] The pore size may also help to explain the selectivity experiment result to CEES which has a typical molecular diameter of approximately 6.98 Å. The selectivity of ZrQ@Zr-BDC may be attributed to the control and limitation of pores with average diameters above 7 Å. The average diameter of Zr-BDC is 7.6 Å suggesting physisorption of CEES can occur which helps to explain the poor selectivity observed. These pores become occupied by ZrQ preventing physisorption of larger chemical warfare agents, such as CEES. A previous study using activated carbon fabrics determined that the optimal mean pore diameter for adsorption of CEES is 29 Å.^[55] ZrQ fills any potential mesopores and larger micropores within the Zr-BDC framework preventing adsorption of CEES and contributing to the enhanced selectivity.

The adsorption of DMMP occurs as a result of hydrogen bonding between oxygen on the phosphoryl groups and open hydroxyl groups on the MOF.^[13] This was verified by Raman and especially evident in the ZrQ@Zr-BDC sample. The adsorption replaces pre-adsorbed water molecules and limits the effect of humidity on the sensing performance. The formation of phosphorus bonds is also observed from FTIR. The use of Zr-BDC for DMMP sensing has been studied before in literature using resonance cantilevers.^[52] However, the complex design and fabrication involved in creating patterned microcantilevers poses substantial challenges to eventual application and commercialization.



Figure 4: (a) Synthesis and encapsulation process of ZrQ in Zr-BDC; (b) DMMP sensing mechanism using ZrQ@Zr-BDC.

The phosphorylation of 8-Q by chemical nerve agent simulants has also been previously demonstrated in literature.^[56] This is verified by FTIR after sensing experiments, and helps to explain the increased selectivity to DMMP using 8-Q as opposed to fluorescein from previous works. Phosphorylation of ZrQ@Zr-BDC is also expected to contribute to the sensing mechanism. The formation of ZrQ may yield additional OH groups that aid in the bonding of the analyte DMMP, as previously reported.^[57] Photo-induced electron transfer of both ZrQ and Zr-BDC help to explain the enhanced sensing performance. Simulations have shown preferential adsorption of DMMP to

Lewis acidic sites of Zr₆ nodes rather than the ligand.^[52] Therefore, it is expected that the ZrQ contributes more to the proposed sensing mechanism given it is the primary fluorescent material. The most plausible mechanism for chemical detection with Zr-BDC is the cleavage of the metallinker bonds which is typically the weakest bond in UiO-66.^[58] This results in loss of stability, functionalization by analytes and the observed fluorescence quenching. The irreversibility of fluorescence quenching in the ZrQ@Zr-BDC suggests that static quenching is occurring in the nanocomposite. However, the exact mechanism for fluorescence quenching requires additional studies. The resulting hydrogen bonds form non-fluorescent complexes that dramatically reduce the fluorescence emission. However, the simplicity of the fabrication method and detection method help to compensate for the irreversibility. The material could instead be used as a disposable sensor like pH paper.

3.4 Assumptions and Limitations

The primary challenge with the fluorescent sensors using 8-Q is the poor stability of metal/8-Q compounds including ZnQ and AlQ.^[59,60] The degradation of ZrQ can also be observed in supporting information Figure S5. The crystalline framework appears intact after sensing experiments, so the optical color change of the ZrQ@Zr-BDC composite is likely from encapsulated ZrQ. Furthermore, changes in the overall chemical structure of the material can be observed from Figure 1 and supporting information Figure S1. Therefore, this material is best treated as a one-time sensor which is possible owing to the facile synthesis process. Coating the gel onto a substrate such as filter paper may be beneficial to achieve real-world applications, as shown in previous works with comparable materials.^[59] Future works may look at testing different synthesis conditions and concentrations to determine the impact on sensing properties. Additional testing may also help to verify whether the sensor is reusable. This may be achieved by attempting to imitate synthesis conditions and applying external heat to reform the MOFs. This was not attempted due to the facile synthesis method compared to regenerating the used sensing material. Zr-BDC, or UiO-66, has also shown fluorescence quenching to metal cations, especially Fe³⁺.^[43,61] Future works may look to test the interference of metal cations in CEES detection.

4. Conclusion

In conclusion, Zr-BDC is successfully synthesized with a rapid, reproducible and simple technique. It is functionalized with ZrQ to form ZrQ@Zr-BDC for DMMP detection via fluorescence quenching. The change in the fluorescence of ZrQ upon encapsulation inside Zr-BDC

is studied. Encapsulation is verified by FTIR, Raman, XRD, SEM, as well as water contact angle measurements. The material exhibits selectivity to DMMP against VOCs such as hexane and other CWAs such as CEES that have previously been detected by Zr-BDC. The manipulation of pore volumes and phosphorylation of 8-Q are the two primary mechanisms for increased sensitivity and selectivity. A strong linear correlation between the responses and DMMP concentration are observed from the Stern-Volmer plot. ZrQ@Zr-BDC exhibits strong selectivity and a LOD of 1.04 ppb. By comparison, Zr-BDC does not exhibit selectivity and only has a LOD of ~ 3 ppm. The primary mechanism leading to the improved sensing performance is the introduction of ZrQ controlling larger micropores, while introducing sufficient defects to maximize DMMP affinity.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no conflict of interest.

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