

Proceeding Paper

Aqueous Medium Fluoride Anion Sensing by Fluorophore Encapsulated UiO-66 Type Zirconium Metal–Organic Framework[†]

Rana Dalapati and Ling Zang * 

Department of Materials Science and Engineering, Nano Institute of Utah, University of Utah, Salt Lake City, UT 84112, USA; rana.dalapati@utah.edu

* Correspondence: lzung@eng.utah.edu

† Presented at the 1st International Electronic Conference on Chemical Sensors and Analytical Chemistry, 1–15 July 2021; Available online: <https://csac2021.sciforum.net/>.

Abstract: A well-known fluorophore molecule, pyrene was encapsulated into a stable metal organic framework by in situ encapsulation method. The existing metal-organic framework (MOF) called UiO-66 (UiO = University of Oslo) served as host material for pyrene fluorophore. The fluorescence of pyrene was quenched after encapsulation inside the porous host. Recovery of quenched fluorescence was accomplished by anion induced host dissolution, followed by the release of the fluorophore molecule. Using this anion induced dissolution, a selective sensing of fluoride anion in pure aqueous was achieved.

Keywords: metal-organic framework; pyrene; fluoride anion sensing



Citation: Dalapati, R.; Zang, L. Aqueous Medium Fluoride Anion Sensing by Fluorophore Encapsulated UiO-66 Type Zirconium Metal–Organic Framework. *Chem. Proc.* **2021**, *5*, 86. <https://doi.org/10.3390/CSAC2021-10551>

Academic Editor: Ye Zhou

Published: 1 July 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

For the past few decades, a tremendous effort has been dedicated by the scientific community towards the development of a modest strategy for the selective and precise sensing of anions [1], as they perform a key role in biological systems, health, and environment [2]. Among the anions present in biological systems, the smallest fluoride anion has drawn significant attention, due to its biological and environmental impact [3]. Currently, the presence of fluoride in drinking water and commercial household products is the emerging concern for public health [4]. Although fluoride is considered as a micronutrient [5], the excess uptake of fluoride can cause fluorosis [6], and even chronic renal failure [7]. As such, there is an urgent necessity for selective and precise determination of fluoride anions in fluoride-contaminated water.

Metal-organic framework (MOF), a new class of porous materials, have received tremendous attention for their potential applications in gas storage [8], chemical separation [9], catalysis [10], and drug delivery [11]. The UiO-66 framework (UiO = University of Oslo) is one typical Zr-MOF, constructed with $Zr_6O_4(OH)_4$ clusters and 1,4-benzenedicarboxylate, BDC linkers [12]. With a higher surface area, thermal resistivity, and an exceptional structural stability in water, this becomes an ideal molecular host material [13]. The triggered release of a guest molecule by host dissolution is one of the efficient strategies for molecular recognition [14]. Recently Bein et al. reported fluoride sensing by using the hybrid composite of the metal-organic framework NH_2 -MIL-101(Al) and fluorescein [15].

Herein, we report a selective and precise sensing of fluoride ions in a pure aqueous medium by a fluoride triggered release of pyrene fluorophore from Zirconium based MOF, UiO-66 [16]. First, in one step we have synthesized pyrene encapsulated UiO-66. Where the Zr-O or μ_3 -oxo bond of UiO-66 framework acts as a reactive probe and the pyrene molecule acts as a signal transducer. Upon encapsulating, the inside of the pore of the framework fluorescence of pyrene was found to be completely quenched. The addition of the fluoride

ion provoked the decomposition of the host UiO-66 and the released pyrene provides a turn-on fluorescence.

2. Methods

All the starting materials were of reagent grade and used as they were received from the commercial suppliers.

2.1. Synthesis

Syntheses of the pyrene containing UiO-66 framework were performed as reported by Biswas et al. with modification [17]. In brief, a mixture of $ZrCl_4$ (72.24 mg, 0.31 mmol), Benzene-1,4-dicarboxylic acid (H₂BDC) (0.31 mmol), pyrene (10 mg, 0.05 mmol), and formic acid (1.2 mL, 3.18 mmol) in Dimethylacetamide (DMA) (3 mL) was placed in a Pyrex tube. The tube was sealed and heated in a preheated heating block to 150 °C for 24 h. The reaction mixture was then cooled to room temperature. Finally, the precipitate was collected by filtration, washed with acetone, and dried in an air oven (60 °C).

2.2. Fluorescence Titration Measurement

For fluorescence titration measurements, a stock solution of pyrene@UiO-66 (1 mg/mL) was diluted in water (final concentration of 99 μ g/mL) in a quartz glass cuvette at room temperature. A 4 mm solution of different anions was used. All the titration fluorescence emission was monitored using an excitation wavelength of 337 nm.

3. Results and Discussion

3.1. Material Characterization

Pyrene encapsulated UiO-66 (pyrene@UiO-66) was synthesized by a single step in situ encapsulation method. Initially, a certain amount of pyrene was added with $ZrCl_4$ and H₂BDC during the synthesis process. The pyrene@UiO-66 material was well characterized by various instrumental techniques, such as X-ray powder diffraction (XRPD), Fourier-transform infrared spectroscopy (FT-IR), and N₂ sorption analysis.

XRPD experiments showed that UiO-66 and pyrene@UiO-66 possessed very similar XRPD patterns (Figure 1a). The similarities between the patterns simulated and found during the experiments of XRPD confirmed the formation of pure UiO-66.

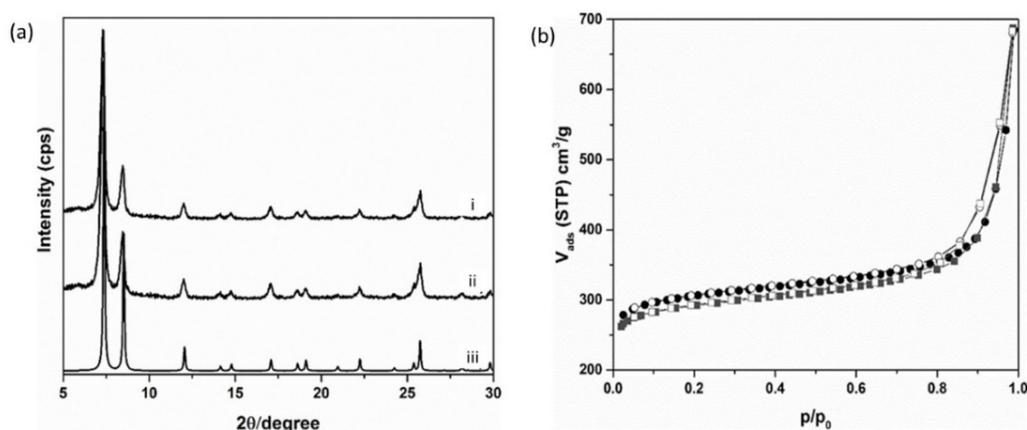


Figure 1. (a) XRPD pattern of (i) pyrene@UiO-66; (ii) only UiO-66; (iii) simulated pattern of UiO-66 MOF. (b) Nitrogen adsorption (filled symbols) and desorption (empty symbols) isotherms of UiO-66 (circle) and pyrene@UiO-66 (square) collected at -196 °C.

The N₂ sorption isotherms of pyrene@UiO-66 (Figure 1b) exhibited an insufficient decrease in the surface area, compared to UiO-66, which indicated the successful encapsulation of the pyrene into the pore framework of UiO-66. Pyrene encapsulated UiO-66

showed a surface area of $898 \text{ cm}^3/\text{g}$, which was lower than the guest-free UiO-66 material ($955 \text{ cm}^3/\text{g}$).

3.2. Anion Sensing Experiment

The fluorescence emission spectra of pyrene@UiO-66 in water was recorded upon the gradual addition of sodium (Na^+) salts of various anions (F^- , Cl^- , Br^- , I^- , NO_2^- , NO_3^- , AcO^- , $\text{S}_2\text{O}_3^{2-}$, HSO_3^- , SO_4^{2-} , HSO_4^- , SO_3^{2-} , ClO_4^- , SCN^- , and HCO_3^-). Figure 2 shows the “turn-on” response of F^- anion towards pyrene@UiO-66 in water. There were almost no changes observed in the fluorescence emission spectra for all other anions. The bar plot in Figure 3a summarized the selectivity of pyrene@UiO-66 towards F^- anion over all other anions.

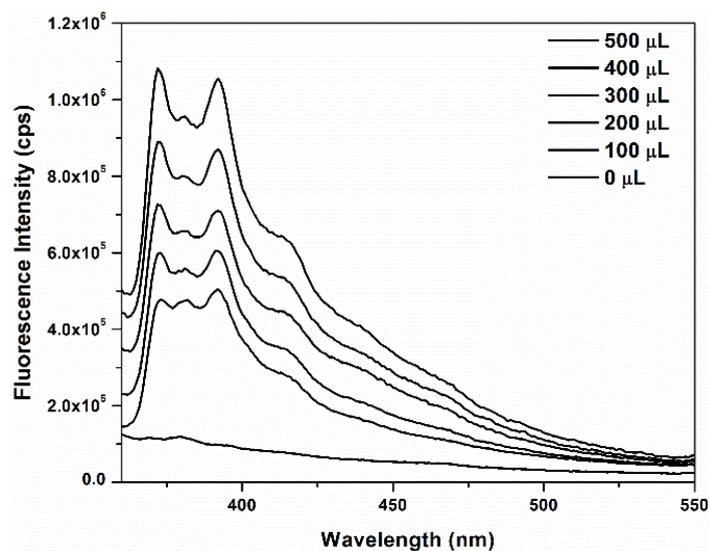


Figure 2. Change in fluorescence intensity with the gradual addition of the F^- solution to a suspension of pyrene@UiO-66 in aqueous medium.

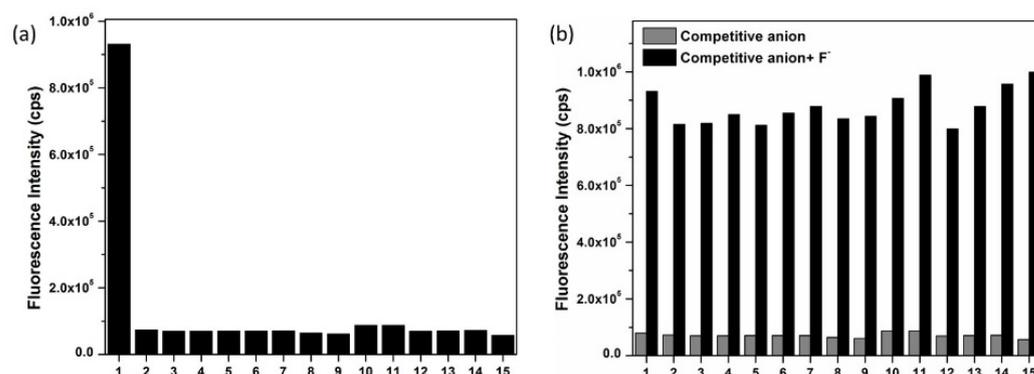


Figure 3. (a) Change in the fluorescence intensity of pyrene@UiO-66 upon the incremental addition of different anions. (b) Change in the fluorescence intensity of pyrene@UiO-66 upon the addition of F^- solution in the absence and presence of different anions. (F^- (1), Cl^- (2), Br^- (3), I^- (4), NO_2^- (5), NO_3^- (6), AcO^- (7), $\text{S}_2\text{O}_3^{2-}$ (8), HSO_3^- (9), SO_4^{2-} (10), HSO_4^- (11), SO_3^{2-} (12), ClO_4^- (13), SCN^- (14), and HCO_3^- (15)).

To examine the sensitivity of the pyrene@UiO-66 sensor material towards fluoride ions, even in the presence of other known interfering ions generally present in water, competitive experiments were performed by monitoring the fluorescence emission intensity of pyrene@UiO-66 in the absence and presence of other anions. During these experiments, solutions of interfering anions were added first to a water of pyrene@UiO-66, followed by

the addition of the F^- anion. The change of the fluorescence intensity of pyrene@UiO-66 upon the addition of the F^- anion, in absence and presence of other interfering anions, are displayed in Figure 3b. In all cases, the interfering anions did not show any interference in their sensing of the F^- anion.

3.3. Mechanism for Anion Sensing

Until now, few mechanisms have been proposed for anion sensing via metal-organic framework. Some include: (1) anion induced coordination to metal-oxygen cluster [18], (2) hydrogen bonding formation with solvated framework [19], and (3) anion induced structural decomposition [15]. To understand the mechanism of fluoride sensing, XRPD and FT-IR measurement was carried out. To check the fluoride induced UiO-66 framework decomposition, MOF material was soaked in the fluoride anion solution. From Figure 4a it was shown that after the fluoride treatment, the characteristic diffraction peak for UiO-66 framework vanished, which confirmed the collapse of the framework in presence of fluoride. However, no change was observed in XRPD pattern after treatment with other anions in aqueous solution (data not shown).

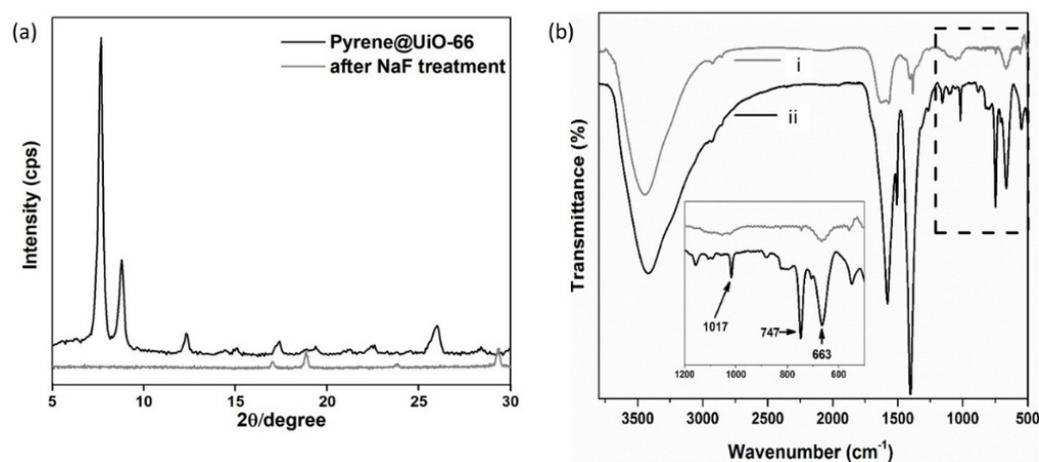


Figure 4. (a) The XRPD pattern and (b) FT-IR spectra of pyrene@UiO-66 before and after fluoride treatment.

The UiO-66 structure consisted of an octahedron of zirconium atom. These octahedrons were capped by μ_3 -oxo and μ_3 -hydroxy groups in an alternating fashion. Carboxylate group from benzenedicarboxylate linker (H_2BDC) connected these octahedral edges. The peak in FT-IR (between 1100 – 1000 cm^{-1}) $\sim 1020\text{ cm}^{-1}$ could be assigned as Zr-OH bending vibration [20], which vanished after fluoride treatment (Figure 4b). Thus, the initial replacement of the hydroxyl group may be responsible for the fluoride sensitivity of the MOF. A peak in FT-IR near 747 cm^{-1} and 663 cm^{-1} was responsible for a Zr- μ_3 -oxo bond that almost disappeared, which also suggested fragmentation of the μ_3 -oxo bond. Observation suggested that fluorescence enhancement occurred via zirconium and fluoride coordination, which led to the release of pyrene from the framework host.

4. Conclusions

We have demonstrated that fluoride induced UiO-66 framework decomposition can be successfully used as a selective sensing probe for the same. Although this system is not reversible in nature, the simple one-step synthesis protocol, high stability, and low toxicity makes this material a promising candidate for fluoride sensing in an aqueous medium.

Author Contributions: Conceptualization, L.Z. and R.D.; methodology, R.D.; formal analysis, R.D.; investigation, R.D.; resources, R.D.; data curation, R.D.; writing—original draft preparation, R.D.; writing—review and editing, R.D.; visualization, R.D.; supervision, L.Z.; project administration, R.D.; funding acquisition, L.Z. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are highly grateful to University of Utah for instrumental facilities and other support.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The support from the University of Utah is acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Busschaert, N.; Caltagirone, C.; van Rossom, W.; Gale, P.A. Applications of Supramolecular Anion Recognition. *Chem. Rev.* **2015**, *115*, 8038–8155. [[CrossRef](#)] [[PubMed](#)]
2. Gale, P.A.; Caltagirone, C. Anion sensing by small molecules and molecular ensembles. *Chem. Soc. Rev.* **2015**, *44*, 4212–4227. [[CrossRef](#)] [[PubMed](#)]
3. Zhou, Y.; Zhang, J.F.; Yoon, J. Fluorescence and Colorimetric Chemosensors for Fluoride-Ion Detection. *Chem. Rev.* **2014**, *114*, 5511–5571. [[CrossRef](#)] [[PubMed](#)]
4. Jagtap, S.; Yenkie, M.K.; Labhsetwar, N.; Rayalu, S. Fluoride in Drinking Water and Defluoridation of Water. *Chem. Rev.* **2012**, *112*, 2454–2466. [[CrossRef](#)] [[PubMed](#)]
5. Nielsen, F.H. Micronutrients in parenteral nutrition: boron, silicon, and fluoride. *GASTAB* **2009**, *137*, S55–S60. [[CrossRef](#)] [[PubMed](#)]
6. Burgmaier, G.M.; Schulze, I.; Attin, T. Fluoride uptake and development of artificial erosions in bleached and fluoridated enamel in vitro. *J. Oral Rehabil.* **2002**, *29*, 799–804. [[CrossRef](#)] [[PubMed](#)]
7. Chandrajith, R.; Dissanayake, C.; Ariyaratna, T.; Herath, H.; Padmasiri, J. Dose-dependent Na and Ca in fluoride-rich drinking water—Another major cause of chronic renal failure in tropical arid regions. *Sci. Total Environ.* **2011**, *409*, 671–675. [[CrossRef](#)] [[PubMed](#)]
8. Alezi, D.; Belmabkhout, Y.; Suyetin, M.; Bhatt, P.M.; Weseliński, Ł.J.; Solovyeva, V.; Adil, K.; Spanopoulos, I.; Trikalitis, P.N.; Emwas, A.-H. MOF Crystal Chemistry Paving the Way to Gas Storage Needs: Aluminum-Based soc-MOF for CH₄, O₂, and CO₂ Storage. *J. Am. Chem. Soc.* **2015**, *137*, 13308–13318. [[CrossRef](#)] [[PubMed](#)]
9. Stock, N.; Biswas, S. Synthesis of Metal–Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. *Chem. Rev.* **2011**, *112*, 933–969. [[CrossRef](#)] [[PubMed](#)]
10. Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C.-Y. Applications of metal–organic frameworks in heterogeneous supramolecular catalysis. *Chem. Soc. Rev.* **2014**, *43*, 6011–6061. [[CrossRef](#)] [[PubMed](#)]
11. Horcajada, P.; Chalati, T.; Serre, C.; Gillet, B.; Sebrie, C.; Baati, T.; Eubank, J.F.; Heurtaux, D.; Clayette, P.; Kreuz, C. Porous metal–organic–framework nanoscale carriers as a potential platform for drug delivery and imaging. *Nat. Mater.* **2010**, *9*, 172–178. [[CrossRef](#)] [[PubMed](#)]
12. Cavka, J.H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K.P. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851. [[CrossRef](#)] [[PubMed](#)]
13. Liu, X.; Demir, N.K.; Wu, Z.; Li, K. Highly Water-Stable Zirconium Metal–Organic Framework UiO-66 Membranes Supported on Alumina Hollow Fibers for Desalination. *J. Am. Chem. Soc.* **2015**, *137*, 6999–7002. [[CrossRef](#)] [[PubMed](#)]
14. Ma, X.; Zhao, Y. Biomedical Applications of Supramolecular Systems Based on Host–Guest Interactions. *Chem. Rev.* **2014**, *115*, 7794–7839. [[CrossRef](#)] [[PubMed](#)]
15. Hinterholzinger, F.M.; Rühle, B.; Wuttke, S.; Karaghiosoff, K.; Bein, T. Highly sensitive and selective fluoride detection in water through fluorophore release from a metal–organic framework. *Sci. Rep.* **2013**, *3*, 2562. [[CrossRef](#)] [[PubMed](#)]
16. Huang, Y.; Qin, W.; Li, Z.; Li, Y. Enhanced stability and CO₂ affinity of a UiO-66 type metal–organic framework decorated with dimethyl groups. *Dalton Trans.* **2012**, *41*, 9283–9285. [[CrossRef](#)] [[PubMed](#)]
17. Biswas, S.; der Voort, P.V. A General Strategy for the Synthesis of Functionalised UiO-66 Frameworks: Characterisation, Stability and CO₂ Adsorption Properties. *Eur. J. Inorg. Chem.* **2013**, *2013*, 2154–2160. [[CrossRef](#)]
18. Yang, J.; Dai, Y.; Zhu, X.; Wang, Z.; Li, Y.; Zhuang, Q.; Shi, J.; Gu, J. Metal–organic frameworks with inherent recognition sites for selective phosphate sensing through their coordination-induced fluorescence enhancement effect. *J. Mater. Chem. A* **2015**, *3*, 7445–7452. [[CrossRef](#)]
19. Chen, B.; Wang, L.; Zapata, F.; Qian, G.; Lobkovsky, E.B. A Luminescent Microporous Metal–Organic Framework for the Recognition and Sensing of Anions. *J. Am. Chem. Soc.* **2008**, *130*, 6718–6719. [[CrossRef](#)] [[PubMed](#)]
20. Wang, C.; Liu, X.; Chen, J.P.; Li, K. Superior removal of arsenic from water with zirconium metal–organic framework UiO-66. *Sci. Rep.* **2015**, *5*, 16613. [[CrossRef](#)] [[PubMed](#)]