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Aqueous medium fluoride anion sensing by fluorophore encapsulated UiO-66 type zirconium metal–organic framework

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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) was 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 release of 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

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1. Introduction

From past few decade, a tremendous effort has been dedicated by scientific community towards development of a modest strategy for selective and sensitive sensing of anions[1], as they play a key role in biological system, health and environment[2]. Among the anions present in biological system, smallest fluoride anion has drawn a significant attention due to its biological and environmental issue[3]. Nowadays presence of fluoride in drinking water and commercial household product is the emerging concern for public health[4]. Although the fluoride is considered as a micronutrient[5], but, the excess uptake of fluoride causes fluorosis[6] and even chronic renal failure[7]. So, there is an urgent necessity for selective and sensitive determination of fluoride anion in fluoride-contaminated water.

Metal-Organic Framework (MOF), a new class of porous material have received tremendous attention for their potential applications in gas storage[8], chemical separation[9], catalysis[10] and drug delivery[11]. 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]. Higher surface area, thermal resistivity, exceptional structural stability in water makes this as ideal molecular host material[13]. Triggered release of guest molecule by host dissolution is one of the efficient strategy for molecular recognition[14]. Recently Bein *et al.* has 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 sensitive sensing of fluoride ion in pure aqueous medium by fluoride triggered release of pyrene fluorophore from Zirconium based MOF, UiO-66[16]. First, we have synthesized in one step pyrene encapsulated UiO-66. Where Zr-O or μ_3-oxo bond of UiO-66 framework acts as a reactive probe and pyrene molecule as a signal transductor. Upon encapsulating inside the pore of framework fluorescence of pyrene was completely quenched. The addition of fluoride ion provoked the decomposition of the host UiO-66 and released pyrene provides a turn-on fluorescence.

2. Methods:

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

2.1. Synthesis

Syntheses of the pyrene containing UiO-66 framework were performed by as reported by Biswas et.al. with modification [17].

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 µg/mL) in a quartz glass cuvette at room temperature. A 4mM solution of different anions were 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 single step in situ encapsulation method. A certain amount of pyrene was added initially with $ZrCl_4$ and H_2BDC during synthesis. The pyrene@UiO-66 material was well characterized by various instrumental techniques such as X-ray powder diffraction (XRPD), FT-IR, and N_2 sorption analysis.

XRPD experiments showed that UiO-66 and pyrene@UiO-66 possess very similar XRPD patterns (Figure 1a). The similarity between the XRPD patterns of simulated and experimental confirms that the formation of pure UiO-66.

The N_2 sorption isotherms of pyrene@UiO-66 (Figure 1b) exhibited a little decrease in the surface area from as compared to UiO-66, which indicates the successful encapsulation of the pyrene into the pore of framework of UiO-66. Pyrene encapsulated UiO-66 shows a surface area of 898 cm^3/g which is lower than the guest free UiO-66 material (955 cm^3/g).

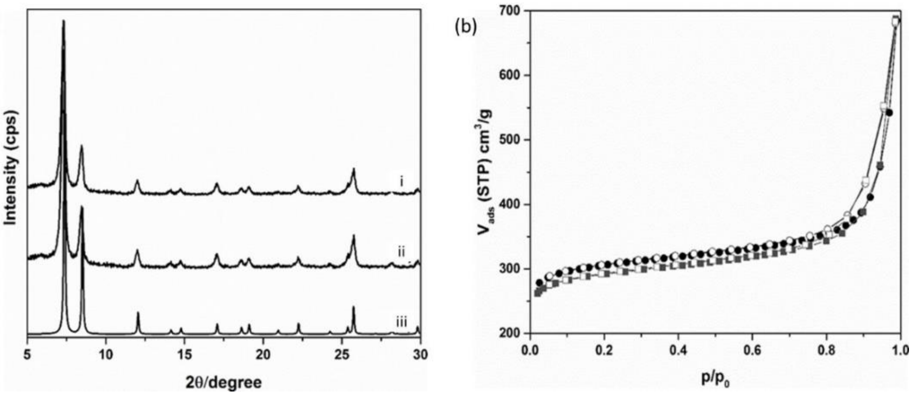

Figure 1. (a) XRPD pattern of (i) pyrene@UiO-66, (ii) only UiO-66 and (iii) simulated pattern of UiO-66 MOF. (b) Nitrogen adsorption (filled symbols) and desorption (empty symbols) isotherms of UiO-66 (circle) and pyrene@UiO-66 (square) collected at –196 °C.

3.2. Anion sensing experiment

The fluorescence emission spectra of pyrene@UiO-66 in water was recorded upon gradual addition of sodium (Na^+) salts of various anions (F^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, AcO^-, $S_2O_3^{2-}$, 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 was almost no change were observed in fluorescence emission spectra for other anions. The bar plot in Figure 3a summarized the selectivity of pyrene@UiO-66 towards F^- anion over other anions.

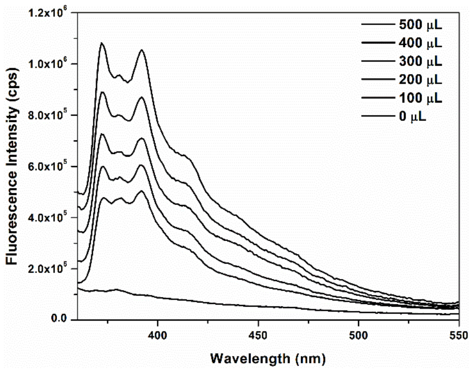

Figure 2: Change in fluorescence intensity with gradual addition of F^- solution to a suspension of pyrene@UiO-66 in aqueous medium.

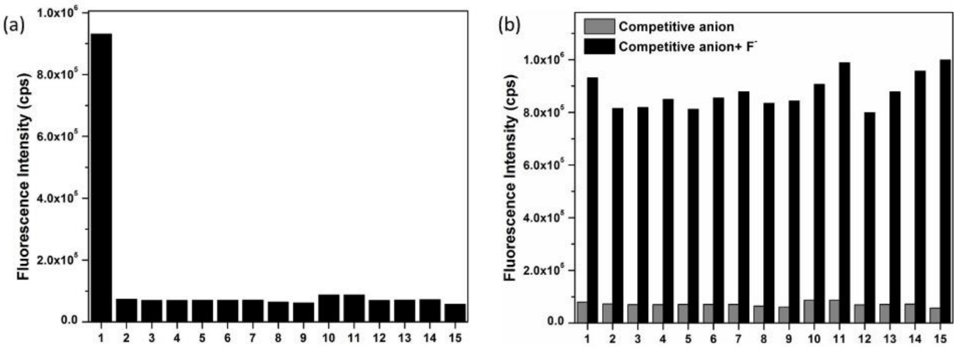

Figure 3: (a) Change in the fluorescence intensity of pyrene@UiO-66 upon incremental addition of different anions. (b) Change in the fluorescence intensity of pyrene@UiO-66 upon addition of F^- solution in the absence and presence of different anions. (F^- (1), Cl^- (2), Br^- (3), I^- (4), NO_2^- (5), NO_3^- (6), AcO^- (7), $S_2O_3^{2-}$ (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 pyrene@UiO-66 sensor material towards fluoride ion even in presence of other interfering ion generally present in water, competitive experiments were performed by monitoring the fluorescence emission intensity of pyrene@UiO-66 in 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 $F-$ anion. The change of the fluorescence intensity of pyrene@UiO-66 upon addition of $F-$ 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 sensing of $F-$ anion.

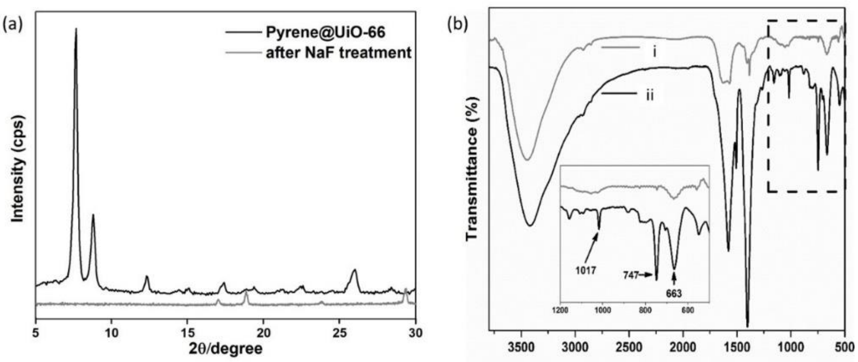

Figure 4: (a) The XRPD pattern and (b) FT-IR spectra of pyrene@UiO-66 before and after fluoride treatment.

3.3. Mechanism for anion sensing

Until now, few mechanisms have been proposed for anion sensing via Metal-Organic framework. Some of them are 1) anion induced coordination to metal-oxygen cluster[18] 2) hydrogen bonding formation with solvated framework[19] 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 fluoride anion solution. From Figure 4a it was shown that after fluoride treatment characteristic diffraction peak for UiO-66 framework vanished, which confirms the collapse of framework in presence of fluoride. Whereas no change was observed in XRPD pattern after treatment with other anions in aqueous solution (data not shown).

UiO-66 structure consist of an octahedron of zirconium atom. These octahedrons are capped by μ_3-oxo and μ_3-hydroxy group in an alternating fashion. Carboxylate group from benzenedicarboxylate linker (H_2BDC) connects these octahedral edges. The peak in FT-IR (between 1100-1000 cm^{-1}) ~1020 cm^{-1} can be assigned as Zr-OH bending vibration[20], which is vanished after fluoride treatment (Figure 4b). Thus, initially replacement of hydroxyl group may be responsible for the fluoride sensitivity of the MOF. Peak in FT-IR near 747 cm^{-1} and 663 cm^{-1} responsible for Zr-μ_3-oxo bond also almost disappeared. Which also suggest that fragmentation of μ3-oxo bond. Observation suggests that fluorescence enhancement in occurred *via* zirconium and fluoride coordination which leads the release of pyrene from framework host.

3. 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, but the easy, one step synthesis protocol, high stability, low toxicity makes this material as a promising candidate for fluoride sensing in aqueous medium.

Informed Consent Statement: Not applicable.

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

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