



Post-synthetic modification of a metal-organic framework with fluorescent-tag for dual naked-eye sensing in aqueous medium

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ABSTRACT

The existing metal-organic framework (MOF) called UiO-66-NH₂ (**1**; UiO = University of Oslo) was post-synthetically modified by condensation with 1-pyrenecarboxaldehyde. The pyrene-tagged MOF (**1'**) exhibited ~3-fold enhancement in fluorescence intensity over the un-functionalized one with a new emission peak at 470 nm due to the formation pyrene excimer within the framework of the MOF. **1'** showed fast response time, excellent selectivity and sensitivity for sensing of biologically active anions like F⁻ and H₂PO₄⁻ in pure aqueous medium via fluorescence 'turn-on' mechanism with detection limits of 8.2×10^{-7} M and 7.3×10^{-7} M, respectively. The fluorescence enhancement and the distinctive blue shifts in the emission bands of **1'** in presence of the anions are attributed to strong hydrogen bonding interactions and static pyrene excimer formation, respectively. **1'** also displayed rapid, selective and sensitive detection of 2,4,6-trinitrophenol (TNP) in aqueous medium via fluorescence 'turn-off' mechanism with a detection limit of 2.1×10^{-7} M. The highly selective fluorescence quenching is ascribed to electron and energy transfer processes as well as molecular interactions (π - π and electrostatic) of the MOF with TNP. The excellent detection performance of **1'** in aqueous medium makes it a promising dual sensor material for real-field applications.

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1. Introduction

Selective and sensitive detection of anions is a great concern among the scientific community, since they are universal in biological systems and play significant roles in wide areas of biology and pharmacy [1]. Development of a fluorescence-based anion sensor has aroused tremendous scientific interests, since fluorescence techniques are highly sensitive and easy to operate. Among the biologically active anions, fluoride and phosphate ions are attractive targets because of their considerable significance in health and environmental issues [2,3]. Digestion of excess fluoride can result in fluorosis, urolithiasis or even cancer [4]. US Environmental Protection Agency (EPA) has set a limit for fluoride that can be present in public-drinking water supplies to 4.0 mg/L (maximum contaminant level, MCL) with a secondary maximum contaminant level (SMCL) of 2 mg/L to protect against dental fluorosis [5]. Therefore, sensitive detection and quantification of the fluoride level in drinking water are highly desirable. Along the same line, phosphate anion is engaged in several biological processes such as transport across membranes, DNA synthesis, cell signaling, energy or

electron-transfer processes [6–8]. However, the opposing effect of excess phosphate in blood also causes some diseases such as hyperphosphatemia and cardiovascular complications resulting from the development of metastatic calcifications at the cardiac level [9]. Therefore, the development of fluorescent probes for the recognition of phosphate anions has received considerable attention.

However, despite the large number of anion sensor materials investigated so far in the literature, there exists only a handful of sensor systems with high selectivity and affinity, which can be easily adapted for practical applications [10–14]. This is specifically true when anion recognition in water is under consideration. The distinctive properties of water (e.g. polarity, H-bonding ability, etc.) [15] impose immense complications when the binding of anions in such media by sensor molecules has to be achieved. Most of the reported sensor materials work only in mixed organic-aqueous solution (with a content of 5–40% of an organic co-solvent such as dimethyl sulfoxide, acetonitrile or ethanol) [16–19]. Thus, they are not suitable for real-world applications. Hence, the development of a simple and inexpensive method for anion detection in aqueous medium is still a challenging task [20].

On the other hand, selective, sensitive and fast detection of nitroaromatic explosives (NAEs) is of vital importance for homeland security, environmental safety and human health [21]. Among various NAEs, 2,4,6-trinitrophenol (TNP, also known as picric acid)

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is a powerful explosive (even stronger than 2,4,6-trinitrotoluene or TNT) [22]. TNP is widely employed in leather, fireworks, pharmaceutical and dye industries. Therefore, the compound is a major environmental pollutant, if it is released to the environment by the industrial processes. Moreover, the discharge of TNP can cause numerous health problems such as skin irritation, anemia, and abnormal liver functions [23]. The existing detection methods for NAEs utilize sophisticated instruments, which are expensive, complex and have limited portability [24]. Therefore, there is an urgent need to develop low-cost, simple and field-applicable fluorescent probes for the rapid, selective and sensitive sensing of NAEs.

As a new generation of crystalline porous materials, metal-organic frameworks (MOFs) [25,26] have received tremendous attention in recent years not only owing to their intriguing structures but also for their potential applications in gas storage [27], chemical separation [28], heterogeneous catalysis [29] and drug delivery [30]. Another potential application of MOF materials is their use as fluorescent sensors. The tunable porosity, functional pore surfaces and bulk conjugated backbones of luminescent MOFs can propagate the host-guest interactions to detectable changes, making them promising candidates for sensing applications. One strategy for designing a MOF for fluorescence sensing applications is to attach fluorescent tags (e.g., pyrene, naphthalene, perylene, etc.) with the organic ligands [31]. Although numerous MOF-based sensors for nitroaromatic explosives have been developed till date [32–35], MOF-based anion recognition in pure aqueous medium still remains largely unexplored [36,37] considering the sensing of fluoride anion [38,39]. Herein we report, for the first time, a post-functionalized MOF with pyrene-tagged ligands which can selectively recognize biologically active anions, such as fluoride and dihydrogen phosphate as well as nitroaromatic explosives like TNP in pure aqueous medium. The pyrene-tagged MOF showed retention of the unique photophysical property of the pyrene fluorophore. The spatial arrangement of the pyrene moieties inside the framework and their accessibility towards various analytes were thoroughly investigated by steady-state as well as time-resolved fluorescence experiments. A comprehensive study indicated that molecular interactions (electrostatic, hydrogen bonding and π - π stacking) as well as electron and energy transfer processes are responsible for the dual sensing phenomena exhibited by this MOF material.

2. Experimental

Caution! TNT is potentially explosive, and caution should be exercised when dealing with such materials. However, the small quantities used in this study were not found to present a hazard.

2.1. Materials

All the starting materials were of reagent grade and used as received from the commercial suppliers. In order to avoid any explosion, TNT was synthesized in 50 mg by following a previously published procedure [40]. Milli-Q water was used as a medium in all the fluorescence titration experiments.

2.2. Characterization

Ambient temperature X-Ray powder diffraction (XRPD) patterns were recorded on a Bruker D2 Phaser X-ray diffractometer operated at 30 kV, 10 mA using Cu-K α ($\lambda = 1.5406 \text{ \AA}$). Thermogravimetric analysis (TGA) was performed with a Mettler-Toledo TGA/SDTA 851e thermogravimetric analyzer in a temperature range of 30–700 °C under air atmosphere at a heating rate of 5 °C min⁻¹. The nitrogen sorption isotherms up to 1 bar were measured using a Quantachrome Autosorb iQ-MP gas sorption

analyzer at –196 °C. Prior to the sorption experiments, the compounds were degassed at 120 °C for 12 h under dynamic vacuum. Fluorescence emission studies were carried out 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 fluorescence decays were analyzed by reconvolution method using the FAST software provided by Edinburgh Instruments. Liquid-state ¹H NMR spectra were measured with a Bruker DPX 500 spectrometer at ambient temperature in the solvent of d₆-DMSO using TMS as internal reference. The solid state cross-polarization magic angle spinning (CP/MAS) ¹³C NMR spectrum was recorded on a Bruker Avance III 400 NMR spectrometer. Field emission scanning electron microscopy (FE-SEM) images were recorded on a Hitachi 4700 field emission scanning electron microscope. Mass spectrum was recorded by Waters Q-ToF Premier Liquid Chromatography–Mass Spectroscopy (LC–MS) system.

2.3. Synthesis of UiO-66-NH₂ (**1**)

Synthesis of **1** was performed by the literature procedure, as reported by Biswas *et al.* [41]. In brief, a mixture of ZrOCl₂·8H₂O (100 mg, 0.31 mmol), formic acid (1.2 mL, 3.18 mmol) and *N,N*-dimethylacetamide (3 mL) was sonicated for 30 min. Then, 2-aminoterephthalic acid (denoted as H₂L hereafter) ligand (56 mg, 0.31 mmol) was added to the clear solution. The resulting solution was heated in a sealed glass tube at 150 °C for 24 h using a block heater. After spontaneous cooling to room temperature, the bright yellow precipitate was collected by centrifugation. Yield: 70 mg (77%). The as-synthesized **1** was activated by using the same literature method [41].

2.4. Post synthetic modification of **1**

A mixture of 60 mg (0.2 mM of –NH₂) of **1** and 50 mg (0.21 mM) of 1-pyrenecarboxaldehyde was placed in round bottom flask containing 15 mL of dry methanol. The resulting mixture refluxed under nitrogen atmosphere for 6 h. After cooling to room temperature, the solid was separated by filtration and washed with *N,N*-dimethylformamide. The filtered solid was stirred in methanol at room temperature for 24 h. After that the Schiff base modified orange colored material was collected by filtration and dried at 60 °C for 12 h in a conventional oven. Yield: 52 mg (76%). Hereafter, this post-synthetically modified solid and the corresponding ligand are denoted as **1'** and H₂L', respectively.

2.5. Fluorescence titration experiments

For fluorescence titration measurements, a suspension of **1'** in water with a concentration of 1 mg/mL was prepared by ultrasonic treatment for 30 min. Subsequently, 100 μ L of this suspension was diluted with 2900 μ L of water (final concentration of 33 μ g/mL) in a quartz cuvette and the solutions of different analytes were incrementally added. For all the titration measurements, emission was monitored at 470 nm, using an excitation wavelength of 360 nm. For anion and nitroaromatic explosives initially ~10 mM solution was prepared in water (minimum amount of ethanol was used to dissolve the less soluble nitroaromatics in water). Desired concentration of analyte was obtained by proper dilution. The titration experiments for sensing anions were performed by incremental addition of 3 mM solution of various TBA salts (TBA⁺X⁻) to a 3 mL well-dispersed aqueous suspension of **1'**. For the detection of nitroaromatic explosives, the titration measurements were carried out by incremental addition of 1 mM solution of different nitroaromatic explosives to a 3 mL aqueous suspension of **1'**. The quenching efficiency was calculated by using $(1 - I/I_0) \times 100\%$, where I_0 is the

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