



Fluoride detection with a redox-active naphthalene diimide metal–organic framework

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ABSTRACT

Fluoride is commonly added to drinking water supplies for dental health; however, exposure to elevated fluoride levels can cause significant health problems. Therefore, it is important to develop simple and robust methods for monitoring fluoride in solution. Metal–organic frameworks (MOFs) have been targeted as ideal materials for next-generation sensing technologies, due to their combination of high surface area and chemical tunability. Here we report that a mesoporous MOF with redox-active naphthalene diimide-based ligands exhibits a selective and reversible color-change response to fluoride anion. The incorporation of fluoride sensing organic molecules into a MOF allows for the development of solid-state sensor devices that offer advantages relative to solution-phase methods.

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1. Introduction

Porous metal–organic frameworks (MOFs) have recently been explored as functional materials for next-generation chemical sensors [1–3]. MOFs are in many ways an ideal platform for the development of “designer” sensing materials, due to a combination of high surface area and modular synthetic design. In particular, redox-active MOFs display great promise for sensing, including electronic sensor devices [1,3–6].

While fluoride is commonly added to drinking water supplies to promote dental health, it is well known that exposure to elevated levels of fluoride in drinking water raises the risk of dental fluorosis [7–11]. Therefore, effort has been devoted to developing selective and sensitive methods of fluoride detection [12–17]. One strategy that has received significant attention has been the colorimetric sensing of fluoride using variously substituted naphthalene diimide (NDI) molecules [18–23]. In some examples, the color change results from the reduction of NDIs to differently colored $\text{NDI}^{\cdot-}$ radical anions or NDI^{2-} dianions. The Saha group proposed that a selective π -anion interaction between NDI-based receptors and fluoride can lead to an electron transfer that generates $\text{NDI}^{\cdot-}$ or NDI^{2-} , depending on the amount of fluoride added [24,25]. The observed response could be further promoted through a synthetic design that preorganizes two NDI units in an overlapping conformation. Others have pointed out, however, that direct reduction of NDI by fluoride is unlikely on thermodynamic grounds

[21,26,27], and the Gabbai group has put forth an alternate explanation that fluoride’s basicity leads to deprotonated solvent side-products that ultimately serve to reduce NDI [28]. While the mechanistic details of fluoride-induced NDI reduction are still unclear, the selective and dramatic response of NDIs towards fluoride remains a potentially useful approach for fluoride sensing.

We envisioned that solution-phase fluoride sensing using NDI molecules could be translated to solid-state fluoride sensor devices, via the incorporation of NDI-based ligands into a porous MOF. Organization of the NDI subunits in the rigid crystalline structure of the MOF could also serve to enhance the sensing response. Solid-state sensor materials and devices offer practical advantages as compared to solution-phase sensor/receptor molecules. Additionally, the development of strategies for fluoride sensing with redox-active MOFs could ultimately lead to advances such as MOF-based fluoride sensitive electrodes [29,30].

2. Experimental

2.1. Materials and methods

All manipulations were carried out under ambient atmosphere, using reagent-grade chemicals and solvents, unless otherwise noted. Reagents and solvents were purchased from Sigma Aldrich and used as received.

NMR spectra were recorded on a Bruker Avance spectrometer operating at 300 MHz for ^1H acquisitions. UV–vis spectra were measured on a Varian Cary 5000 spectrophotometer. EPR spectra were collected on a Bruker EMX spectrometer operating at X-band

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frequency; samples were measured in 2 mm quartz tubes at ambient temperature. PXRD data were recorded on a PANalytical XPert3 diffractometer with a Cu K α X-ray source and PIXcel 1d detector, in a Bragg-Brentano geometry.

2.2. Synthesis of H₄NDISA

The H₄NDISA ligand was synthesized according to the procedure in Ref. [34].

Under an Ar atmosphere, 1,4,5,8-naphthalenetetracarboxylic dianhydride (1.0 g, 3.7 mmol, 1.0 equiv), 5-amino-2-hydroxybenzoic acid (1.2 g, 7.8 mmol, 2.1 equiv), and anhydrous DMF (35 mL) were added to a 100 mL Schlenk flask. The reaction mixture was stirred at 130 °C for 12 h, then cooled to room temperature and opened to ambient atmosphere. The resulting orange solid was isolated via vacuum filtration, washed with DMF, diethyl ether, and methanol, and then dried under vacuum to afford the product as an orange powder. ¹H NMR analysis was consistent with the previously reported data.

2.3. Synthesis of Ni-NDISA

Ni-NDISA (powder or thin film) was synthesized according to the procedure in Ref. [34].

Powder: To a 20 mL vial was added H₄NDISA (55 mg, 0.094 mmol), Ni(NO₃)₂·6H₂O (104 mg, 0.36 mmol), DMF (7.5 mL), EtOH (0.5 mL), and H₂O (0.5 mL). The vial was capped, and the reaction mixture was heated at 120 °C for 12 h. After cooling, the solid product was isolated by vacuum filtration and washed with fresh DMF. The solids were then stored under DMF prior to use.

Thin films: To a 20 mL vial was added H₄NDISA (55 mg, 0.094 mmol), Ni(NO₃)₂·6H₂O (90 mg, 0.31 mmol), anhydrous DMF (10 mL) and anhydrous MeOH (1 mL). A glass slide was submerged in the reaction mixture, then the vial was capped and placed at 120 °C for 20 min. After cooling to room temperature, the glass slide was removed and carefully washed with fresh DMF. The MOF-coated slides were stored under DMF prior to use.

Note: Extensive drying under vacuum, or extended storage as a dry powder, results in decomposition of Ni-NDISA as determined by PXRD analysis. We find that best results are obtained when the MOF is stored under DMF after synthesis and purification, then isolated via vacuum filtration immediately prior to weighing.

2.4. Procedure for ion detection experiments

20 mg of Ni-NDISA was added to a 20 mL vial, and then suspended in 3 mL of DMF. Tetra-*n*-butylammonium halide (TBAX; X = F, Cl, Br, I) was then added (3 equiv, relative to equivalents of NDI in the MOF), and the suspension was briefly swirled. No changes were observed for X = Cl, Br, I, whereas a rapid color change to black was observed for X = F (see Fig. 3).

Note: All ion detection experiments were conducted under ambient atmosphere, using reagent-grade solvents that were neither dried nor deoxygenated.

2.5. Fabrication of paper fluoride test strips

Paper fluoride test strips were made by cutting filter paper (VWR Grade 413) into strips (1 × 6 cm). Each strip was first saturated with DMF. A suspension of Ni-NDISA (20 mg) in DMF (5 mL) was immersed in an ultrasonic bath for 5 min to disperse the solids. The end of a paper strip was then held in the MOF suspension, and sonication was continued for 1–2 min to embed the MOF solids into the paper. The MOF-infused paper strips were kept wet with DMF until use.

3. Results and discussion

3.1. Choice of suitable MOF for fluoride sensing

In targeting a suitable MOF for fluoride detection in solution, we considered several design criteria: high porosity to allow for efficient ion transport; accessibility of the NDI subunits to fluoride ions in the MOF pores; and stability of the MOF towards fluoride. We also chose not to use the large number of NDI-based MOFs that exhibit photochromism [31–33], in order to avoid potentially competing responses between fluoride and ambient light. From surveying the literature, we identified the mesoporous MOF-74 analogs M-NDISA (M = Mg, Ni) as promising candidates [34]. Synthesis of M-NDISA, as either polycrystalline bulk samples or as thin films, is accomplished via standard solvothermal methods from M (NO₃)₂ and the free ligand H₄NDISA (Fig. 1, top). The H₄NDISA ligand is synthesized in one step from commercially available starting materials. Thin films of M-NDISA have previously been shown to exhibit fast and reversible electrochromic switching from transparent to dark states, based on redox activity of the NDI ligands. We anticipated that intercalation of fluoride via the ~3.3 nm mesopores of the MOF should allow for a selective response via reduction of the NDI subunits of the ligands (Fig. 1, bottom).

3.2. Evaluation of M-NDISA stability towards fluoride

Initial tests were conducted using bulk polycrystalline samples of the MOF. The as-synthesized M-NDISA MOFs were suspended in DMF, after which tetra-*n*-butylammonium fluoride (TBAF) was added to the suspension. In accordance with results from previous studies using molecular NDI-based fluoride sensors [24], fluoride amounts in the range of ≤5 equivalents were used (equivalents of fluoride were calculated with respect to the NDI subunits in the MOF, using the reported molecular formulae for M-NDISA). We found that Mg-NDISA was unstable towards fluoride: addition of TBAF to suspensions of Mg-NDISA quickly resulted in dissolution of the framework. Gratifyingly, however, Ni-NDISA displayed stability towards fluoride solutions over the course of several hours, as established by powder X-ray diffraction (PXRD). Diffraction patterns measured for Ni-NDISA matched well with the simulated pattern, and no change was observed after fluoride exposure (Fig. 2). Longer exposure times (e.g. several days) did lead to eventual degradation of Ni-NDISA.

3.3. Response of Ni-NDISA to anion solutions

In order to evaluate the response of Ni-NDISA towards fluoride and other halide anions, suspensions of Ni-NDISA were prepared in DMF, and then 3 equivalents of halide (fluoride, chloride, bromide, and iodide) were added as their tetra-*n*-butylammonium salts. Addition of TBAF produced a rapid and dramatic color change in the MOF solids from red/orange to black. Addition of other halide salts did not produce an observable color change as compared to the as-synthesized MOF (Fig. 3, left). These results are consistent with previous studies on molecular NDI-based fluoride sensors, and show that selective fluoride-induced reduction of NDIs can also take place in a solid-state framework. The rapid response also suggests facile ion transport through the mesopores of the MOF. Leaching of the colored NDI ligand into solution was not seen on the timescale of our experiments (minutes to hours), in line with the observed stability of Ni-NDISA towards fluoride. Interestingly, when the MOF solids were isolated by filtration after fluoride exposure, the color quickly reverted back to orange. Removal from the

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