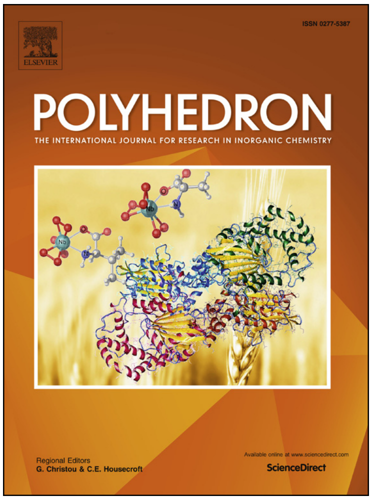

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Fluoride Detection with a Redox-Active Naphthalene Diimide Metal–Organic Framework

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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.

Keywords: metal–organic frameworks; fluoride; sensors

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 NDI$^{\bullet-}$ 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 NDI$^{\bullet-}$ 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 Gabbaï 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 ^{1}H 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 frequency; samples were measured in 2 mm quartz tubes at ambient temperature. PXRD data were recorded on a PANalytical XPert3 diffractometer with a Cu Kα X-ray source and PIXcel 1d detector, in a Bragg-Brentano geometry.

2.2 Synthesis of ***H_4NDISA***

The **H_4NDISA** ligand was synthesized according to the procedure in reference 34. Under an Ar atmosphere, 1,4,5,8-napthalenetetracarboxylic 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 hours, 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. ^{1}H 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 reference 34.

Powder: To a 20 mL vial was added H_4NDISA (55 mg, 0.094 mmol), $Ni(NO_3)_2{\bullet}6H_2O$ (104 mg, 0.36 mmol), DMF (7.5 mL), EtOH (0.5 mL), and H_2O (0.5 mL). The vial was capped, and the reaction mixture was heated at 120 °C for 12 hours. 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 H_4NDISA (55 mg, 0.094 mmol), $Ni(NO_3)_2{\bullet}6H_2O$ (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 minutes. 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 Figure 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 minutes to disperse the solids. The end of a paper strip was then held in the MOF suspension, and sonication was continued for 1–2 minutes 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 analogues 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 $M(NO_3)_2$ and the free ligand H_4NDISA (Figure 1, top). The H_4NDISA 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 (Figure 1, bottom).

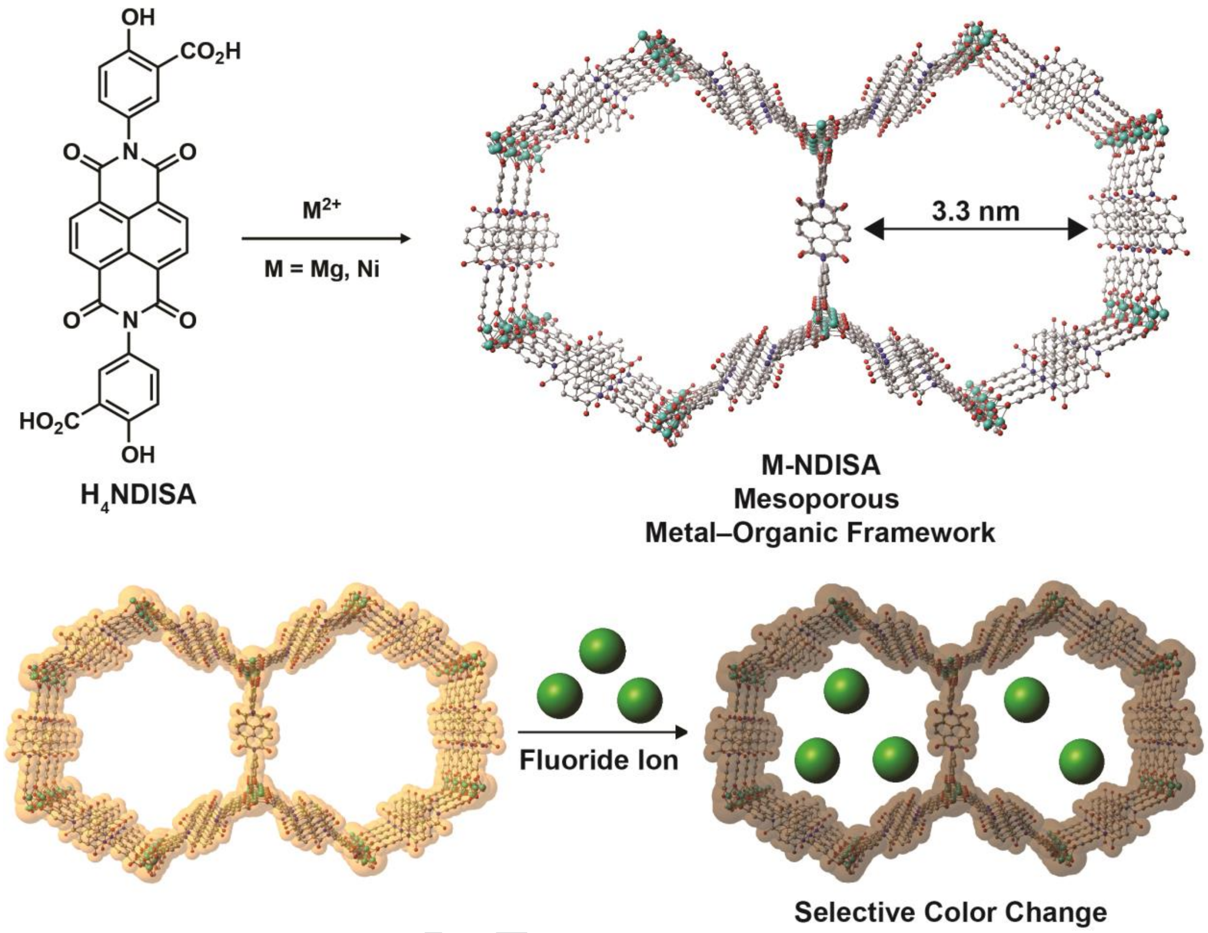

Figure 1. Synthesis and structure of the mesoporous MOFs M-NDISA (top); conceptual schematic of fluoride-induced reduction to produce a selective color change response (bottom).

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 (Figure 2). Longer exposure times (e.g. several days) did lead to eventual degradation of Ni-NDISA.

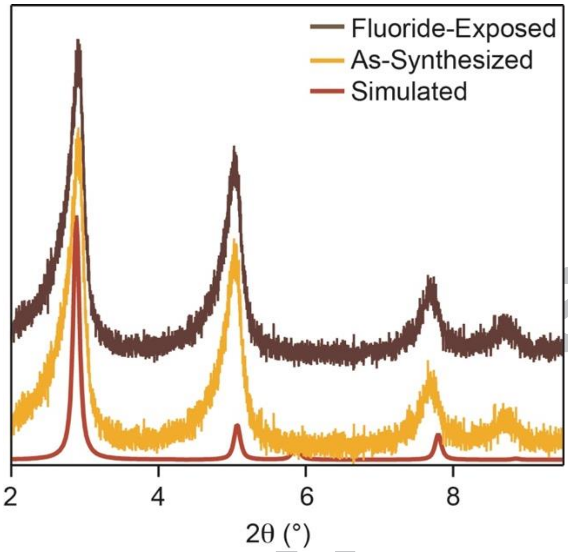

Figure 2. PXRD data for Ni-NDISA: simulated diffraction pattern (bottom); as-synthesized Ni-NDISA (middle); Ni-NDISA after exposure to a solution of TBAF in DMF (top).

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 (Figure 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 fluoride-containing solution likely allows for re-oxidation of the NDI ligands by air.

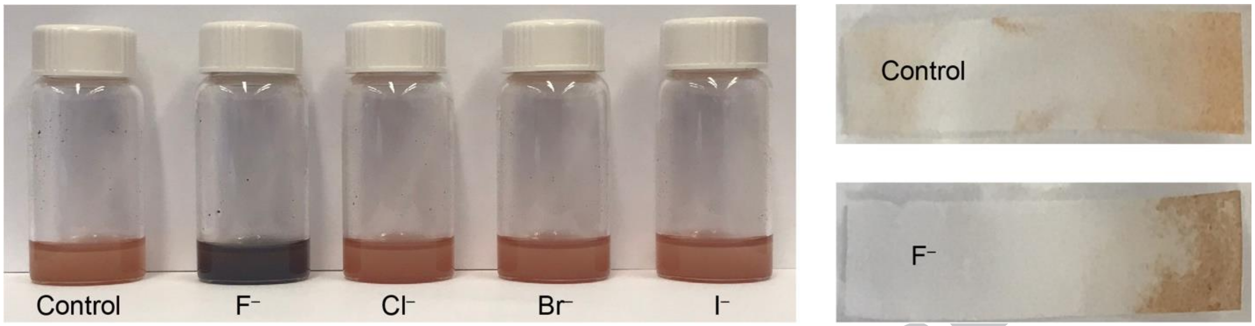

Figure 3. Optical images of Ni-NDISA suspensions before and after exposure to halide anions in DMF solutions (left); paper test strips fabricated from Ni-NDISA, showing a color change after exposure to fluoride in solution (right).

For practical applications, fluoride sensing in aqueous solutions is important. We therefore explored the effect of water on the response of Ni-NDISA towards fluoride. Exposure of Ni-NDISA to fluoride in pure water was not successful due to the limited stability of Ni-NDISA in water, so we tested mixed solvent systems. We found that addition of water to DMF solutions completely shut down reactivity of the MOF with fluoride: if Ni-NDISA was suspended in a 85/15 mixture of DMF/H_2O, addition of TBAF produced no response; similarly, after TBAF was added to a suspension of Ni-NDISA in DMF, subsequent addition of water reversed the observed color change. If DMSO was used in place of DMF, the color change response upon addition of TBAF was nearly identical (Figure 4, left). Unlike DMF, however, a mixed solvent system of 85/15 DMSO/H_2O still led to a color change response upon addition of TBAF, albeit less pronounced (Figure 4, right). This solvent-dependent behavior is consistent with the hypothesis that acid/base reactivity with solvent mediates NDI reduction in the presence of fluoride [28].

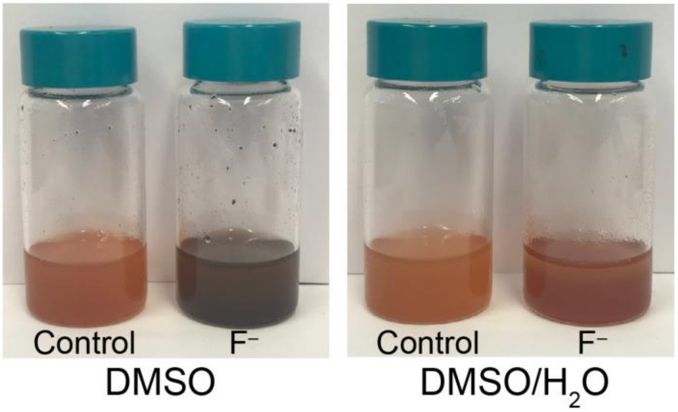

Figure 4. Optical images of Ni-NDISA suspensions before and after exposure to TBAF in DMSO solutions, showing the effect of added water.

3.4 Paper Test Strips for Fluoride Detection

Previously reported examples of molecular NDI-based fluoride sensors have primarily focused on solution-phase reactivity, which limits practical applications [18–25]. We envision that a significant advantage of incorporating the NDI moiety into a porous MOF is the ability to develop solid-state fluoride sensor devices. As a proof-of-concept demonstration, we have fabricated simple “dip strip” papers using Ni-NDISA. Strips of filter paper were infused with solid Ni-NDISA by immersing the ends of the paper in a DMF suspension of Ni-NDISA, in an ultrasonic bath. The MOF-infused paper strips displayed a pale orange color, which selectively turned dark brown after dipping into a DMF solution of TBAF (Figure 3, right). We found that the color change was less dramatic for the paper strips, as compared to suspensions of Ni-NDISA. This is primarily due to the reversibility of the color change: as with the bulk solids, the “dip strips” rapidly lost their dark color after removal from the fluoride solution.

3.5 Spectroscopic Characterization

The selective color change of the MOF in the presence of fluoride anion was probed using electronic absorption spectroscopy. Thin films of Ni-NDISA were grown on the surface of glass slides. Transmission UV-vis spectra were then acquired before and after exposure to a TBAF solution in DMF (Figure 5). As with the bulk solids, Ni-NDISA thin films displayed a selective transparent-to-dark color change response to fluoride (Figure 5, inset). The spectrum before fluoride exposure is consistent with previous data for Ni-NDISA and displays characteristic peaks for $\pi \rightarrow \pi^*$ transitions of the neutral NDI core (λ_{max} = 342, 363, and 385 nm) [34,35]. Exposure to fluoride produces new absorption maxima throughout the visible region of the spectrum (λ_{max} = 474, 607, 700, and 780 nm). The spectral features that appear after fluoride exposure are nearly identical to spectroelectrochemical data for films of Ni-NIDSA in which the ligands have been reduced to the $NDI^{\bullet-}$ radical anion form [34]. In contrast to solution-phase fluoride sensing with NDI-based molecules, peaks corresponding to the NDI^{2-} dianion were not observed, even after extended exposure times to a larger excess of TBAF [24]. After removing the Ni-NDISA film from the TBAF solution, the color faded within seconds, and the UV-vis spectrum was identical to the as-synthesized material. This could be repeated for several cycles of TBAF exposure, although after a few cycles the film began to delaminate from the glass substrate. The observed reversibility is promising for the development of reusable MOF-based fluoride sensors.

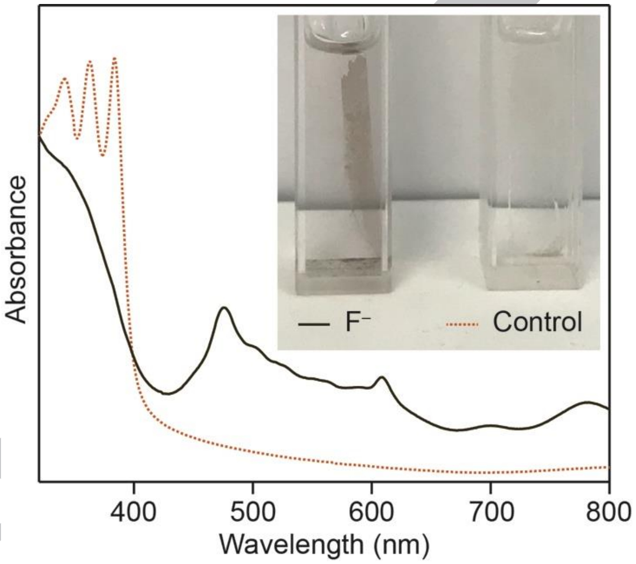

Figure 5. Normalized transmission UV-vis spectra of Ni-NDISA thin films before and after exposure to a solution of TBAF in DMF; the inset shows optical images of the films on glass slides inside of quartz cuvettes.

Consistent with the UV-vis data, electron paramagnetic resonance (EPR) spectroscopy clearly indicates the formation of radical anion ligands after fluoride exposure. While the as-synthesized Ni-NDISA MOF is EPR silent, exposure to fluoride results in the appearance of a signal centered at approximately g = 2.006 (Figure 6). Typical of $NDI^{\bullet-}$ radical anions, a 13-line pattern is observed, due to coupling with two equivalent nitrogen nuclei and four equivalent protons in the NDI core [35]. The combined data show that fluoride exposure results in reduction of the MOF ligands to their radical anion form, without destruction of the MOF framework.

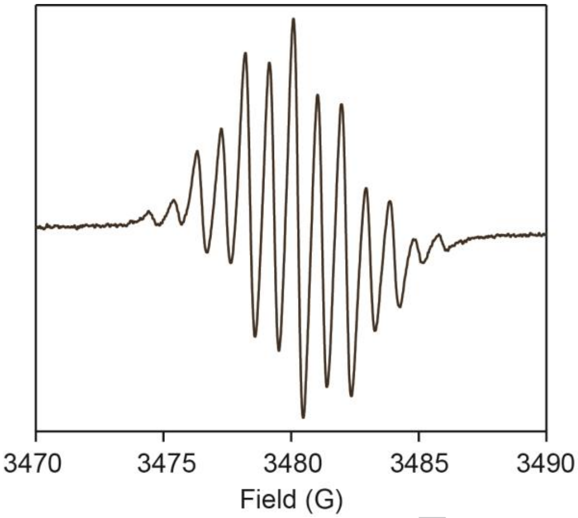

Figure 6. X-band EPR spectrum of Ni-NDISA after exposure to a solution of TBAF in DMF (100 kHz modulation frequency, 0.2 G modulation amplitude); no signal is observed prior to fluoride exposure.

Because fluoride exposure generates ligand-based radicals, we were also curious about the electrical response of Ni-NDISA in the presence of fluoride. We performed preliminary electrical conductivity studies on Ni-NDISA before and after fluoride exposure and observed slight increases in conductivity. However, these efforts were hampered by the fact that the color change response does not persist if the MOF is isolated from the fluoride-containing suspension, which complicates device fabrication. Additionally, under our measurement conditions, the change in conductivity was not anion-specific. Exposure to TBACl also produced a comparable increase in conductivity. Future studies in our lab will aim to further explore the electrical response of NDI-based MOFs to fluoride exposure – the development of new fluoride-sensitive electrodes based on redox-active MOFs would be a significant advance.

4. Conclusions

We have reported the first example of using a redox-active MOF for the detection of fluoride anions in solution. Incorporation of naphthalene diimide-based ligands into a mesoporous MOF allows for rapid and selective color-change response in the presence of fluoride, which represents a practical advantage over previously reported solution-phase systems. We anticipate that future work will result in improved MOF-based technologies for monitoring fluoride levels in solution. In particular, the development of water-stable, redox-active MOFs that exhibit a selective electrical response towards fluoride in aqueous solutions would provide a platform for next-generation fluoride sensors.

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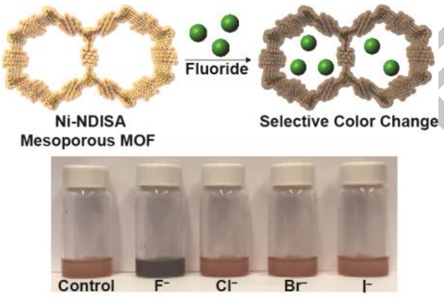
Graphical abstract



Synopsis: We report the first example of using a redox-active metal–organic framework (MOF) for the detection of fluoride anions in solution. These results provide a platform for the development of improved MOF-based fluoride sensor devices.