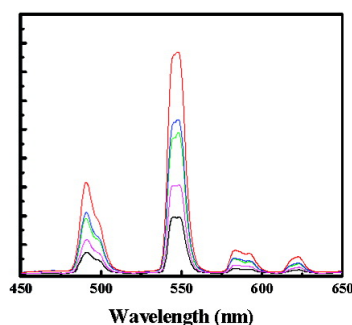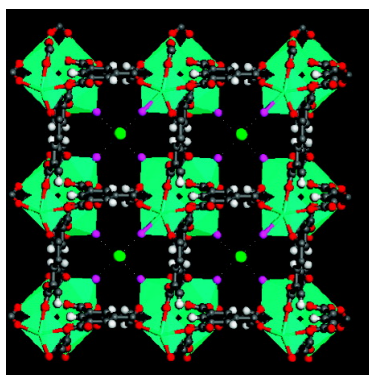Communication

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A Luminescent Microporous Metal−Organic Framework for the Recognition and Sensing of Anions

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There has been extensive interest in recognition and sensing of anions because of their important roles in biological and environmental systems.[1] The receptors developed for such anion recognition have mainly focused on organic and metal−organic supramolecules in which N−H and O−H organic groups are utilized to direct their differential hydrogen bonding with anions.[2] The emerging microporous metal−organic frameworks (MOFs) have attracted wide attention for their superior functional properties and application in gas storage, separation, and heterogeneous catalysis,[3] while their sensing function has rarely been realized, particularly the sensing of anions.[4−11] Given the richness of N−H and O−H containing organic linkers and terminal organic solvents within MOFs to induce hydrogen bonding interactions with anions, microporous MOFs are expected to be very promising solid materials for the recognition and sensing of anions. Such a recognition event can be readily transformed into an external luminescence intensity change once luminescent metal sites and/or organic linkers have been incorporated into the luminescent MOFs. Herein we report a prototype luminescent MOF, Tb(BTC)·G (**MOF-76**: BTC = benzene-1,3,5-tricarboxylate, G = guest solvent),[12] for the recognition and sensing of anions, exhibiting a high-sensitivity sensing function with respect to fluoride.

The basic structural feature of **MOF-76** is the one-dimensional channels of about 6.6×6.6 Å^2 along the c axis in which the terminal solvent molecules partially occupy the pores (Figure 1). Its high stability has allowed us to easily remove the terminal solvents at 150 °C under high vacuum and then to reintroduce organic solvents back to Tb^{3+} sites once the evacuated Tb(BTC) are immersed in organic solvents.

The evacuated Tb(BTC) was immersed in methanol solution containing different amounts of NaX (X = F$^-$, Cl$^-$, and Br$^-$) and Na$_2$X (X = CO$_3^{2-}$ and SO$_4^{2-}$) to form the anion incorporated Tb(BTC)·G (**MOF-76b**, G = methanol) microcrystalline solids for luminescence studies. The excitation and photoluminescence (PL) spectra of **MOF-76b** are shown in Figure 2. The excitation peak around 353 nm is assigned to the absorption of BTC ligands and the fluorescence peaks at 620, 584, 548, and 492 nm could be attributed to $^5D_4 \rightarrow {}^7F_3$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_5$, and $^5D_4 \rightarrow {}^7F_6$ transitions of Tb^{3+} ion, respectively. The most interesting feature is that the luminescence intensity of the anion incorporated **MOF-76b** is significantly enhanced, particularly for the F$^-$ incorporated MOF. The luminescence intensity of the F$^-$ incorporated **MOF-76b** activated from 10^{-2} M NaF methanol solution is about four times stronger than that of non-F$^-$ incorporated **MOF-76b** (Figures 2 and 3), underlying the potential of **MOF-76** for anion sensing.

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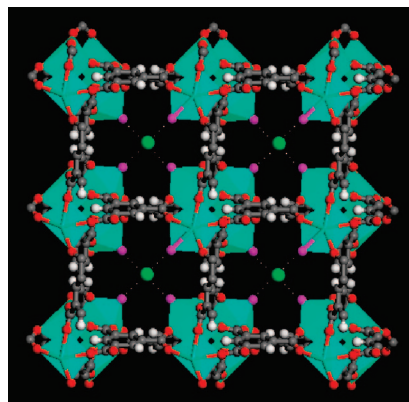‡ Zhejiang University.
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Figure 1. Single crystal X-ray structure of **MOF-76b** activated in methanol containing NaF with the model of fluoride (green) at the center of the channel involving its hydrogen-bonding interaction with terminal methanol molecules (methanol oxygen, purple; the methyl group from methanol is omitted for clarity).
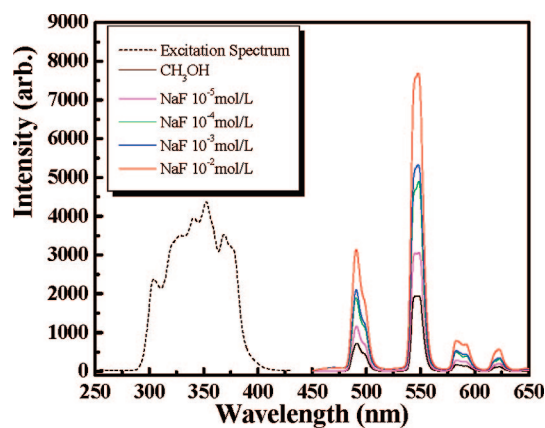

Figure 2. Excitation (dotted) and PL spectra (solid) of **MOF-76b** solid activated in different concentrations of NaF methanol solution (excited and monitored at 353 and 548 nm, respectively).

To elucidate the mechanism for such luminescence enhancement with the addition of anions, the evacuated Tb(BTC) was immersed in methanol solution containing NaF (Tb(BTC)/NaF mole ratio = 1:1) to form F$^-$ incorporated **MOF-76b** crystal solids for energy dispersive spectroscopy (EDS) and single crystal X-ray diffraction studies. EDS studies clearly indicate that the fluoride has been incorporated into the framework solids (S3), while the terminal Tb−O bond distance of 2.48 Å revealed in the single crystal X-ray structure excludes the possible direct coordination of F$^-$ with Tb^{3+}, given the fact that the typical Tb−F bond distances are in the range
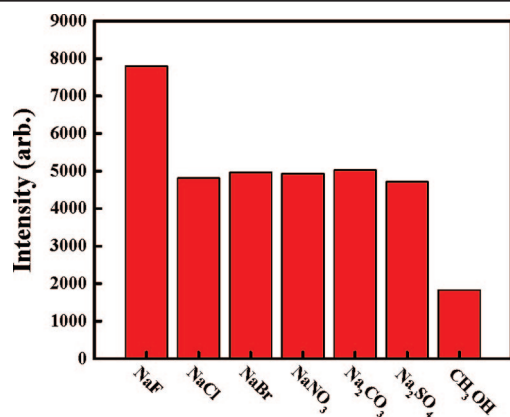
Figure 3. $^5D_4 \rightarrow {}^7F_5$ transition intensities of **MOF-76b** activated in different types of 10^{-2} M NaX and Na$_2$X methanol solution (excited and monitored at 353 and 548 nm, respectively).

of 2.1−2.2 Å.[13] It is speculated that the F$^-$ anions are immobilized within micropores to form hydrogen bonding interactions with the terminal methanol molecules. Suppose that the F$^-$ anions are located at the center of the micropores (Figure 1), the F$^-$···O (from methanol) distances will be around 2.78 to 3.24 Å which are reasonably in the range of hydrogen bonding distance for F$^-$···H−OCH$_3$.[14] Tb^{3+}, BTC^{3-}, methanol, and F$^-$ within **MOF-76b** work collaboratively to fulfill the sensing function. Tb^{3+} provides the basic luminescence arising from the electronic transitions among the 4f orbitals. Such luminescence can be sensitized by intramolecular energy transfer by employing light-harvesting BTC organic ligands (so-called antenna chromophores).[15] To make use of the hydrogen bonding interactions between methanol molecules and F$^-$, the quenching effect of O−H bond stretching within the terminal methanol on the luminescence intensity can be tuned by a differential amount of F$^-$, thus addition of F$^-$ can enhance the luminescence intensity. The detailed luminescence mechanism is provided in Supporting Information (S5−6). The stronger hydrogen-bonding interaction between the F$^-$ and methanol has led to its higher luminescence enhancement.

The as-synthesized Tb(BTC)·G (**MOF-76a**, G = DMF) was also examined for the fluoride sensing function. The corresponding luminescence intensity of the F$^-$ incorporated **MOF-76a** solid activated from 10^{-2} M NaF methanol solution is about twice that of non-F$^-$ incorporated **MOF-76a** (Figure S4). The terminal DMF molecules in the as-synthesized **MOF-76a** are expected to induce weaker interactions with fluorides. Furthermore, the C−H and C=O bonds in DMF are less sensitive than the O−H bond in methanol for the luminescence response, leading to lower sensitivity of as-synthesized **MOF-76a** for fluoride sensing.

The **MOF-76b** examined after sensing studies can be partially regenerated by immersion of the F$^-$ incorporated **MOF-76b** in pure methanol for 1 day followed by further anion sensing. The regenerated **MOF-76b** still exhibits a differential luminescence response once NaF has been added (Figure S5). To tune the interactions between the terminal solvents and fluoride anions by

changing the pore structures and curvatures, more reversible luminescent MOFs might be realized for such anion sensing.

The mechanism of **MOF-76** for the recognition and sensing of anions reported here is to make use of O−H moieties within the terminal solvents for their recognition of anions, which is quite different from that of Tb$_2$(Mucicate)$_3$ in which O−H groups within organic linkers have been utilized for the recognition and sensing event.[8] The easy access to luminescent MOFs with a variety of terminal solvents and pore structures to tune their sensing function with specific anions, together with the promise for reversible anion sensing will make such a new strategy very practical and useful in exploring luminescent microporous anion sensors. We are now targeting some robust luminescent microporous MOFs for their reversible anion sensing in aqueous solution.

Supporting Information Available: (a) X-ray structure data in CIF format; (b) details of experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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