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Post-modification of a MOF through a fluorescent-labeling technology for the selective sensing and adsorption of Ag^+ in aqueous solution†

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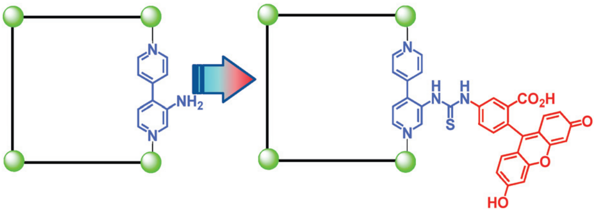
A new approach inspired by fluorescent labeling technology to fluorescently functionalize MOFs *via* post-modification is reported. A fluorescein-containing MOF FITC@BTPY–NH_2 was synthesized for selective sensing and adsorption of Ag^+ in aqueous solution.

Metal–organic frameworks (MOFs) have attracted considerable attention and become one of the most widely studied hybrid porous materials for their large pore volumes, accessible through the porous networks, to topologies resulting from the bonding of multi-dentate ligands to metal centers.[1,2] As MOFs have a degree of structural predictability and well-defined environments for luminophores in crystalline form, they offer a unique platform for the development of solid-state luminescent materials.[3] In particular, the combination of synthesis flexibility with respect to both the organic and inorganic components means MOFs exhibit several advantages over other luminescent materials.[4] Furthermore, the ability to absorb molecules into pores allows the species to be immobilized in close proximity to luminescent centers.[5] In this context, the combination of luminescence and accessible porosity within MOFs bring the capability to sensitise the host–guest chemistry to detectable changes in their luminescence and makes them promising candidates for chemical sensing applications.[6] However, the incorporation of intense fluorescence within the stable pores of MOFs is still a big challenge, because most of the bright luminophores are not compatible with the MOF synthetic conditions or exhibiting groups interfere with the formation of the desired MOFs.[7]

Fluorescent labeling is one of the most common methodologies used for bioanalytical purposes.[8,9] The organic fluorophores may form covalent or noncovalent linkages with the sample to be analyzed, producing the respective conjugates or complexes that show fluorescence from short to long wavelengths, depending on the marker used. Of the widely used labels, fluorescein, a poly-cyclic fluorophore with absorption and fluorescence maxima in the visible region, is one of the most common labels used in biological applications.[10] Recently, Cohen's group has shown that the superior chemical stability of MILs allowed for the synthesis of reactive isocyanate and isothiocyanate groups on the organic components of the framework.[11] Under suitable conditions, these reactive groups readily combine with species diffusing through the porous structure, generating new functionalized MIL. Bearing these in mind, herein, we try to label a large porous $[Zn_6\ (btb)_4(bipy–NH_2)_3]$ (**BTPY**–NH_2) with fluorescein isothiocyanate (FITC) to obtain a dye-functionalized MOF **FITC@BTPY**–NH_2 (btb = benzene-1,3,5-tribenzoate, bipy–NH_2 = 3-amino-4,4′-bipy-ridine) (Scheme 1) .[12] Fluorescein and its derivatives were always used in the fluorescent detection of transition metal ions in aqueous solutions and living cells,[13] and the molecules containing thiocarbamide moiety have been used to bond thiophile metal ions (*e.g.* Ag^+, Hg^{2+}).[14] We anticipated that our dye-functionalized MOF could be used in the selective and sensitive sensing of thiophile metal ions in aqueous media. The new functionalized MOF is also expected to be used in the separation, removal and enrichment of heavy-transition metal ions from drinking water because of its heterogeneous features.[15]



Scheme 1 Post-modification of **BTPY**–NH_2 with **FITC** showing the dye-functionalized fluorescent MOF **FITC@BTPY**–NH_2.

Crystals of **BTPY**–NH_2 were obtained by the solvothermal reaction of benzene-1,3,5-tribenzoate (29.4 mg, 0.067 mmol), 3-amino-4,4′-bipyridine (8.6 mg, 0.05 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (30 mg, 0.1 mmol) in 6 mL of DMF at 85 °C for 3 days. Single-crystal X-ray diffraction revealed that **BTPY**–NH_2 had a similar cubic lattice to FJL-1, which was reported by Hong's group.[16] It comprised Zn(II) paddle-wheel SBUs (Fig. 1), each of which was linked by four benzene-1,3,5-tribenzoate ligands. The ends of the axial sites of each SBU were occupied by two different bipy–NH_2 ligands, such that there were two different types of pores in the crystals of **BTPY**–NH_2. The pore and window sizes of the bigger pores were about 27 Å and 14 Å in diameter,

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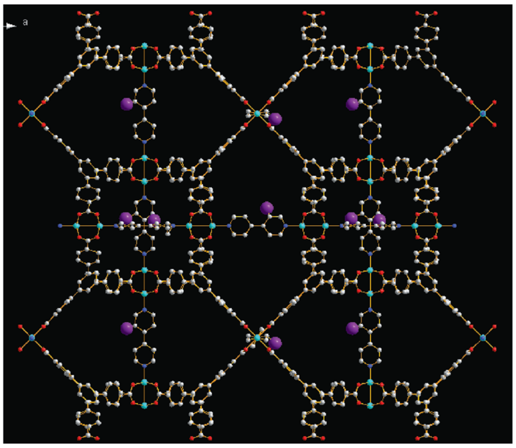

Fig. 1 The structure of **BTPY**–NH_2, viewed along the *y* axis. The gray, red, blue and cyan balls represent the carbon, oxygen, nitrogen and zinc atoms, except the amino groups are drawn in purple. H-atoms have been omitted for clarity.

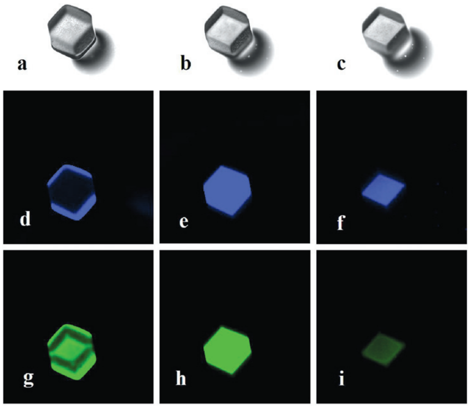

Fig. 2 Brightfield images (a)–(c) and confocal laser scanning micrographs at λ_{ex} = 405 nm (d)–(f) and λ_{ex} = 488 nm (g)–(i) of **FITC@BTPY**–NH2. (d)–(f) and (g)–(i) each show three slices from the top down. The slices chosen for (d)–(f) and (g)–(i) were in about 75 μm distance, with crystals of *ca.* 260 μm dimension in the *z* direction.

respectively, derived from the structure data. PLATON calculation of **BTPY**–NH_2 indicated that the solvent accessible volume accounted for 81.2% of the crystal volume, which was a high level among existing MOFs. The amino group in bipy–NH_2 could not be located in the Fourier difference map, owing to the statistical disorder over four sites coupled with likely conformational disorder at each of these sites. However, ^{1}H NMR spectroscopy on digested crystals indicated that this group remained intact in the MOF.

Furthermore, the characteristic peaks of amino groups could be observed in the IR spectroscopy (3423 cm^{-1}, 3220 cm^{-1}). Analysis of the residual electron density within the framework voids was consistent with its presence. The atoms of this unit were placed in calculated positions to complete the refinement. The phase purity of **BTPY**–NH_2 was established by powder XRD; the observed diffraction pattern closely matched that simulated from the single-crystal structure.

The isothiocyanate groups on **FITC** molecules can react with arylamine groups in high yield under mild conditions, which makes **FITC** a frequently used fluorescence label in protein studies. Comparing the dimensions of the **FITC** molecule (5 × 10 × 10 $Å^3$) with that of the pore and the window sizes of **BTPY**–NH_2, it is suggested that molecules of **FITC** possibly diffuse into pore channels and react with the amino groups. To further establish the feasibility of the chemical reaction, 3-amino-4,4′-bipyridine and **FITC** molecules were mixed in DMF at room temperature and stirred in the dark. The formation of the desired conjugate was confirmed by electrospray ionization mass spectrometry, which exhibited two main peaks corresponding to $[M + H]^+$, *m/z* = 561.2 and $[M + Na]^+$, *m/z* = 583.1.

The post modification of **BTPY**–NH_2 with **FITC** was then performed by using similar conditions. The fresh crystals of **BTPY**–NH_2 were incubated in DMF solutions containing **FITC**. The mixture was then shaken in a dark place at room temperature. The products were washed with DMF scrupulously in order to remove any physisorbed **FITC** molecules from the surface of **BTPY**–NH_2. The identity and phase purity of the **BTPY**–NH_2 crystals before and after modification were confirmed by powder X-ray diffraction, which showed no lattice distortion. The wt% of **FITC** in the functionalized MOF was measured at about 5–10% through comparing the UV-vis absorption with that of pure **FITC**.[17] ^{1}H NMR of the digested **FITC@BTPY**–NH_2 suggested that *ca.*7.5% of the amino groups were converted to isothiocyanate groups, which indicated that FITC was bound to **BTPY**–NH_2 covalently.

We also studied **FITC@BTPY**–NH_2 with fluorescence microscopy (FM) and confocal laser scanning microscopy (CLSM) (Fig. 2). The blue fluorescence was attributed to bipy–NH_2 ligands, and a strongly increased green fluorescence (λ_{ex} = 488 nm) confirms the successful labeling of FITC molecules inside the MOF crystals. Furthermore, CLSM excites only the focal layer, thereby providing a layer-by-layer imaging of dye distribution in and on the MOF crystals. A rather uniform distribution of **FITC** molecules throughout the crystal resulted.[12] It is suggested that **FITC** penetrated deeply into the crystal rather than staying on the external surface owing to the large pores and windows sizes of **BTPY**–NH_2.

In order to study the recognition property of **FITC@BTPY**–NH_2, the fluorescence titration of the suspension in water with various cations was conducted. As shown in Fig. 3, the addition of 50 μM relevant cations, including Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+} did not cause significant fluorescence quenching of the hybrid material **FITC@BTPY**–NH_2. Only the presence of Ag^+ and Hg^{2+} quenched the fluorescence of **FITC@BTPY**–NH_2 directly, and Ag^+ has a higher quenching efficiency on the fluorescence of **FITC@BTPY**–NH_2 compared with that of Hg^{2+}. This result is similar to those of the reported homogeneous sensors containing thiourea groups for sensing Ag^+.[14] Meanwhile, it was found that the fluorescence of **FITC@BTPY**–NH_2 was nearly proportional to the concentration of silver ions in a wide concentration range. The detection limit of the material towards Ag^+ is established at or below 0.1 ppm under the experimental conditions used here (25% quenching efficiency). To the best of our knowledge, this is the first heterogeneous probe that can detect less than 0.1 ppm of Ag^+ in aqueous solution. Interestingly, the presence of the above mentioned metal ions, except Hg^{2+}, did not interfere with the luminescence responses toward Ag^+, demonstrating the

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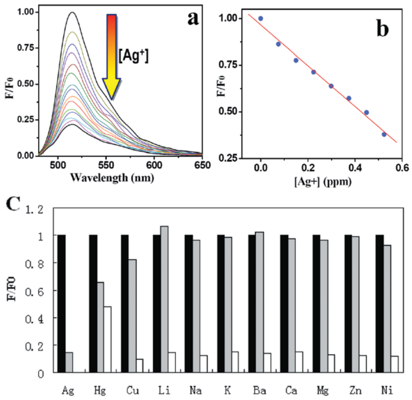

Fig. 3 (a) The emission spectra of **FITC@BTPY**–NH_2 (1 mg mL^{-1}) upon addition of various amounts of Ag^+ in HEPES buffer (pH = 7.0). (b) Emission intensities at 520 nm **FITC@BTPY**–NH_2 as a function of the [Ag^+] in the range of 0.07–0.75 ppm. λ_{ex} = 490 nm. (c) Fluorescence responses of **FITC@BTPY**–NH_2 in HEPES buffer at pH 7.0 towards metal ions interested. For each sample, a 1 mg mL^{-1} suspension of the sensor (black bar) was mixed with 50 μM of the cation of interest (gray bar) and then subsequently treated with 50 μM $AgNO_3$ (white bar).

selectivity of **FITC@BTPY**–NH_2 towards Ag^+ over alkali-, alkaline-earth metals, and the first-row transition metals Ni^{2+}, Zn^{2+} and Cu^{2+}. This can be attributed to the thiourea groups, which tend to interact with the more polarizable heavy metal ions, especially Ag^+, due to cation-*p* interactions.[18]

As excessive silver ion intake can lead to the long-term accumulation of insoluble precipitates in the skin, eyes and other organisms,[19] the detection of Ag^+ has received considerable attention.[20] Accordingly, the adsorption ability of **FITC@BTPY**–NH_2 in solid–liquid phase was estimated in order to evaluate its potential as a practical absorbent material for Ag^+ in drinking water. Solutions of two different Ag^+ concentrations (0.18 ppm/50 mL; 0.06 ppm/50 mL) were treated with 20 mg of **FITC@BTPY**–NH_2 overnight at room temperature, after filtration the concentrations of residual Ag^+ in the filtrate were analyzed by inductively coupled plasma (ICP) source mass spectrometry. Most of the Ag^+ was adsorbed in both solutions by **FITC@BTPY**–NH_2, only 0.046 ppm and 0.02 ppm Ag^+ remained in the water for the two samples, respectively. The amount of adsorbed Ag^+ for **FITC@BTPY**–NH_2 is about 0.35 mg per gram. The Ministry of Environmental Protection of the P.R. China has set a national standard for Ag^+ in daily drinking water of 0.05 ppm,[21] integrated wastewater discharge of 0.5 ppm.[22] Current reported Ag^+ adsorbents (*e.g.* activated carbon) are often used in separation of silver from ores. The recovery of ionic silver by these is only useful for ionic silver concentrations greater than 20 ppm.[23] The adsorbed quality of **FITC@BTPY**–NH_2 is lower than these reported adsorbents, but it can be useful for reducing the ionic silver concentration to below 0.02 ppm. Therefore, **FITC@BTPY**–NH_2 is a promising material in the recovery and monitoring of waste water.

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