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# Dual Sensing of Copper Ion and Chromium (VI) Oxyanions by Benzotriazole Functionalized UiO-66 Metal-Organic Framework in Aqueous Media

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Graphical abstract



Fluorescence quenching of benzotriazole functionalized UiO-66 by copper and chromium oxyanions.

## Highlights

- A new dual chemosensor based on the UiO-66 (University of Oslo) Metal –Organic Framework, containing benzotriazole functionalized dicarboxylate struts.
- This MOF based chemosensor is highly selective and ultrasensitive to Cu<sup>2+</sup> ion and chromium oxyanions (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and CrO<sub>4</sub><sup>2-</sup> anions) in aqueous media.

- This sensor showed a detection limit of 16.9 ppb for  $Cu^{2+}$  ion, 280 ppb for  $Cr_2O_7^{2-}$  and 47.7 ppb (0.4  $\mu$ M) for  $CrO_4^{2-}$  anions.
- This chemosensor has quenching constants  $(K_{sv})$  of  $1.1 \times 10^5 \text{ M}^{-1}$ ,  $3.9 \times 10^3 \text{ M}^{-1}$ , and  $6.7 \times 10^3 \text{ M}^{-1}$  for  $\text{Cu}^{2+}$ ,  $\text{Cr}_2 \text{O7}^{2-}$ , and  $\text{CrO4}^{2-}$  respectively.
- This sensor also demonstrated a regenerative property for five consecutive cycles.

**Abstract:** A new dual chemosensor UiO-66-NH-BT (BT=1-methylenebenzotriazole) based on the UiO-66 (University of Oslo) framework, containing benzotriazole functionalized dicarboxylate struts was synthesized and characterized. This isoreticular Metal-Organic Framework (MOF) was found to be a very selective and ultrasensitive for copper ion and chromium oxyanions in aqueous media. It showed a detection limit of 16.9 ppb (0.266  $\mu$ M) for Cu<sup>2+</sup> ion, 280 ppb (1.3  $\mu$ M) for Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and 47.7 ppb (0.411  $\mu$ M) for CrO<sub>4</sub><sup>2-</sup> anions. The quenching constants (K<sub>sv</sub>) for Cu<sup>2+</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup> was found to be 1.1x10<sup>5</sup> M<sup>-1</sup>, 3.9x10<sup>3</sup> M<sup>-1</sup>, and 6.7x10<sup>3</sup> M<sup>-1</sup> respectively. The covalently bonded benzotriazole moiety with the UiO-66 framework not only produces an emission peak at 491 nm but also act as an intrinsic binding site for both cations and anions. The nature of the coordinative interaction between the analytes and the UiO-66-NH-BT has also been elaborated with the help of ICP and FTIR. This chemosensor also demonstrated a regenerative property without the loss in performance for five consecutive cycles.

Keywords: Dual chemosensor, Isoreticular, Metal-Organic Framework, Ultrasensitive, Benzotriazole.

### 1. Introduction

Metal–Organic Frameworks (MOFs) with porous structure and high surface area has been extensively used for the capture and storage of carbon dioxide, hydrogen and methane [1-3]. The finely tuned pores with functional sites have enabled us to use MOF in developing materials for separations of small and large molecules, sensing of different analytes, drug delivery, carbon dioxide conversion and heterogeneous catalysis [4-9]. These pore environments can be engineered by using functionalized linkers for different potential applications [10]. The functionalization of the linkers can be achieved in two ways postsynthetic modification (PSM), [10 -13] or postsynthetic exchange (PSE), [14] and by direct solvothermal synthesis using presynthetically functionalized organic linkers. Thus these isoreticular MOFs have gained extensive importance as the functionality and metrics of an extended porous structure can be need fully modified without changing its underlying topology [15].

Copper is an omnipresent metal ion and an essential trace element for the growth and development of human beings. Thus low concentration of copper effects the enzyme activity owing to the redox-active nature [16] while excessive accretion of copper cause damage to the liver and kidney, hepatolenticular degeneration (Wilson's disease), Alzheimer's diseases, Menkes syndrome, neutropenia and myelopathy [17]. Thus the U.S. Environmental Protection Agency (EPA) has set the limit of copper concentration in drinking water to be 1.3 ppm (~20  $\mu$ M) [18]. There are several analytical techniques for detection of copper ions, such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), activated carbon or natural zeolite adsorption etc [17,19]. MOFs and their composites have also been used for the detection of copper ions in aqueous solution [20-23]. But these methods

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have their own disadvantages such as low selectivity, tedious and troublesome analysis methods, complicated synthetic procedure and lack of practical applicability.

Chromium as an oxidant has large industrial applications such as chromium electroplating, metallurgy, pigment production, leather tanning, detergent manufacturing, welding, steel manufacturing, and wood preservation [24]. This chromium exists as oxyanions in its most stable oxidation states of Cr(VI) ions in the environment as highly soluble, non-biodegradable pollutants [25,26]. Cr(VI) is a carcinogenic species with higher oxidation potential and diffusible cell membrane size [26]. Chromate ion can cause allergic reaction in human and prolonged exposure results in chrome ulcer, contact dermatitis, and irritant dermatitis [27]. Due to the exposure potential and toxicity the U.S. Environmental Protection Agency (EPA) has set the maximum concentration level of Cr(VI) in drinking and ground water to be 0.1 ppm (100  $\mu$ g/L) and 0.05 ppm (50  $\mu$ g/L) respectively [28]. Several feasible analytical techniques have been employed for the detection of these chromium species such as inductively coupled plasma mass spectrometry, atomic absorption spectrometry, etc [27,29,30]. However, these methods have their own impediment such as selectivity, prolonged sample preconditioning, use of expensive and complicated instruments, and lack of practical relevance. Several MOF based optical chromate sensors are also reported, but most of them lack the selectivity with other anions and their detection ability in water [25, 26, 31-33].

Zirconium based MOFs were first synthesized by Cavka et al which exhibited a high thermal, chemical and acidic stability due to the very strong metal ligand bond that arises from high oxidation state of Zr(IV) which results high charge density and bond polarization [34-36]. The benzene ring of the UiO-66 could be easily functionalized

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without disturbing the high thermal and chemical stability of the MOF. This unique feature of UiO-66 makes it a suitable candidate to be used in various applications. In case of most Zirconium based MOFs the fluorescence originates from the organic linkers. Due to the Zirconium clusters amino benzene ring of the framework in UiO-66-NH<sub>2</sub> produce weak emission, it can be functionalized with heteroaromatic rings to produce a strong emission as well as good binding sites for analytes [37].

In this paper, we report the synthesis and characterization of a benzotriazole functionalized UiO-66-NH<sub>2</sub> nanocrystalline MOF (UiO-66-NH-BT) and its application in the sensing of heavy metal copper and chromium (VI) oxyanions. A new benzotriazole functionalized 2-aminoterphthalic acid linker (H<sub>2</sub>L) was used to prepare the UiO-66-NH-BT by hydrothermal methods. This MOF was then characterized with powdered XRD, FTIR, SEM, TGA, BET, and digestion NMR. The absorption and the emission properties of this MOF were studied and were found to be highly selective for copper ion and chromium oxyanions in aqueous media (Figure 1).



Figure 1. Schematic representation of UiO-66-NH<sub>2</sub> and UiO-66-NH-BT.

### 2. Experimental

### 2.1. Materials and General Methods

**Chemicals used in this work:** 2 aminoterephthalic acid (98% purity), benzotriazole (99% purity), formaldehyde (99% purity), methanol (99.9% purity), ethanol (97.2% purity), *N*,*N*-dimethylformamide (DMF; 99.8% purity), dichloromethane (99.8% extra dry grade), potassium hydroxide (98% purity), all other nitrates or chlorides of the metal salts, and the sodium or potassium salts of the anions were purchased from Sigma Aldrich Corporation. NMR solvents: dimethyl sulfoxide-*d*6 (DMSO-*d*6; 99.9% purity) were purchased from Cambridge Isotope. All chemicals were used without further purification. Water used in this work was double distilled and filtered through a Millipore membrane. The solutions of metal ions were prepared from their nitrate and chloride salts and anions were prepared from their sodium and potassium salts (analytical grade) followed by subsequent dilution to prepare the working solutions.

**Instrumentation:** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AM-400 spectrometer using Me<sub>4</sub>Si as the internal standard. Elemental microanalyses (EA) were performed using a PerkinElmer-EA 2400 elemental analyzer. Powdered X-ray diffraction patterns of the samples were recorded using a Rigaku MiniFlex diffractometer, which was equipped with Cu-Kα radiation. The data were acquired over the 2θ range of 5° and 30°. The FT-IR spectra of UiO-66-NH-BT were obtained using a Nicolet 6700 Thermo Scientific instrument in the range of 400-4000 cm<sup>-1</sup>, using KBr. Thermogravimetric analysis (TGA) of the samples were performed using a TA Q500. In this study, an activated sample of UiO-66-NH-BT (10 mg) was heated in alumina pan under airflow (60 mL min<sup>-1</sup>) with a gradient of 10 °C min<sup>-1</sup> in the temperature range of 30 - 800 °C. The BET surface areas of the MOFs were calculated by using Micromeritics ASAP 2020

instrument. The surface morphology of these materials were discerned using a field emission scanning electron microscope (FESEM, LYRA 3 Dual Beam, Tescan), which operated at 30 kV. The FESEM samples were prepared from suspension in ethanol. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) of the copper and chromate treated samples of UiO-66-NH-BT were carried in Thermo Scientific XSeries 2 ICP-MS. The absorption spectra of the MOF were studied using a Jasco V-670 spectrophotometer. Fluorescence spectra were measured using a Horiba, Fluorolog-3 fluorescence spectrophotometer, which was equipped with a xenon discharge lamp and 1 cm quartz cells with slit width 2 nm for both the source and the detector. The quantum yield and chromaticity studies were done using Fluoromax-4 equipped with Quanta-Phi integration sphere (Horiba) by using liquid sample holder at room temperature. The solutions at different pH were prepared under adjustment by a Mettler Toledo pH meter.

**Sample preparation for photophysical studies:** In a typical luminescence-sensing experimental setup, 0.001 g of UiO-66-NH-BT powder was dispersed in 1 ml of water. In a 1 cm quartz cuvette, 3 mL of dispersed aqueous solution of UiO-66-NH-BT was placed and the absorption and emission responses were measured in-situ after incremental addition of freshly prepared analyte solutions. The mixtures were sonicated for 5 minutes after each incremental addition of the analytes for uniform dispersion during the luminescent measurements. All of the measurements were performed at 298 K.

#### 2.2. Synthesis:



Scheme 1. Synthesis of the linker H<sub>2</sub>L.

#### Synthesis of Compound 2

A solution of 2-aminoterephthalic acid (0.5 g, 2.8 mmol) in methanol (10 mL) and 2 drops of HCl was refluxed for 10 h. The solvent was removed under vacuum and the residue was diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by SiO<sub>2</sub> column chromatography (elution with EtOAc:hexane-1:3) to give 1 in 87% yield. A mixture of 1 (0.45 g, 2.2 mmol), benzotriazole (0.255 g, 2.2 mmol), formaldehyde (37%) (0.065 g, 2.2 mmol) in Ethanol: water (1:3) (10 mL) was stirred for 24 h. The solvent was removed under vacuum and the residue was diluted with water and extracted with ethyl acetate. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by SiO<sub>2</sub> column chromatography (elution with EtOAc:hexane-1:1) to give 2 in 70% yield. <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$  3.83 (s, 6H), 6.37 (d, J = 5.2 Hz, 2H), 7.19 (d, J = 6.4Hz, 1H), 7.37 (t, J = 6.4 Hz, 1H), 7.56 (t, J = 6.0 Hz, 1H), 7.83-7.86 (m,1H), 7.88 (s, 1H), 8.00 (d, J = 6.4 Hz, 1H), 8.13 (d, J = 6.4 Hz, 1H), 8.89 (bs, 1H, NH); <sup>13</sup>C NMR  $(DMSO-d_6)$   $\delta$  56.25, 59.68, 115.12, 117.18, 118.59, 121.00, 123.2, 128.22, 131.49, 135.77, 136.23, 138.6, 149.37, 151.8, 169.63, 171.14; Anal. Calcd for C<sub>17</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>: C, 60.00; H, 4.74; N, 16.46; Found: C, 60.17; H, 4.91; N, 16.52 (Figure S1, S2).

# Synthesis of linker 2-((1H-benzo[d][1,2,3]triazol-1-yl)methylamino)terephthalic acid H<sub>2</sub>L

Compound **2** (0.3 g, 0.9 mmol) was refluxed with an ethanolic solution of KOH for 12 h. The solvent was removed under vacuum, the residue was diluted with water, and the pH was adjusted to 5.0 by addition of HCl (1 M). The off-white solid precipitated was filtered with a Buchner base washed with water and recrystallized from ethanol to give linker **H**<sub>2</sub>**L** in 80% yield. <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$  6.37 (d, *J* = 5.5 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.85 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 9.07 (bs, 1H, NH), 12.95 (s, 2H, COOH); <sup>13</sup>C NMR (DMSO- $d_6$ )  $\delta$  70.71, 111.57, 113.59, 115.79, 117.66, 119.64, 124.64, 127.86, 132.50, 136.14, 145.86, 148.54, 151.68, 167.29, 169.52; Anal. Calcd for C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>: C, 57.69; H, 3.87; N, 17.94; Found: C, 57.77; H, 3.94; N, 18.07 (Figure S3, S4).

#### Synthesis of UiO-66-NH<sub>2</sub>

UiO-66-NH<sub>2</sub> was synthesized by dissolving ZrCl<sub>4</sub> (0.125 g, 0.54 mmol) and 2-amino-1,4benzenedicarboxylic acid (0.134 g, 0.75 mmol) in DMF (20 mL) with ultrasonic vibration for 30 min then 0.5 mL of acetic acid was added. The as-obtained mixture was transferred to a 50 mL vial and heated at 393 K for 24 h. Then the vial was cooled in air to room temperature. The resulting UiO-66-NH<sub>2</sub> was washed three times with DMF (5-10 mL) using a centrifuge (10,000 rpm for 30 min), and then sequentially immersed in methanol (5-10 mL three times per day) for three 24 h periods. Finally, UiO-66-NH<sub>2</sub> was activated by removing the solvent under vacuum for 24 h at 100 °C. FT-IR (KBr, cm<sup>-1</sup>): 3430, 1662, 1570, 1434, 1383, 1261, 1098, 768, 663. Anal. Calcd for C<sub>54</sub>H<sub>52</sub>N<sub>8</sub>O<sub>36</sub>Zr<sub>6</sub>

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(Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(2-NH<sub>2</sub>BDC)<sub>6</sub>(DMF)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>): C, 33.49; H, 2.71; N, 5.79; Zr, 28.27; Found: C, 33.57; H, 2.94; N, 6.01; Zr, 28.68.

### Synthesis of UiO-66-NH-BT

UiO-66-NH-BT was synthesized in a similar way as above by dissolving ZrCl<sub>4</sub> (0.125 g, 0.54 mmol) and 2-((1H-benzo[d][1,2,3]triazol-1-yl)methylamino)terephthalic acid (0.234 g, 0.75 mmol) in DMF (20 mL) with ultrasonic vibration for 30 min then 0.5 mL of acetic acid was added. The as-obtained mixture was transferred to a 50 mL vial and heated at 393 K for 24 h. Then the vial was cooled in air to room temperature. The resulting UiO-66-NH-BT was washed in the same way as the previous method by three times with DMF (5-10 mL) using a centrifuge (10,000 rpm for 30 min), and then sequentially immersed in methanol (5-10 mL three times per day) for three 24 h periods. Finally, UiO-66-NH-BT was activated by removing the solvent under vacuum for 24 h at 100 °C. FT-IR (KBr, cm<sup>-1</sup>): 3342, 1700, 1606, 1548, 1482, 1421, 1340, 1250, 1185, 1096, 1043, 772, 651, 582. Anal. Calcd for C<sub>96</sub>H<sub>82</sub>N<sub>26</sub>O<sub>36</sub>Zr<sub>6</sub> (Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(2-NHCH<sub>2</sub>BT-BDC)<sub>6</sub>(DMF)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>): C, 42.34; H, 3.04; N, 13.37; Zr, 20.10; Found: C, 42.43; H, 3.31; N, 13.79; Zr, 20.61.

### 3. Results and Discussion

### 3.1. Characterization of the linker H<sub>2</sub>L

In this work, we have presynthetically modified the 2-aminoterephthalic acid linker by covalently appending it with a benzotriazole moiety to give H<sub>2</sub>L (Figure 2). This new linker was synthesized by reacting methyl ester of 2-aminoterephthalic acid with benzotriazole in the presence of formaldehyde to give compound **2**, followed by the deprotection of the diacid by alkaline hydrolysis to give H<sub>2</sub>L in good yield as shown in Scheme 1. The structures of **2** and H<sub>2</sub>L were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, (Figure

S1-S4 of Supporting Information (SI)) and elemental analyses data. The <sup>1</sup>H NMR spectra of **2** and H<sub>2</sub>L exhibited doublet peak at  $\delta$  6.38 ppm that is assigned to the (-CH<sub>2</sub>-) protons that bridges the 2-aminoterephthalic acid with the benzotriazole, another peak is observed





at 8.9 ppm that corresponds to the NH proton of the 2-aminoterephthalic acid.

### 3.2. Characterization of UiO-66-NH2 and UiO-66-NH-BT



**Figure 3.** Powered XRD patterns of UiO-66-NH<sub>2</sub> obtained from cif file, UiO-66-NH<sub>2</sub> as synthesized, UiO-66-NH-BT as synthesized, UiO-66-NH-BT after addition of copper, and UiO-66-NH-BT after addition of chromate ion.

The powdered XRD pattern of UiO-66-NH<sub>2</sub>, was persistent with that documented in the literature (Figure 3) [34]. UiO-66-NH-BT was also synthesized with the same high crystallinity and characteristic peaks of UiO-66-NH<sub>2</sub> at  $2\theta = 7.78^{\circ}$ , 8.92° (Figure 3). This establishes the fact that functionalization of the 2-aminoterephthalic acid with benzotriazole did not disturb the framework and connectivity of UiO-66-NH<sub>2</sub>.

The IR spectrum of UiO-66-NH-BT (Figure S5, SI) shows a sharp peak at 772 cm<sup>-1</sup> that represents the stretching vibration of the C—H bond in the two benzene rings. The two peaks at 1043 cm<sup>-1</sup> and 1096 cm<sup>-1</sup> indicate the stretching vibration of two adjacent N—C bonds on the benzene ring of the benzotriazole. The peak at 1250 cm<sup>-1</sup> is strong, and corresponds to the stretching vibration of —N=N— of the benzotriazole. The peaks at 1295 cm<sup>-1</sup> and 1349 cm<sup>-1</sup> represents the vibrations of the bond between aromatic carbon and nitrogen of the 2-aminoterephthalate. The peaks at 1606 cm<sup>-1</sup> and 1700 cm<sup>-1</sup> represent –COO asymmetrical stretching. The broad peak at 3342 cm<sup>-1</sup> corresponds to the symmetric vibrations of NH bond of the organic linker. Additionally, the alkaline digestion <sup>1</sup>HNMR of the UiO-66-NH-BT confirmed the presence of the linker H<sub>2</sub>L in the framework. After digesting the UiO-66-NH-BT with KOH solution, peaks at chemical shifts matching H<sub>2</sub>L were observed (Figure S6, SI).





The thermal stability of the UiO-66-NH<sub>2</sub> and UiO-66-NH-BT materials, were measured by thermogravimetric analysis (TGA) under an airflow with a heating rate of  $5^{\circ}$ C min<sup>-1</sup> (Figure 4). Both samples show identical thermal behavior with the initial mass loss of 5.3% and 4.3% for UiO-66-NH<sub>2</sub> and UiO-66-NH-BT below 150 °C. This mass loss is assigned to the removal of trapped solvents molecules from the pores of the structure. The total weight loss for UiO-66-NH<sub>2</sub> and UiO-66-NH-BT are 46.5% and 48.5% respectively occurs at a temperature of 410 °C indicating that both MOFs are stable up to 410 °C. The final residue of 44.3% and 34.7% for UiO-66-NH<sub>2</sub> and UiO-66-NH-BT respectively corresponds to the zirconium oxides. The ICP-MS of the samples showed the content of Zirconium in UiO-66-NH<sub>2</sub> is 31% while in UiO-66-NH-BT is 25%. These results clearly indicate that the introduction of the benzotriazole functional groups does not influence the thermal stability.



**Figure 5.** N<sub>2</sub> adsorption isotherms of UiO-66-NH-BT and UiO-66-NH<sub>2</sub>. The filled and open circles represent the adsorption and desorption branches, respectively.

Nitrogen sorption experiments of UiO-66-NH-BT showed that it is Type I and had a very significant uptake at relative low pressure (P/P<sub>0</sub>) of 0 to 0.05 which is indicative of the microporous nature like UiO-66-NH<sub>2</sub>. The BET surface area and the pore volume of UiO-66-NH-BT was found to be  $384 \text{ m}^2\text{g}^{-1}$  and  $0.275 \text{ cm}^3\text{g}^{-1}$  respectively. These were very small as compared to the pristine UiO-66-NH<sub>2</sub> (BET surface area= 1067 m<sup>2</sup>g<sup>-1</sup> and pore volume=  $0.517 \text{ cm}^3\text{g}^{-1}$ ) due to the presence of the appended benzotriazole moleties that block the pores and reduced the surface area (Figure 5). The SEM image of the UiO-66-NH-BT shows that they are uniformly distributed bipyramidal shaped particle with 125-150 nm in size (Figure S7, SI).

#### 3.3. Optical properties of UiO-66-NH-BT

The absorbance and emission studies of UiO-66-NH-BT were carried out in aqueous solution as an emulsion. In general, 2-aminoterephthalate is luminescent but in UiO-66-NH<sub>2</sub> it has a low emission, due to the ligand-to-metal charge transfer (LMCT), on coordination with the Zr-O clusters [37]. But in case of UiO-66-NH-BT the emission peak is produced at 491 nm, at an excitation wavelength of 360 nm, which is 58 nm red shifted from the emission peak of UiO-66-NH<sub>2</sub> ( $\lambda_{em}$ =449 nm) (Figure S8, SI). Thus functionalization of UiO-66-NH<sub>2</sub> with benzotriazole produces a redshift and enhanced emission due to the electron transfer (ET) from the benzotriazole to the benzene ring in the main structural framework of UiO-66 (Scheme 1) [38,39]. Moreover, the benzotriazole with the NH- moiety provide selective binding sites for metal ions. The absolute quantum yield of UiO-66-NH-BT, calculated from the integrated sphere, was found to be 0.56 and the CIE coordinates of the chromaticity diagram, are persistent with the experimentally derived emission results (Figure S9, SI).

#### 3.4. Cation sensing properties of UiO-66-NH-BT

In order to check the cation sensing properties, UiO-66-NH-BT was screened with different cations and the change in its absorbance properties were noted. It was found that on addition of different cations only copper ion produces a change in the absorbance of UiO-66-NH-BT. All the optical sensing experiments were carried out using  $10^{-2}$  M aqueous solutions of copper salt. Upon slow addition of Cu<sup>2+</sup> to a suspension of UiO-66-NH-BT the absorbance increased and an additional new peak is formed at 284 nm along with the peaks at 256 and 360 nm (Figure S10). The formation of this new peak indicates a coordinative interaction of the copper with the nitrogen rich benzotriazole. The

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stoichiometry of binding between UiO-66-NH-BT and  $Cu^{2+}$  was confirmed by Job's plot, which concluded that a 1:1 stoichiometric complex is formed between UiO-66-NH-BT and  $Cu^{2+}$  (Figure S11, SI) [40,41].



**Figure 6.** Changes in fluorescence emission spectra of UiO-66-NH-BT with the incremental addition of Cu(NO<sub>3</sub>)<sub>2</sub> (10<sup>-2</sup> M) in water ( $\lambda_{exe}$ = 360 nm). Inset: Fluorogenic changes in UiO-66-NH-BT upon addition of Cu<sup>2+</sup> in water upon illumination at 365 nm.

In order to further understand the chemosensing properties of UiO-66-NH-BT, the changes in the fluorescence emission intensity were examined as a function of increasing Cu<sup>2+</sup> concentration at an excitation wavelength of 360 nm. The emission was quantitatively quenched with increasing concentrations of Cu<sup>2+</sup> and was observed to be completely quenched when a 1:1 UiO-66-NH-BT: Cu<sup>2+</sup> molar ratio was achieved (Figure 6, Figure S12, SI). This complete quenching signifies that full complexation occurred between Cu<sup>2+</sup> and the nitrogen rich benzotriazole moiety of the linker. Cu<sup>2+</sup> being a paramagnetic cation, with open shell d-orbitals, inhibit the electron transfer (ET) from the benzotriazole to the benzene ring in the main structural framework of UiO-66 thus

resulting in quenching of fluorescence (Scheme 2). The quenching efficiency was then elucidated from the Stern–Volmer constant [41,42]. The Stern–Volmer constant, K<sub>SV</sub>, obtained from the titration curve shown in Figure 6, was calculated to be  $1.1 \times 10^5$  (Figure S13, SI). The sensitivity of UiO-66-NH-BT towards Cu<sup>2+</sup> was determined from the calculated detection limit, which was found to be 16.9 ppb (0.266  $\mu$ M) (Section S6, Determination of the detection limit, Figure S24). It was found that this detection limit were quiet comparable with the recently published results on the MOF based copper ion sensors and is lower than the limit set by the U.S. Environmental Protection Agency (EPA) (Table S1, SI). The powdered XRD of the copper bounded UiO-66-NH-BT showed that the crystallinity of the MOF is intact (Figure 3). The selectivity and tolerance of UiO-66-NH-BT towards Cu<sup>2+</sup> as compared to other metal contaminants was investigated by immersion of UiO-66-NH-BT in solutions of different





metal ions (e.g. Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Rb<sup>2+</sup>, Cs<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Ag<sup>+</sup>, Pd<sup>2+</sup>, Al<sup>3+</sup>, Ga<sup>3+</sup>, and Pb<sup>2+</sup>) (Figure S14). As shown in Figure 7, the fluorescence emission remained same for all metal ions tested, except for Cu<sup>2+</sup> where the emission was completely quenched. This high selectivity for Cu<sup>2+</sup> ion is due to the fact that copper being the highest occupant on the Irving–Williams series leads to the formation of the most stable complex with the benzotriazole as compared to other metal ions. To explore the possibility of using UiO-66-NH-BT in practical purpose competitive binding experiments with to 200  $\mu$ L of different metal ions (10<sup>-2</sup> M) in the presence of 200  $\mu$ L Cu<sup>2+</sup> ion was carried out which exhibited that none of the metal ions interfere with the quenching of UiO-66-NH-BT by Cu<sup>2+</sup> (Figure S15, SI).

### 3.5. Anion sensing properties of UiO-66-NH-BT

Anion sensing properties of UiO-66-NH-BT was also investigated with the aqueous potassium or sodium salts solutions  $(10^{-2} \text{ M})$  of the anions,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\Gamma$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{MnO}_4^-$ ,  $\text{CrO}_4^{2-}$ , and  $\text{Cr}_2\text{O}_7^{2-}$ . Screening with these anions showed that optical properties of UiO-66-NH-BT are selectively sensitive to  $\text{CrO}_4^{2-}$ , and  $\text{Cr}_2\text{O}_7^{2-}$  anions. The absorbance studies showed that the peak of UiO-66-NH-BT at 360 nm is redshifted to 372 and 382 nm for  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  ions respectively (Figure S16 and S17, SI). The Job's methods confirmed that the stoichiometry of binding of UiO-66-NH-BT with  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  ions are 1:1 (Figure S18 and S19, SI). The fluorescence emission spectroscopy analysis of UiO-66-NH-BT with the chromium oxyanions showed that  $\text{Cr}_2\text{O}_7^{2-}$  ion produces partial quenching (Figure 8) while the  $\text{CrO}_4^{2-}$  ion produce a complete quenching (Figure 9) of the emission spectra indicating that a partial and full complexation was realized between the chromate oxyanions and the benzotriazole.



**Figure 8.** Changes in fluorescence emission spectra of UiO-66-NH-BT with the incremental addition of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (10<sup>-2</sup> M) in water ( $\lambda_{exe}$ = 360 nm).



**Figure 9.** Changes in fluorescence emission spectra of UiO-66-NH-BT with the incremental addition of K<sub>2</sub>CrO<sub>4</sub> (10<sup>-2</sup> M) in water ( $\lambda_{exe}$ = 360 nm).



**Figure 10.** Change in the normalized fluorescence emission of UiO-66-NH-BT in water upon addition of 200  $\mu$ L of different anionic species (10<sup>-2</sup> M).

Moreover, the powdered XRD demonstrate that complete complexation of the chromate with the MOF did not produce any change in the crystallinity of the UiO-66-NH-BT (Figure 3). The quenching constant  $K_{sv}$  calculated for  $Cr_2O_7^{2-}$  and  $CrO_4^{2-}$  were  $3.9x10^3$ and  $6.7x10^3$  respectively (Figure S20 and S21, SI). The sensitivity of UiO-66-NH-BT towards the chromium oxyanions ( $Cr_2O_7^{2-}$  and  $CrO_4^{2-}$ ) was calculated to be 280 ppb (1.3  $\mu$ M) and 47.7 ppb (0.411  $\mu$ M) respectively (Section S6, Determination of the detection limit Figure S25 and S26). It was found that this detection limit were quiet comparable with the recently published results on the MOF based chromium oxyanion sensors and is lower than the limit set by the U.S. Environmental Protection Agency (EPA) (Table S2, SI).In order to check the selectivity of the material it was tested with aqueous solution of different anions. It was realized that only the chromium oxyanions ( $Cr_2O_7^{2-}$  and  $CrO_4^{2-}$ )

causes quenching of the fluorescence emission of UiO-66-NH-BT (Figure 10, Figure S22 of SI). The competitive binding experiments showed that none of the anions interfere with the quenching effects of  $CrO_4^{2-}$  even when added in excess (Figure S23, SI). The UV-vis absorption spectrum (Figure S27 of SI) shows that two possible mechanisms are responsible for quenching with the chromate ions. Firstly the wide absorption bands of the chromate ions aqueous solution covers the absorption bands of the UiO-66-NH-BT thus there is a competition of absorption of the excitation wavelength energy between the chromate ions and the MOF. This will prevent the energy transfer to the framework that will result in quenching. Secondly there exists an overlap between the aqueous solution of chromate ions and the emission spectrum of the UiO-66-NH-BT (Figure S27 of SI) which indicates that there is energy transfer between the chromate ion, bonded by coordinative interaction to the nitrogen of the triazole ring, and UiO-66-NH-BT that leads to quenching [43,44]. A successful chemosensor should be effective in aqueous media with widely varying pHs. The emission properties of UiO-66-NH-BT remained unaltered within a pH range of 6.0-10.0 (Figure S28, SI). Beyond this range, the emission properties are lost probably due to the decomposition of the structure of UiO-66-NH-BT.



Scheme 2. Schematic illustration of the mechanism of fluorescence in UiO-66-NH-BT.

The interaction between the UiO-66-NH-BT and the analytes  $(Cu^{2+}/CrO_4^{2-})$  were studied with the help of ICP and FTIR. UiO-66-NH-BT was accumulated after sensing experiments and then wash with water to remove the analytes adhered to the surface of the MOF, and then dried. The ICP analysis of the washed and dried samples concluded the presence of Cu and Cr in addition to the metal of the framework. It was found that 0.517 mg of Cr and 13.675 mg of Cu was recovered per 100 mg of the Zirconium. FTIR analysis of the washed and dried UiO-66-NH-BT samples obtained after sensing experiments offered us with significant information about the nature of the interaction between the host framework and the analytes ( $Cu^{2+}/CrO_4^{2-}$ ). The coordination of the  $Cu^{2+}$ ion with the nitrogen of the benzotriazole in UiO-66-NH-BT is mirrored in the shifting of the -N=N- stretching vibration from 1253 to 1243 cm<sup>-1</sup>. The C-H stretching of the aromatic ring of the benzotriazole at 1097 cm<sup>-1</sup> and 1043 cm<sup>-1</sup> of the pristine MOF is shifted to 1088 cm<sup>-1</sup> and 1034 cm<sup>-1</sup> respectively after interaction with the Cu<sup>2+</sup>. The Cu<sup>2+</sup> ion also binds with the lone pair of the NH moiety of the framework thus shifting the N-H stretching frequency of the pristine UiO-66-NH-BT from 3348 cm<sup>-1</sup> to 3282 cm<sup>-1</sup> (Figure S29 and S30, SI). In the case of the chromate ions we can see new peaks are formed at 626, 738, and 1316 cm<sup>-1</sup> that corresponds to the bending vibrational modes of O-Cr-O bond, that confirms the incorporation of the chromate ion within the framework. There is a shift in the -N=N- stretching from 1253 cm<sup>-1</sup> to 1242 cm<sup>-1</sup> due to the binding of the chromium ion with the nitrogen rich benzotriazole. The shift in the NH peak of the pristine UiO-66-NH-BT from 3348 cm<sup>-1</sup> to 3313 cm<sup>-1</sup> is due to the H-bonding of the chromate oxygen with the NH proton of the framework (Figure S31 and S32, SI). Thus while ICP confirmed the presence of the analytes within the framework of UiO-66-NH-

BT the FTIR gave us information about the nature of interaction between the analytes and the different functional groups of the framework.

#### 3.6. Reusable properties of UiO-66-NH-BT

In order to measure the recyclable sensing ability of UiO-66-NH-BT the fluorescence sensing experiments were repeated with the same materials recovered after the first set of experiments followed by washing with 1.0 M aqueous solution of EDTA, water, and then drying at  $100 \, {}^{0}$ C for 1 hour. The recovered UiO-66-NH-BT showed no significant variation in the fluorescence intensities and sensitivity towards sensing of ions for five consecutive cycles (Figure S33, SI).

#### 4. Conclusion

In this paper we prepared a benzotriazole appended new linker H<sub>2</sub>L that was used to develop isoreticular MOF UiO-66-NH-BT. This presynthetically incorporation of the benzotriazole moiety in the UiO-66-NH<sub>2</sub> framework not only enhanced its intrinsic fluorescence emission properties but also introduce additional coordinating sites that help in the selective and sensitive detection of  $Cu^{2+}$  and  $CrO_4^{2-}/Cr_2O_7^{2-}$  ions in aqueous solution with a detection limit of 16.9 ppb, 280 ppb and 47.7 ppb for  $Cu^{2+}$ ,  $Cr_2O_7^{2-}$ , and  $CrO_4^{2-}$  respectively. We studied the interaction of the analytes with the functionalities of the framework and also found that the sensor is recyclable for five consecutive cycles with the respective analytes.

#### **Conflict of interests**

The authors declare that there is no conflict of interests.

#### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### 5. References

- 1. H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, The Chemistry and Applications of Metal–Organic Frameworks, Science 341 (2013) 1230444.
- K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. –H. Bae, J. R. Long, Carbon Dioxide Capture in Metal–Organic Frameworks, Chem. Rev. 112 (2012) 724–781.
- H. Li, K. Wang, Y. Sun, C. T. Lollar, J. Li, H. –C. Zhou, Recent advances in gas storage and separation using metal–organic frameworks, Mater. Today 21 (2018) 108-121.
- C. Wang, D. Liu, W. Lin, Metal–Organic Frameworks as A Tunable Platform for Designing Functional Molecular Materials, J. Am. Chem. Soc. 135 (2013) 13222–13234.
- G.-Y. Jeong, A. K. Singh, M.-G. Kim, K.-W. Gyak, U. J. Ryu, K. M. Choi, D.-P. Kim, Metal-organic framework patterns and membranes with heterogeneous pores for flow-assisted switchable separations, Nat. Commun. 9 (2018) 3968-3976.
- D. Kukkara, K. Vellingiric, K.–H. Kim, A. Deep, Recent progress in biological and chemical sensing by luminescent metal-organic frameworks, Sens. Actuators B: Chem. 273 (2018) 1346–1370.
- A. U. Czaja, N. Trukhan, U. Müller, Industrial Applications of Metal–Organic Frameworks, Chem. Soc. Rev. 38 (2009) 1284–1293.

- C. A. Trickett, A. Helal, B. A. Al-Maythalony, Z. H. Yamani, K. E. Cordova, O. M. Yaghi, The chemistry of metal-organic frameworks for CO<sub>2</sub> capture, regeneration and conversion, Nat. Rev. Mater. 2 (2017) 17045-17060.
- L. Zhu, X.-Q. Liu, H.-L. Jiang, L.-B. Sun, Metal–Organic Frameworks for Heterogeneous Basic Catalysis, Chem. Rev. 117 (2017) 8129–8176.
- P. Deria, J. E. Mondloch, O. Karagiaridi, W. Bury, J. T. Hupp, O. K. Farha, Beyond post-synthesis modification: evolution of metal–organic frameworks *via* building block replacement, Chem. Soc. Rev. 43 (2014) 5896–5912.
- Z. Wang, S. M. Cohen, Postsynthetic modification of metal–organic frameworks, Chem. Soc. Rev. 38 (2009) 1315–1329.
- S. –Y. Zhu, B. Yan, A novel sensitive fluorescent probe of S<sub>2</sub>O<sub>8</sub><sup>2–</sup> and Fe<sup>3+</sup> based on covalent post-functionalization of a zirconium(iv) metal–organic framework, Dalton Trans., 47, (2018) 11586-11592.
- S. –Y. Zhu, B. Yan, Highly Sensitive Luminescent Probe of Aniline and Trace Water in Organic Solvents Based on Covalently Modified Lanthanide Metal– Organic Frameworks, Ind. Eng. Chem. Res. 57 (2018) 16564-16571.
- 14. S. M. Cohen, The Postsynthetic Renaissance in Porous Solids, J. Am. Chem. Soc.139 (2017) 2855–2863.
- 15. R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe, O. M. Yaghi, Control of Pore Size and Functionality in Isoreticular Zeolitic Imidazolate Frameworks and their Carbon Dioxide Selective Capture Properties, J. Am. Chem. Soc. 131 (2009) 3875-3877.

- L. M. Gaetke, H. S. ChowJohnson, C. K. Chow, Copper: Toxicological relevance and mechanisms, Arch. Toxicol. 88 (2014) 1929–1938.
- J. A. Jr. Cotruvo, A. T. Aron, K. M. Ramos-Torres, C. J. Chang, Synthetic fluorescent probes for studying copper in biological systems, Chem. Soc. Rev. 44 (2015) 4400-4414.
- 18. 2018 Edition of the Drinking Water Standards and Health Advisories Tables, EPA
  822-F-18-001 Office of Water U.S. Environmental Protection Agency
  Washington, DC.
- M. Kobya, E. Demirbas, E. Senturk and M. Ince, Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone, Bioresour. Technol., 96 (2005) 1518-1521.
- 20. F. -Y. Yi, D. Chen, M. -K. Wu, L. Han, H. -L. Jiang, Chemical Sensors Based on Metal-Organic Frameworks, Chem.Plus.Chem. 81 (2016) 675-690.
- 21. C. F. Qiao, X. N. Qu, Q. Yang, Q. Wei, G. Xie, S. P. Chen and D. S. Yang, Instant high-selectivity Cd-MOF chemosensor for naked-eye detection of Cu(II) confirmed using *in situ* microcalorimetry, Green Chem., 18 (2016) 951-956.
- 22. J. Lia, X. Yuan, Y.-N. Wu, X. Ma, F. Li, B. Zhang, Y. Wang, Z. Lei, Z. Zhang, From powder to cloth: Facile fabrication of dense MOF-76(Tb) coating onto natural silk fiber for feasible detection of copper ions, Chem. Eng. Sci. 350 (2018) 637-644.
- 23. L. L. Liu, Y. Z. Yu, X. -J. Zhao, Y. R. Wang, F. Y. Cheng, M. K. Zhang, J. J. Shu, L. Liu, A robust Zn(II)/Na(I)-MOF decorated with [(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub><sup>2n-</sup>

anions for the luminescence sensing of copper ions based on the inner filter effect, Dalton Trans., 47 (2018) 7787–7794.

- 24. B. Dhal, H. N. Thatoi, N. N. Das, B. D. Pandey, Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: A review, J. Hazard. Mater. 250-251 (2013) 272–291.
- 25. T. Y. Gu, M. Dai, D. J. Young, Z. G. Ren, J. P. Lang, Luminescent Zn(II) Coordination Polymers for Highly Selective Sensing of Cr(III) and Cr(VI) in Water, Inorg. Chem. 56 (2017) 466-4678.
- 26. B. Parmar, Y. Rachuri, K. K. Bisht, E. Suresh, Mixed-Ligand LMOF Fluorosensors for Detection of Cr(VI) Oxyanions and Fe<sup>3+</sup>/Pd<sup>2+</sup> Cations in Aqueous Media, Inorg. Chem. 56 (2017) 10939-10949.
- 27. R. Rakhunde, L. Deshpande, H.D. Juneja, Chemical speciation of chromium in water: a review, Crit. Rev. Environ. Sci. Technol. 42 (2012) 776–810.
- 28. A.A. Mohamed, A.T. Mubarak, Z.M.H. Marstani, K.F. Fawy, A novel kinetic determination of dissolved chromium species in natural and industrial wastewater, Talanta 70 (2006) 460–467.
- 29. S. Mohandossa, J. Sivakamavallib, B. Vaseeharanb, T. Stalina Host-guest molecular recognition based fluorescence On-Off-On chemosensor for nanomolar level detection of  $Cu^{2+}$  and  $Cr_2O_7^{2-}$  ions: Application in XNOR logic gate and human lung cancer living cell imaging, Sens Actuators B 234 (2016) 300-15.

- 30. A. Prakash, S. Chandra, D. Bahadur, Structural, magnetic, and textural properties of iron oxide-reduced graphene oxide hybrids and their use for the electrochemical detection of chromium, Carbon 50 (2012) 4209–4219.
- 31. Y. Lin, X. Zhang, W. Chen, W. Shi, P. Cheng, Three Cadmium Coordination Polymers with Carboxylate and Pyridine Mixed Ligands: Luminescent Sensors for FeIII and CrVI Ions in an Aqueous Medium. Inorg. Chem. 56 (2017) 11768–11778.
- 32. R. Lv, J. Wang, Y. Zhang, H. Li, L. Yang, S. Liao, W. Gu, X. Liu, An aminodecorated dual-functional metal–organic framework for highly selective sensing of Cr(iii) and Cr(vi) ions and detection of nitroaromatic explosives, J. Mater. Chem. A 4 (2016) 15494-15500.
- 33. W.-H. Huang, J.-Z. Li, T. Liu, L.-S. Gao, M. Jiang, Y.-N. Zhang, Y.-Y. Wang, A stable 3D porous coordination polymer as multi-chemosensor to Cr(iv) anion and Fe(iii) cation and its selective adsorption of malachite green oxalate dye, RSC Adv. 5 (2015) 97127-97132.
- 34. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K.
  P. Lillerud, A New Zirconium Inorganic Building Brick Forming Metal Organic
  Frameworks with Exceptional Stability, J. Am. Chem. Soc. 130 (2008) 13850–
  13851.
- 35. M. Zhang, Y.-P. Chen, M. Bosch, T. Gentle, K. Wang, D. Feng, Z. U. Wang and H.-C. Zhou, Symmetry-Guided Synthesis of Highly Porous Metal–Organic Frameworks with Fluorite Topology, Angew. Chem. Int. Ed. 53 (2014) 815–818.

29

- 36. Y. Bai, Y. Dou, L.-H. Xie, W. Rutledge, J. –R. Li, H. –C. Zhou, Zr-based metal– organic frameworks: design, synthesis, structure, and applications, Chem. Soc. Rev. 45 (2016) 2327-2367.
- 37. J. Yang, Y. Dai, X. Zhu, Z. Wang, Y. Li, Q. Zhuang, J. Shi, J. Gu, Metal-Organic Frameworks with inherent recognition sites for selective phosphate sensing through their coordination-induced fluorescence enhancement effect, J. Mater. Chem. A 3, (2015) 7445–7452.
- 38. A. Kumar, H.-S. Kim, N-(3-Imidazolyl)propyl dansylamide as a selective Hg<sup>2+</sup> sensor in aqueous media through electron transfer, Spectrochim. Acta. A 148 (2015) 250-254.
- A. Kumar, M. K. Ghosh, C.-H. Choi, H.-S. Kim, Selective fluorescence sensing of salicylic acids using a simple pyrenesulfonamide receptor, RSC Adv. 5 (2015) 23613-23621.
- 40. S. Sanda, S. Parshamoni, S. Biswas, S. Konar, Highly Selective Detection of Palladium and Picric Acid by a Luminescent MOF: A Dual Functional Fluorescent Sensor, Chem. Commun. 51 (2015) 6576-6579.
- 41. A. Helal, H. L. Nguyen, A. Al-Ahmed, K. E. Cordova, Z. H. Yamani, An Ultrasensitive and Selective Metal–Organic Framework Chemosensor for Palladium Detection in Water. Inorg. Chem. 58 (2019) 1738–1741.
- 42. M. Zheng, H. Tan, Z. Xie, L. Zhang, X. Jing, Z. Sun, Fast Response and High Sensitivity Europium Metal Organic Framework Fluorescent Probe with Chelating Terpyridine Sites for Fe<sup>3+</sup>, ACS Appl. Mater. Interfaces 5 (2013) 1078–1083.

- 43. S. Chen, Z. Shi, L. Qin, H. Jia, H. Zheng, Two New Luminescent Cd(II)-Metal–Organic Frameworks as Bifunctional Chemosensors for Detection of Cations Fe<sup>3+</sup>, Anions CrO<sub>4</sub><sup>2-</sup>, and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> in Aqueous Solution, Cryst. Growth Des. 17 (2017) 67–72.
- 44. W. Sun, J. Wang, G. Zhang, Z. Liu, A luminescent terbium MOF containing uncoordinated carboxyl groups exhibits highly selective sensing for Fe<sup>3+</sup> ions, RSC Adv. 4 (2014) 55252–55255.