

Cite this: *RSC Adv.*, 2019, 9, 34949

Two-dimensional Cd(II) coordination polymer encapsulated by Tb³⁺ as a reversible luminescent probe for Fe³⁺†

Yuandi Wu,^a Meihua Lin,^a Dongyang Liu,^a Ming Liu^a and Jing Qian^{ID}*^{abc}

A two-dimensional luminescent cadmium(II) coordination polymer, [Cd(modbc)]_n (Cd-P); modbc = 2-methyl-6-oxygen-1,6-dihydro-3,4'-bipyridine-5-carbonitrile, was successfully synthesized by a solvothermal reaction and fully characterized. Cd-P exhibited excellent luminescence emission, and detected Cu²⁺, Co²⁺, Fe²⁺, Hg²⁺, Ni²⁺ and Fe³⁺ ions with high sensitivity and showed good anti-interference performance. After encapsulation of Tb³⁺ ions in Cd-P, the as-obtained fluorescent functionalized Tb³⁺@Cd-P maintained distinct chemical stabilities in different pHs and metal salt solutions. Subsequently, we explored the potential application of Tb³⁺@Cd-P as a probe for Fe³⁺ ions. A new and convenient method for individual identification of Fe³⁺ ions by the combination of Cd-P and Tb³⁺@Cd-P was successfully established. A possible sensing mechanism is discussed in detail.

Received 23rd August 2019
Accepted 22nd October 2019

DOI: 10.1039/c9ra06639j

rsc.li/rsc-advances

1. Introduction

Chemists have been highly successful at developing detection methods for anions, cations, small organic molecules and biological macromolecules. Fluorescent organogels have become novel and promising materials, especially in sensor applications.^{1,2} Metal-organic frameworks (MOFs) can be defined as one of the ideal candidates for chemical sensors.³ Luminescent coordination polymers (CPs) as chemosensors, have also attracted more and more attention for the selective and sensitive detection of some explosives,^{4,5} organic compounds,^{6,7} inorganic ions,^{8,9} etc., through “turn on”¹⁰ or “turn off”¹¹ sensing. Among them, rapid selection and sensitive detection of Fe³⁺ ions has aroused widespread interest because Fe³⁺ ions have important cell functions such as hemoglobin formation and play a vital role in biological systems.^{12–14} Its deficiency or excess over the normal allowable limit can lead to physical diseases such as diabetes, anemia, arthritis, mental decline, cancer and so on.^{15,16} In addition, with the rapid development of industry, a large number of harmful inorganic ions is being released into the environment, and causing adverse effects on people's health.^{17–19} In a word, not only is Fe³⁺ recognized as an

industrial pollutant but also it plays a significant role in living organisms. Therefore, it is an urgent problem to explore the high effective probes to detect Fe³⁺.^{20–23}

3D microporous CPs, which can produce significant fluorescence signals and visible emission colors, and have become the most reported chemical sensors.^{4,7–11,24} At present, compared with the transition-metal-based CPs, Ln-CPs have aroused great interest due to their unique optical characteristics such as large Stokes shift, high color purity, and long fluorescence lifetime *via* the “antenna effect” obtained from the 4f–4f electron transitions.^{7,8,25,26} Recently, an alternative strategy for constructing Ln-CPs and optimizing photoluminescence was proposed by doping lanthanide ions to CPs *via* post-synthesis method (PSM).^{27–29} Any desired fluorescent probes can be acquired by modifying the molar ratio of the starting reactants.^{30–33} In the construction of CPs for the above applications, poly-carboxylic acid and N-donor ligands have been widely chosen as building blocks. However, the achievement of a fast response, practicability, and reproducible performance for Fe³⁺ detection using fluorescence is still challenging.³⁴

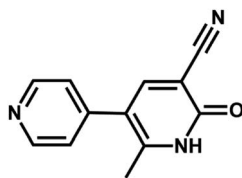
In fact, it was rarely reported that low-dimensional chemical sensors with one-dimensional or two-dimensional structures were considered for selective detection of inorganic ions.^{35,36} In this study, asymmetric unflexible 2-methyl-6-oxygen-1,6-dihydro-3,4'-bipyridine-5-carbonitrile (modbc) containing coordination N and O atoms, was utilized as an anionic ligand (Scheme 1). Then, we report a multifunctional highly luminescent [Cd(modbc)]_n (Cd-P), and obtain a Ln-decorated CP Tb³⁺@Cd-P. Cd-P was fully characterized by IR spectroscopy, elemental analysis, single crystal, XPS, powder X-ray diffraction, thermal and photoluminescence properties. Moreover, selective

^aCollege of Chemistry, Tianjin Normal University, Tianjin 300387, P. R. China. E-mail: qianjing@aliyun.com

^bTianjin Key Laboratory of Structure and Performance for Functional Molecules, Tianjin Normal University, Tianjin 300387, P. R. China

^cKey Laboratory of Inorganic-Organic Hybrid Functional Materials Chemistry, Tianjin Normal University, Ministry of Education, Tianjin 300387, P. R. China

† Electronic supplementary information (ESI) available: Experimental details, crystallographic data, tables, TGA, PXRD, XPS, EDS, and luminescent spectra. CCDC 1881136. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ra06639j



Scheme 1 The structure of modbc.

and sensing properties of Cd-P and Tb³⁺@Cd-P were investigated in H₂O for Fe³⁺ ions in detail.

2. Experimental section

2.1. Synthesis of [Cd(modbc)₂]_n (Cd-P)

Cd-P was obtained by one-pot solvothermal synthesis from CdSO₄ (0.05 mmol, 0.008 g), modbc (0.1 mmol, 0.021 g) in 10 mL of water/DMF (4 : 1). The reactants were placed in a 25 mL reactor, and heated to 120 °C for 72 h under self-generated pressure, then cooled to atmospheric temperature at a rate of 2.0 °C h⁻¹. Light yellow rodlike-shaped crystals suitable for X-ray analysis were obtained, which were filtered, washed and dried (Tables S1 and S2†). Total yield of Cd-P was *ca.* 54% based on CdSO₄. Anal. Calcd for Cd_{0.50}C₁₂H₈N₃O: C, 54.1; H, 3.03; N, 15.77%. Found: C, 53.59; H, 3.47; N, 15.34%. FT-IR (KBr, cm⁻¹): 3377.05 (vs.), 2982.1 (s), 2215.19 (m), 1601.95 (s), 1386.11 (s), 1109.61 (vs.), 983.56 (vs.), 856.65 (s), 617.75 (m), 541.33 (vs.) (Fig. S1†).

2.2. Preparation of Tb³⁺@Cd-P

Tb³⁺@Cd-P was prepared by adding 100 mg powder of Cd-P to the aqueous solution of Tb(NO₃)₃ soaking for 24 h, and separated by centrifugation and washed with deionized water to remove the remaining Tb³⁺. The collected crystal powder was dried for 12 h under vacuum conditions of 60 °C.

2.3. Experiment of luminescent detection

Cd-P and Tb³⁺@Cd-P (0.01 mM) were well-dispersed in 5 mM Tris-HCl/NaCl buffer (pH 7.0) by sonicating for 0.5 h to obtain a solution, which were used for luminescent experiments. The aqueous solutions of nitrate salts or chloride of Na⁺, Ag⁺, Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Hg²⁺, Fe³⁺ (1.0 × 10⁻³ M) were prepared for luminescent experiments. Generally, ferrous salt is easy to be oxidized in the air, but it is relatively stable and not easy to be oxidized after forming double salt, so we chose double salt (NH₄)₂Fe(SO₄)₂ to prepare the aqueous solution of Fe²⁺. In addition, the same concentrations (1.0 × 10⁻³ M) of aqueous solutions containing potassium salts of MnO₄⁻, CO₃²⁻, SO₄²⁻, Cl⁻, and Cr₂O₇²⁻ were also prepared. The Stern-Volmer equation: $I_0/I = 1 + K_{sv}[Q]$ was applied to judge the quenching effect.³⁷ The detection limit was calculated according to $3\sigma/k$ recommended by IUPAC, where the standard deviation, σ value was estimated by fifteen repeated fluorescent measurements of Cd-P and Tb³⁺@Cd-P, and k value was obtained using a calibration curve of I vs. $[Q]$.³⁸ The fluorescence

stability of Cd-P and Tb³⁺@Cd-P in the aqueous solution at different pH values were investigated.

3. Results and discussion

3.1. Structural description

By one-pot solvothermal method, CdSO₄ combined with modbc produced a 2D framework at about 54% yield. Single-crystal X-ray diffraction shows that Cd-P crystallizes in the *P*4₃2₁2 space group. The symmetric unit consists of one Cd²⁺ ion and two modbc anions. A six-coordinated Cd²⁺ ion exhibits a distorted octahedron geometry, which is completed by two oxygen atoms and four nitrogen atoms from different modbc molecules (Fig. 1a). Each modbc molecule adopts tridentate mode (Fig. 1b). The Cd-N and Cd-O bond lengths fall in the reasonable range of 2.269–2.501 Å, and adjacent Cd²⁺ ions are bridged by modbc ligands into the cadmium chain. The structural feature of Cd-P is that each cadmium chain serves as a secondary building unit and is further connected by a modbc-ligand into a 2D framework, containing tetranuclear homometallic Cd₄(modbc)₄ cycles, with different Cd1...Cd1 distances of 10.434 and 14.756 Å (Fig. 1c).

3.2. Property characterization

As shown in Fig. S2,† thermogravimetric analysis (TGA) of Cd-P was measured to evaluate its thermal stability at ≤450 °C. Further, powder X-ray diffraction (PXRD) of Cd-P confirmed the phase purity and excellent stability in H₂O and common organic solvents, as well as in metal salt aqueous system by matching the simulated pattern (Fig. S3†). The samples were heated for 8 h at different temperatures and the corresponding PXRD diagrams were determined. As shown in Fig. S4,† when heated

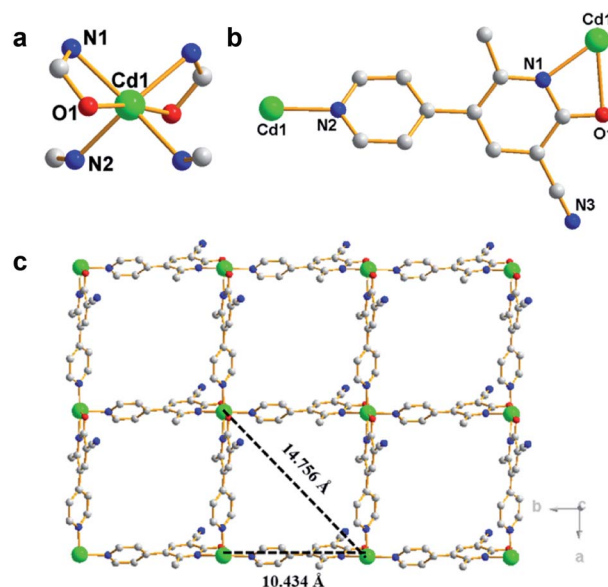


Fig. 1 (a) Coordination environment of Cd²⁺ ion in Cd-P. (b) Coordination mode of modbc molecule. (c) Two-dimensional reticulated structure of Cd-P along the *c* axis; red, O; gray, C; green, Cd1; blue, N. All H atoms are omitted for clarity.



to 180 °C, Cd-P framework still contains excellent chemical stability. High stability of Cd-P may result from the formation of strong bonds between N/O atoms and Cd²⁺ ions based on Pearson's hard/soft acid/base principle,^{39,40} or relatively highly dense 2D framework, and the synergy effect of these factors.⁴¹ Obviously, Cd-P framework with excellent chemical stability offers the possibility for its practical application as a metal ion sensor.

Afterward, Cd-P was soaked in the aqueous solution of Tb(NO₃)₃ to obtain Tb³⁺@Cd-P. The crystalline integrity of Cd-P remained unchanged after the incorporation of Tb³⁺ ion, which was confirmed by PXRD. In order to explore the stability of the Tb³⁺@Cd-P, the sample was treated with FeCl₃ solution. After multiple immersion in FeCl₃ solution for 12 h, the PXRD patterns of Tb³⁺@Cd-P showed the excellent stability of the crystalline integrity (Fig. S5†). To obtain the number of Tb³⁺ ions doping into Cd-P, EDS analysis on Tb³⁺@Cd-P was performed (Fig. S6†). The result showed that the ratio of Cd²⁺ and Tb³⁺ ions was approximately 5 : 1. Further, X-ray photoelectron spectroscopy (XPS) analyses on Tb³⁺@Cd-P and Cd-P were performed. As shown in Fig. S7,† after treatment by Tb³⁺, three new peaks at 1277.6, 1243.4 and 151 eV appeared corresponding to Tb 3d_{3/2}, Tb 3d_{5/2}, Tb 4d, by which the existence of Tb³⁺ ions in the composites can be ascertained.⁴²

3.3. Fluorescence properties

Considering that CPs composed of d¹⁰ metal ions and aromatic organic ligands may be the promising luminescent materials,⁴³ the fluorescence properties of Cd-P were investigated in 5 mM Tris-HCl/NaCl buffer (pH 7.0) at room temperature. Under 318 and 328 nm excitation, the luminescence of Cd-P and Tb³⁺@Cd-P in aqueous solution show the intense emission centered at 400 and 390 nm, respectively, while the luminescence of modbc exhibits a similar emission centered at 475 nm at 412 nm excitation (Fig. S8†). Moreover, the fluorescence emission spectra of Cd-P and Tb³⁺@Cd-P show good fluorescence stability within 12 h. In addition, the fluorescence intensity of Cd-P and Tb³⁺@Cd-P dispersed in aqueous solution is basically unchanged in the range of pH 0.5–14.0 (Fig. S9†). Obviously, Cd-P framework with excellent chemical stability offers the possibility for its practical application based on the fact that industrial effluent and polluted rivers are usually acidic or alkaline.⁴⁴

3.4. Detection of ions

To detect water pollution, we explored the potential detection of Cd-P to various cations and anions. The same concentrations (1.0 × 10^{−3} M) of aqueous solutions of Na⁺, Ag⁺, Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Fe²⁺, Hg²⁺, Fe³⁺, MnO₄[−], CO₃^{2−}, SO₄^{2−}, Cl[−], and Cr₂O₇^{2−} were prepared, and we investigated their effects on the fluorescence intensity of Cd-P. As shown in Fig. 2, Cd-P shows selective sensing ability toward different cations and anions. Obviously, Cu²⁺, Co²⁺, Ni²⁺, Fe²⁺, Hg²⁺ and Fe³⁺ ions present the higher quenching efficiency.

To investigate the fluorescence sensitivity ability of Cd-P for detecting Cu²⁺, Co²⁺, Fe²⁺, Hg²⁺, Ni²⁺ and Fe³⁺ ions, the

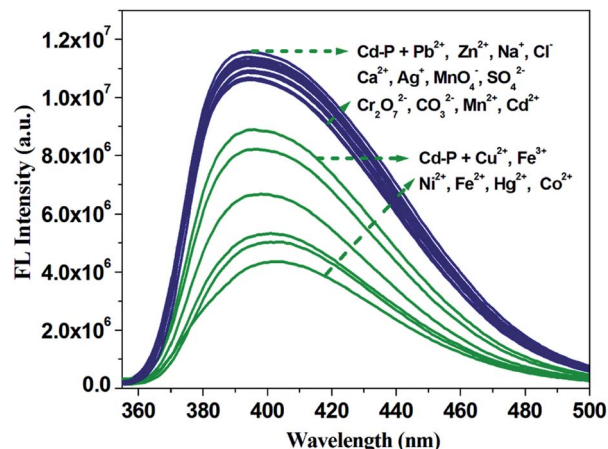


Fig. 2 Luminescence intensity of Cd-P upon different ions at 400 nm in 5 mM Tris-HCl/NaCl buffer (pH 7.0). [Cd-P] = 1.0 × 10^{−5} M and [ions] = 2.5 μM. λ_{ex}: 318 nm, λ_f: 400 nm, slit width: 4 nm.

corresponding luminescence spectra were recorded by ion concentration titration. As shown in Fig. S10,† the remarkable fluorescence declines of Cd-P are observed in ionic concentration range. Furthermore, based on the application requirements of wastewater or pollutant detection, the anti-interference ability of Cd-P sensing for Cu²⁺, Co²⁺, Fe²⁺, Hg²⁺, Ni²⁺ and Fe³⁺ ions to other metal ions was explored at the same fluorescence measurement conditions. It is quite pleasing that the quenching effects by Cu²⁺, Co²⁺, Fe²⁺, Hg²⁺, Ni²⁺ and Fe³⁺ ions on the luminescence intensity of Cd-P are almost not influenced by the interfering metal ions, as shown in Fig. 3 and S11.†

Quantitatively, at low concentrations, the good linearity plots of Co²⁺, Ni²⁺, Fe³⁺, Fe²⁺, Hg²⁺ and Cu²⁺ ions were obtained, as shown in

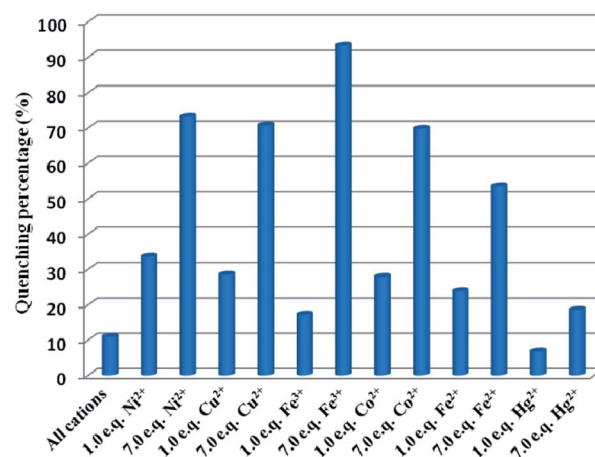


Fig. 3 Comparison of the luminescence intensity of Cd-P in 5 mM Tris-HCl/NaCl buffer (pH 7.0): blank, after addition of mixed ions (Na⁺, Ag⁺, Cd²⁺, Zn²⁺, Pb²⁺, Ca²⁺, Mn²⁺; total concentration of mixed metal ions is 35 μM), and followed by addition of Cu²⁺, Co²⁺, Ni²⁺, Fe²⁺, Hg²⁺ and Fe³⁺ ions, respectively ([analyte] = 5 or 35 μM). λ_{ex}: 318 nm, λ_f: 400 nm, slit width: 4 nm.



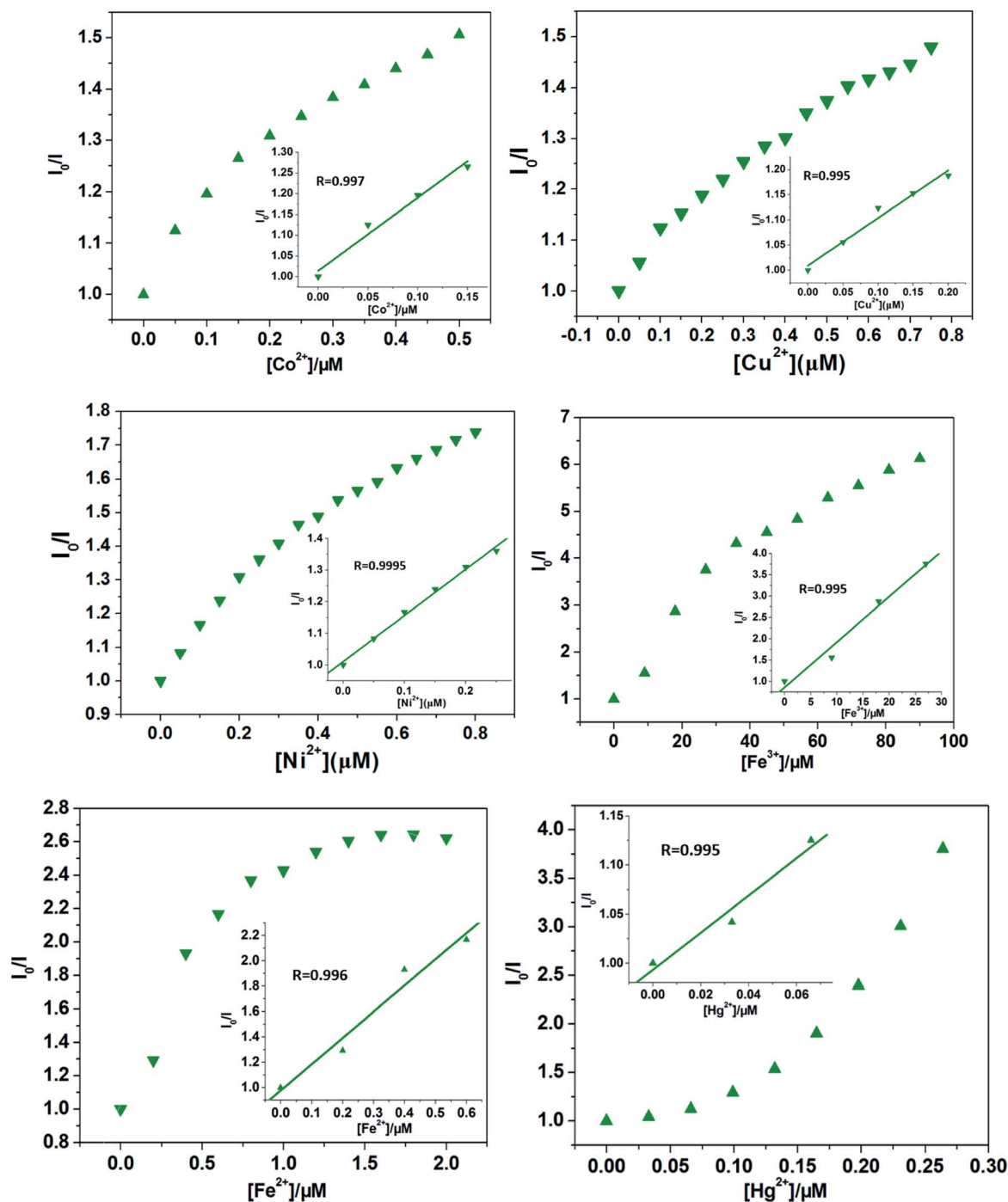


Fig. 4 The Stern–Volmer plot of I_0/I versus Co^{2+} , Ni^{2+} , Fe^{3+} , Fe^{2+} , Hg^{2+} , and Cu^{2+} ions concentration, respectively (insets: the related Stern–Volmer plots at low Co^{2+} , Ni^{2+} , and Cu^{2+} ions concentration). λ_{ex} : 318 nm, λ_{f} : 400 nm, slit width: 4 nm.

Fig. 4. Also, the corresponding quenching constants, K_{sv} , were calculated, $1.76 \pm 0.18 \times 10^6 \text{ M}^{-1}$ for Co^{2+} ions, $0.95 \pm 0.89 \times 10^6 \text{ M}^{-1}$ for Cu^{2+} ions, $1.46 \pm 0.058 \times 10^6 \text{ M}^{-1}$ for Ni^{2+} ions, $1.06 \pm 0.11 \times 10^5 \text{ M}^{-1}$ for Fe^{3+} ions, $2.07 \pm 0.27 \times 10^6 \text{ M}^{-1}$ for Fe^{2+} ions, and $1.89 \pm 0.36 \times 10^6 \text{ M}^{-1}$ for Hg^{2+} ions, respectively. In addition, the LODs based on Cd-P were also obtained and $0.19 \pm 0.06 \text{ }\mu\text{M}$ for Co^{2+} ions, $0.26 \pm 0.04 \text{ }\mu\text{M}$ for Cu^{2+} ions, $0.23 \pm 0.03 \text{ }\mu\text{M}$ for Ni^{2+} ions, $0.047 \pm 0.002 \text{ }\mu\text{M}$ for Fe^{3+} ions, $0.58 \pm 0.013 \text{ nM}$ for Fe^{2+} ions,

and $5.79 \pm 2.0 \text{ mM}$ for Hg^{2+} ions, respectively. However, at higher concentrations, the Stern–Volmer figures deviate from the line maybe due to energy transfer processes or self-absorption.³⁷ In this work, the calculated LOD values of Cd-P for Cu^{2+} , Ni^{2+} and Fe^{3+} ions are far lower than maximum allowable levels (MAL) in drinking water as required by the Environmental Protection Agency (EPA, 15.7, 0.34, and 5.36 μM , respectively).⁴⁵



3.5. Differentiation of Co^{2+} , Ni^{2+} , Fe^{3+} , Fe^{2+} , Hg^{2+} and Cu^{2+} ions

It is worth noting that Cd-P cannot selectively distinguish Cu^{2+} , Co^{2+} , Ni^{2+} , Fe^{2+} , Hg^{2+} and Fe^{3+} ions. To improve the selectivity of Cd-P, $\text{Tb}^{3+}\text{@Cd-P}$ was obtained *via* PSM. As expected, with the concentration titration of Fe^{3+} ions, the luminescence intensity of $\text{Tb}^{3+}\text{@Cd-P}$ is quenched prominently (Fig. S12†). Further, we investigated the selectivity of $\text{Tb}^{3+}\text{@Cd-P}$ toward a wide range of ions. The other measured ions show a negligible influence to the emission intensity of $\text{Tb}^{3+}\text{@Cd-P}$ except Fe^{3+} and Fe^{2+} ions, as shown in Fig. 5. To examine the sensing behavior of $\text{Tb}^{3+}\text{@Cd-P}$ to Fe^{2+} , titration experiment of $\text{Tb}^{3+}\text{@Cd-P}$ with Fe^{2+} was performed (Fig. S13†). On gradual addition of Fe^{2+} , the fluorescence of $\text{Tb}^{3+}\text{@Cd-P}$ solutions significantly enhanced. We also observed that $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ exhibited the fluorescence emission at about 390 nm, as deposited in Fig. S14.† Therefore, we speculate that the luminescence of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ is responsible for the fluorescence enhancement by Fe^{2+} . These results indicate that $\text{Tb}^{3+}\text{@Cd-P}$ can detect Fe^{3+} selectively among coexisting ions.

To further evaluate the anti-interference ability of $\text{Tb}^{3+}\text{@Cd-P}$ as a selective sensor for Fe^{3+} , competitive experiments were conducted in the presence of other metal ions (Fig. 6 and S15†).⁴⁶ No significant differences in luminescence intensity can be observed among these solutions. All these results clearly indicate $\text{Tb}^{3+}\text{@Cd-P}$ has a high selectivity and anti-interference ability in the detection of Fe^{3+} under aqueous conditions.⁴⁷

One unexpected finding is that both Cd-P and $\text{Tb}^{3+}\text{@Cd-P}$ are easily sensitized by Fe^{3+} ions, and the rapid response time of the sensitization process obtained by the experiment is approximately 10 s (Fig. S16†). Compared with Cd-P, the influence of Fe^{3+} ions on the luminescence intensity of $\text{Tb}^{3+}\text{@Cd-P}$ is significantly smaller (Fig. 7a and b). To better analyze and compare with Cd-P, the Stern–Volmer plot of $\text{Tb}^{3+}\text{@Cd-P}$ for detecting Fe^{3+} was obtained (Fig. S17†), a linear presented at lower and higher experimental concentration

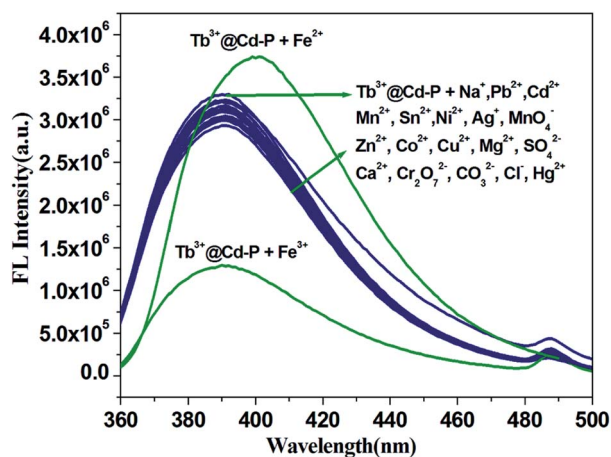


Fig. 5 Luminous intensity of $\text{Tb}^{3+}\text{@Cd-P}$ upon different ions at 390 nm in 5 mM Tris–HCl/NaCl buffer (pH 7.0). [$\text{Tb}^{3+}\text{@Cd-P}$] = 1.0×10^{-5} M and [ions] = 2.5 μM . λ_{ex} : 328 nm, λ_{f} : 390 nm, slit width: 4 nm.

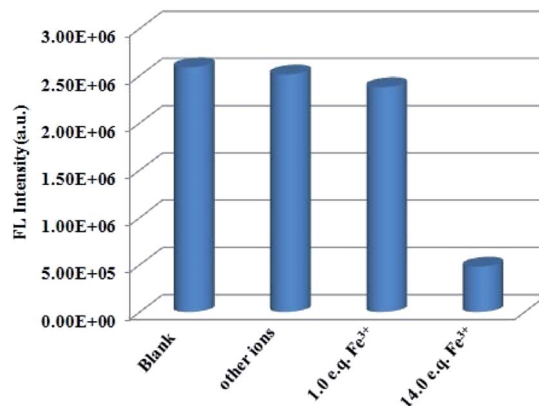


Fig. 6 Comparison of the luminescence intensity of $\text{Tb}^{3+}\text{@Cd-P}$ in 5 mM Tris–HCl/NaCl buffer (pH 7.0): after addition of mixed ions (Na^+ , Ag^+ , Cd^{2+} , Zn^{2+} , Pb^{2+} , Ca^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Sn^{2+} , Mg^{2+} , Hg^{2+} , Fe^{2+} , Mn^{2+} ; total concentration of mixed metal ions is 70 μM), and followed by addition of Fe^{3+} ions ($[\text{Fe}^{3+}] = 5$ or 70 μM). λ_{ex} : 328 nm, λ_{f} : 390 nm, slit width: 4 nm.

range (0–20 μM ; 36–90 μM), and the K_{SV} and LOD values were $1.31 \pm 0.01 \times 10^4 \text{ M}^{-1}$, $1.09 \pm 0.02 \times 10^5 \text{ M}^{-1}$, respectively, displaying the high quenching efficiency of the Fe^{3+} ions.^{48–50} In addition, the LODs based on $\text{Tb}^{3+}\text{@Cd-P}$ were also obtained and $0.66 \pm 0.02 \mu\text{M}$ for Fe^{3+} ions.

For Fe^{3+} ions at lower concentration, the values of $K_{\text{sv}}[\text{Tb}^{3+}\text{@Cd-P}]/K_{\text{sv}}[\text{Cd-P}]$ and $\text{LOD}[\text{Tb}^{3+}\text{@Cd-P}]/\text{LOD}[\text{Cd-P}]$ were 0.12 and 14.04, respectively, which further verify the above conclusion. In short, although Cu^{2+} , Co^{2+} , Fe^{2+} , Hg^{2+} , Ni^{2+} and Fe^{3+} ions can reduce the luminescence intensity of Cd-P, the luminescence quenching of $\text{Tb}^{3+}\text{@Cd-P}$ is only affected by Fe^{3+} ions. In addition, the luminescence quenching degree of $\text{Tb}^{3+}\text{@Cd-P}$ and Cd-P for Fe^{3+} ions is also different. We can selectively differentiate Fe^{3+} ions by combining the changes of the luminescence intensities of $\text{Tb}^{3+}\text{@Cd-P}$ and Cd-P. It exhibits a better performance, and the LODs were estimated to be 10^{-7} M, which also lies well below several MOF fluorescent sensors for detecting Fe^{3+} ion for a specific comparison (Table S3†).

Considering the cost of emitting probes, their regenerative properties play an important role in practical applications. Hence, to obtain $\text{Tb}^{3+}\text{@Cd-P} + \text{Fe}^{3+}$ samples, we dispersed $\text{Tb}^{3+}\text{@Cd-P}$ in the aqueous solution of $\text{Fe}(\text{NO}_3)_3$ (10^{-3} M) for 12 h, and separated by centrifugation then washed with deionized water to remove the remaining Fe^{3+} ions. The emission intensity of recovered $\text{Tb}^{3+}\text{@Cd-P}$ is well comparable to that of the parent sample (Fig. 8 and S18†). Fortunately, after five regeneration cycles, the yield of $\text{Tb}^{3+}\text{@Cd-P}$ to differentiate Fe^{3+} ions reaches about 78%. Above results confirm that $\text{Tb}^{3+}\text{@Cd-P}$ can achieve a differential detection toward Cu^{2+} , Co^{2+} , Ni^{2+} and Fe^{3+} ions, and exhibits high detection sensitivities. Moreover, as an Fe^{3+} ion-responsive probe, the $\text{Tb}^{3+}\text{@Cd-P}$ can exert the anti-interference, regenerative recognition and fast procedure under aqueous solution.



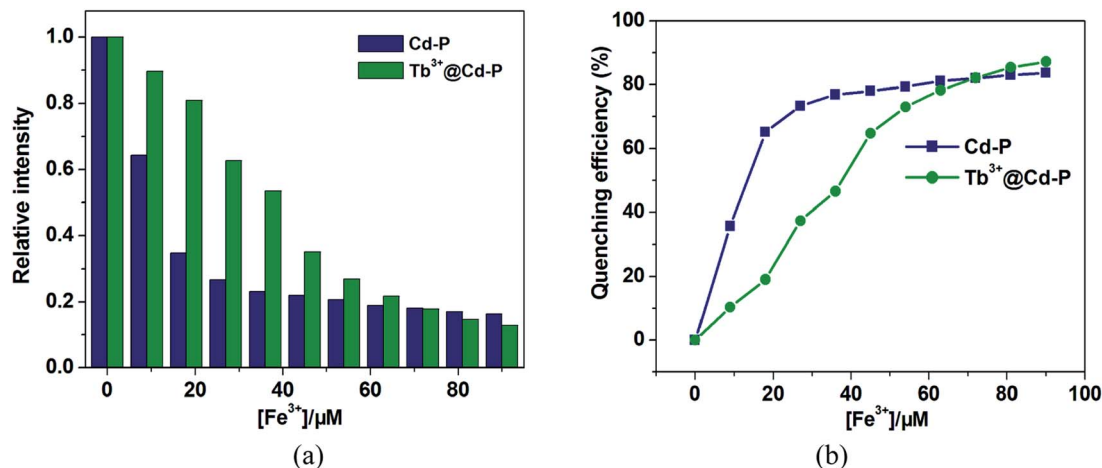


Fig. 7 (a) Relative fluorescence intensity and (b) the corresponding quenching efficiency of Cd-P and Tb³⁺@Cd-P vs. different Fe³⁺ ion concentrations. λ_{ex} : 328 nm, λ_{f} : 390 nm for Tb³⁺@Cd-P, slit width: 4 nm; λ_{ex} : 318 nm, λ_{f} : 400 nm for Cd-P, slit width: 4 nm.

3.6. Discussion of the mechanism

The high stabilities of Cd-P (Fig. S3 and S4†) and Tb³⁺@Cd-P (Fig. S5†) in aqueous solution of metal salts, organic solvents, different temperatures, and the solutions with pH range from 0.5 to 14.0 (Fig. S9†) suggest that the luminescence quenching is not caused by framework collapse. In order to observe whether these metal ions can enter the frame structure of Cd-P, ICP-AES analysis on Cd-P has been performed, as shown in Table S4.† Further, the XPS spectra of Cd-P before and after added Cu²⁺, Co²⁺, Ni²⁺, Fe³⁺ metal salt samples present that both carboxyl oxygen atoms of Cd-P and hydroxyl oxygen atoms of H₂O participate in the coordination of Fe³⁺ *etc* metal ions (Fig. S19†).²⁸

After Cd-P treatment by Tb³⁺ ions, EDS analysis on Tb³⁺@Cd-P shows that the ratio of Cd²⁺ and Tb³⁺ ions is approximately 5 : 1 (Fig. S6†). Fig. S20† shows that the UV-vis absorption band of Tb³⁺@Cd-P presents a significant red shift compared to Cd-P, indicating that Tb³⁺ ions interacts with Cd-P.⁵¹ Further, XPS analyses on Cd-P, Tb³⁺@Cd-P and Tb³⁺@Cd-P + Fe³⁺ also show that the luminescent CPs are high stability, and the luminescence quenching is not caused by framework collapse (Fig. S21† and 9a). Three new peaks at 1277.6, 1243.4 and 151 eV appear corresponding to Tb 3d_{3/2}, Tb 3d_{5/2}, Tb 4d, by which the existence of Tb³⁺ ions in the composites of Tb³⁺@Cd-P can be ascertained (Fig. 9b and c).⁴² The O 1s spectrum of Tb³⁺@Cd-P shown in Fig. 9d can be fitted into two peaks at 530.8 eV and 532.4 eV, which correspond to carboxyl group oxygen atoms and -OH species, respectively. In addition, the binding energy of N 1s does not change (Fig. 9e), implying that the N atom of modbc may not be involved in the coordination interaction with Tb³⁺ ions. The result shows that carboxyl oxygen atoms of Cd-P and hydroxyl oxygen atoms of H₂O participate in the coordination of Tb³⁺ ions.²⁸ Therefore, the emission peak of Tb³⁺@Cd-P shows a significant blue shift from 400 to 390 nm after post-treatment by Tb³⁺ ions, which can be attributed to the O atom of modbc coordinated with Tb³⁺ ions, but does not result in the “antenna effect” obtained from the 4f–4f electron transitions.²⁵ Tb³⁺@Cd-

P after treatment by Fe³⁺ ions, the corresponding Fe 2p peak is found supporting the presence of Fe in Tb³⁺@Cd-P (Fig. 9f). The O 1s peak further shifts to 530.9 eV (Fig. 9d). The fast and simple regeneration method also shows that the binding between Tb³⁺@Cd-P and Fe³⁺ ions should be weaker (Fig. 8 and S18†), which may be that Fe³⁺ ions spread to the frameworks of CPs leading to luminescence quenching.⁷

In addition, Fig. S8 and S20† show that there exists extensive overlap between UV-vis absorbance of Fe³⁺ and the excitation absorbance of Tb³⁺@Cd-P, while negligible for other metal ions.⁵² As well as the absorbance of Fe³⁺ corresponding to the excitation absorbance of Tb³⁺@Cd-P, ultimately lead to the luminescence quenching of Tb³⁺@Cd-P.^{53,54} As shown in Fig. S22 and Table S5,† the lifetimes are shortened from 4.15 to 1.99 ns, 4.15 to 1.94 ns, and 4.15 to 1.98 ns after Cd-P treated with Cu²⁺, Co²⁺, and Ni²⁺ ions, and the downward Stern–Volmer curve at higher Cu²⁺, Co²⁺ or Ni²⁺ ion concentrations demonstrate that both static and dynamic mechanisms operate at higher concentration. However, the lifetimes of Cd-P

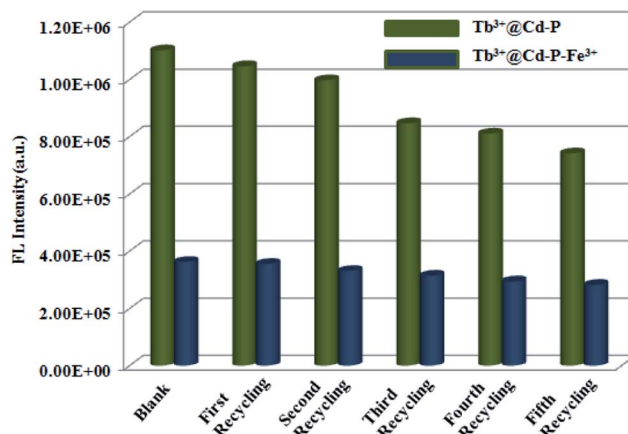


Fig. 8 Five regeneration cycles for detection of Fe³⁺ ions by Tb³⁺@Cd-P. λ_{ex} : 328 nm, λ_{f} : 390 nm, slit width: 4 nm.



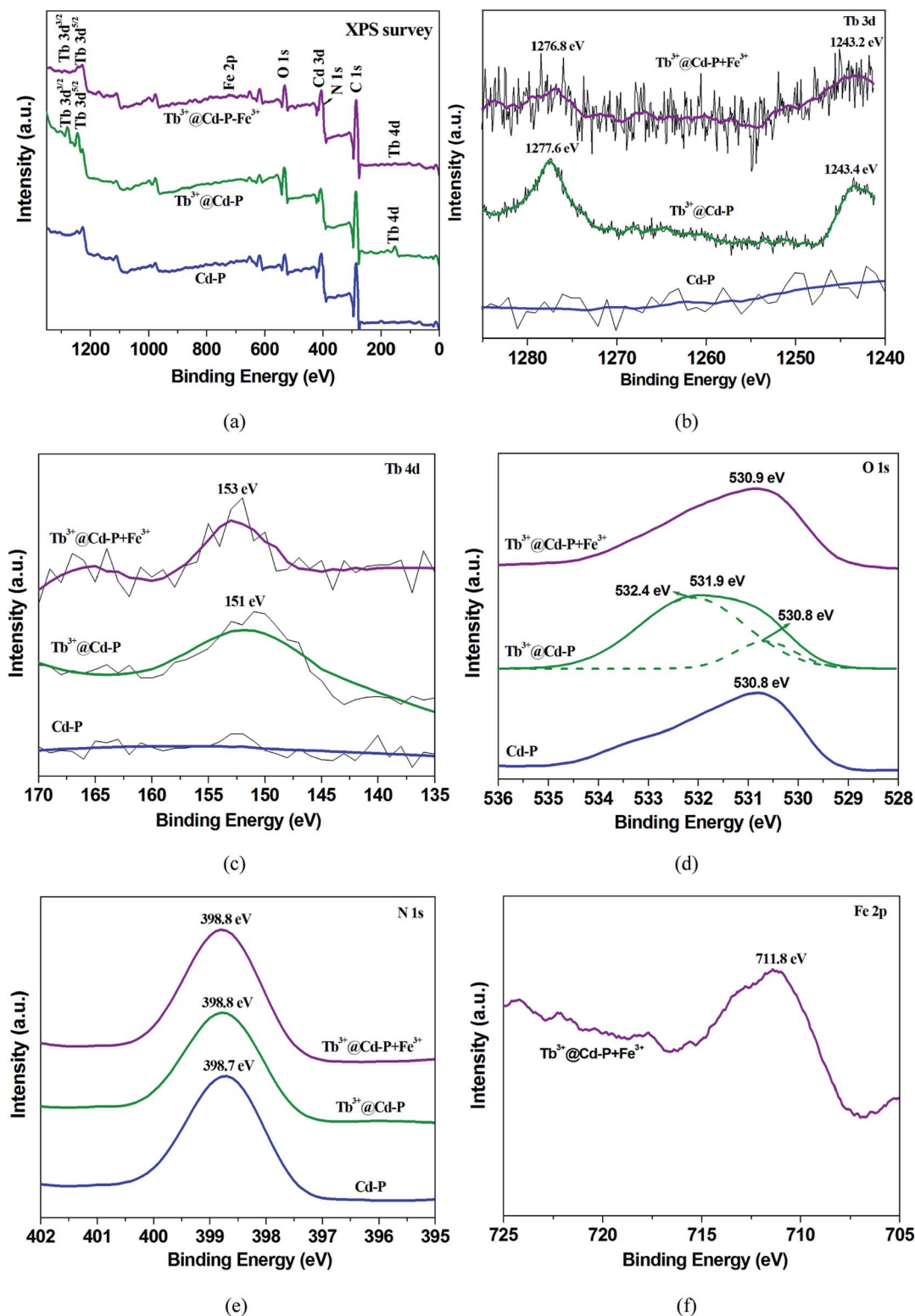


Fig. 9 The XPS spectra of Cd-P, Tb^{3+} @Cd-P, and Tb^{3+} @Cd-P + Fe^{3+} samples: (a) the survey spectrum, the high resolution XPS spectra of (b) Tb 3d, (c) Tb 4d, (d) O 1s, (e) N 1s, and (f) Fe 2p, respectively.

and Tb^{3+} @Cd-P remain in the presence and absence of Fe^{3+} ions (Fig. S22, S23 and Table S4†), and the Stern–Volmer plots are linear at the full experimental concentration region, which

suggest that there are the static quenching mechanisms in selectively differentiate Fe^{3+} ions by combining Tb^{3+} @Cd-P and Cd-P.⁵⁵



4. Conclusion

In summary, a Cd(II)-based polymer framework (Cd-P) was constructed and exhibited high sensitivity ($K_{sv} \sim 10^6 \text{ M}^{-1}$ and LODs $\sim 10^{-7} \text{ M}$) toward Cu^{2+} , Co^{2+} , Hg^{2+} , Fe^{2+} , Ni^{2+} and Fe^{3+} ions via luminescence quenching. In addition, a fluorescent hybrid material, $\text{Tb}^{3+}@\text{Cd-P}$, derived from Cd-P via PSM, which maintains high chemical stability, good selectivity, and excellent response toward Fe^{3+} ions, is most likely associated with the competition between the excitation of $\text{Tb}^{3+}@\text{Cd-P}$ and the absorption of Fe^{3+} ions, wherein there is also the weak interaction of $\text{Tb}^{3+}@\text{Cd-P}$ with Fe^{3+} ions. Also, we can differentiate selectivity Fe^{3+} ions by the combination of Cd-P and $\text{Tb}^{3+}@\text{Cd-P}$. It should be mentioned that the two-dimensional luminescent probes for detecting a trace amount of Fe^{3+} ions (μM) and quick response time ($\sim 10 \text{ s}$) are still few reports. Most importantly, $\text{Tb}^{3+}@\text{Cd-P}$ can act as a reversible luminescent probe for Fe^{3+} ions with potential application.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21571141) and Tianjin Natural Science Foundation, China (No. 15JCYBJC20300).

References

- 1 X. H. Cao, N. Zhao, A. P. Gao, Q. Q. Ding, Y. R. Li and X. P. Chang, *Langmuir*, 2018, **34**, 7404–7415.
- 2 A. Panja and K. Ghosh, *Mater. Chem. Front.*, 2018, **2**, 1866–1875.
- 3 T. L. Mako, J. M. Racicot and M. Levine, *Chem. Rev.*, 2019, **119**, 322–477.
- 4 B. Wang, X. L. Lv, D. Feng, L. H. Xie, J. Zhang, M. Li, Y. B. Xie, J. R. Li and H. C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 6204–6216.
- 5 D. Tian, Y. Li, R. Y. Chen, Z. Chang, G. Y. Wang and X. H. Bu, *J. Mater. Chem. A*, 2014, **2**, 1465–1470.
- 6 L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105–1125.
- 7 W. Yan, C. L. Zhang, S. G. Chen, L. J. Han and H. Zheng, *ACS Appl. Mater. Interfaces*, 2017, **9**, 1629–1634.
- 8 G. F. Ji, J. J. Liu, X. C. Gao, W. Sun, J. Z. Wang, S. L. Zhao and Z. L. Liu, *J. Mater. Chem. A*, 2017, **5**, 10200–10205.
- 9 X. Y. Xu and B. Yan, *Sens. Actuators, B*, 2016, **222**, 347–353.
- 10 M. Zhang, G. Feng, Z. G. Song, Y. P. Zhou, H. Y. Chao, D. Q. Yuan, T. T. Y. Tan, Z. G. Guo, Z. G. Hu, B. Z. Tang, B. Liu and D. Zhao, *J. Am. Chem. Soc.*, 2014, **136**, 7241–7244.
- 11 S. Bhattacharyya, A. Chakraborty, K. Jayaramulu, A. Hazra and T. K. A. Maji, *Chem. Commun.*, 2014, **50**, 13567–13570.
- 12 P. Y. Du, W. Gu and X. Liu, *Inorg. Chem.*, 2016, **55**, 7826–7828.
- 13 S. Y. Moon, N. R. Cha, Y. H. Kim and S. K. Chang, *J. Org. Chem.*, 2004, **69**, 181–183.
- 14 H. Matsumiya, N. Iki and S. T. Miyano, *Anal. Bioanal. Chem.*, 2004, **62**, 337–342.
- 15 X. Liu and E. C. Theil, *Acc. Chem. Res.*, 2005, **38**, 167–175.
- 16 L. Hyman and K. Franz, *Coord. Chem. Rev.*, 2012, **256**, 2333–2356.
- 17 J. L. Bricks, A. Kovalchuk, C. Trieflinger, M. Nofz, M. Büschel, A. I. Tolmachev, J. Daub and K. Rurack, *J. Am. Chem. Soc.*, 2005, **127**, 13522–13529.
- 18 S. R. Zhang, D. Y. Du, J. S. Qin, S. J. Bao, S. L. Li, W. W. He and Z. M. Su, *Chem.–Eur. J.*, 2014, **20**, 3589–3594.
- 19 T. F. Liu, D. W. Feng, Y. P. Chen, L. F. Zou, M. Bosch, S. Yuan, Z. W. Wei, S. Fordham, K. C. Wang and H. C. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 413–419.
- 20 F. Yi, D. Chen, M. Wu, L. Han and H. Jiang, *ChemPlusChem*, 2016, **81**, 675–690.
- 21 Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815–5840.
- 22 W. P. Lustig, S. Mukherjee, N. D. Rudd, A. V. Desai, J. Li and S. K. Ghosh, *Chem. Soc. Rev.*, 2017, **46**, 3242–3285.
- 23 X. Xu and B. Yan, *ACS Appl. Mater. Interfaces*, 2015, **7**, 721–729.
- 24 P. C. Rao and S. Mandal, *Inorg. Chem.*, 2018, **57**, 11855–11858.
- 25 G. Ji, J. Wang, X. Gao, J. Liu, W. Guan, H. Liu and Z. Liu, *Eur. J. Inorg. Chem.*, 2018, **19**, 1998–2003.
- 26 Z. J. Lin, J. Lu, M. Hong and R. Cao, *Chem. Soc. Rev.*, 2014, **43**, 5867–5895.
- 27 G. F. Ji, X. C. Gao, T. X. Zheng, W. H. Guan, H. T. Liu and Z. L. Liu, *Inorg. Chem.*, 2018, **57**, 10525–10532.
- 28 J. N. Hao and B. Yan, *Nanoscale*, 2016, **8**, 12047–12053.
- 29 J. An, C. M. Shade, D. A. C. Czegan, S. Petoud and N. L. Rosi, *J. Am. Chem. Soc.*, 2011, **133**, 1220–1223.
- 30 K. M. Buschbaum, F. Beuerle and C. Feldmann, *Microporous Mesoporous Mater.*, 2015, **216**, 171–199.
- 31 L. V. Meyer, F. Schonfeld and K. Muller-Buschbaum, *Chem. Commun.*, 2014, **50**, 8093–8108.
- 32 Z. Zhang, Y. He, L. Liu, X. Lu, X. Zhu, W. Wong, M. Pan and C. Su, *Chem. Commun.*, 2016, **52**, 3713–3716.
- 33 T. Xia, Y. Cui, Y. Yang and G. Qian, *ChemNanoMat*, 2016, **3**, 51–57.
- 34 R. Lv, H. Li, J. Su, X. Fu, B. Y. Yang, W. Gu and X. Liu, *Inorg. Chem.*, 2017, **56**, 12348–12356.
- 35 D. Basudeb, J. Rajkumar, K. B. Anup, P. R. Partha, S. Chittaranjan and H. M. Mohammad, *Inorg. Chem.*, 2019, **58**, 2686–2694.
- 36 A. Mürsel, *Cryst. Growth Des.*, 2017, **17**, 5499–5505.
- 37 Y. L. Hou, H. Xu, R. R. Cheng and B. Zhao, *Chem. Commun.*, 2015, **51**, 6769–6772.
- 38 L. Li, S. Shen, R. Lin, Y. Bai and H. Liu, *Chem. Commun.*, 2017, **53**, 9986–9989.
- 39 F. Y. Yi, S. C. Wang, M. Gu, J. Q. Zheng and L. Han, *J. Mater. Chem. C*, 2018, **6**, 2010–2018.
- 40 Z. Q. Yao, G. Y. Li, J. Xu, T. L. Hu and X. H. Bu, *Chem.–Eur. J.*, 2018, **24**, 3192–3198.
- 41 C. Yu, Z. Shao and H. Hou, *Chem. Sci.*, 2017, **8**, 7611–7619.



- 42 J. N. Hao and B. Yan, *Adv. Funct. Mater.*, 2017, **27**, 1603856.
- 43 C. Liu and B. Yan, *Photochem. Photobiol. Sci.*, 2015, **14**, 1644–1650.
- 44 L. F. Liang, L. Y. Liu, F. L. Jiang, C. P. Liu, D. Q. Yuan, Q. H. Chen, D. Wu, H. L. Jiang and M. C. Hong, *Inorg. Chem.*, 2018, **57**, 4891–4897.
- 45 WHO, *WHO Guidelines for Drinking-Water Quality*, 4th edn, WHO Press, Geneva, 2011.
- 46 Z. Y. Zhang, S. Z. Lu, C. M. Sha and D. M. Xu, *Sens. Actuators, B*, 2015, **208**, 258–266.
- 47 C. C. Hu, Q. Gao, Z. X. Zhu, L. L. Chang, W. J. Zhou, K. S. Xia, B. Han and C. G. Zhou, *Sens. Actuators, B*, 2018, **259**, 411–419.
- 48 G. X. Wen, Y. P. Wu, W. W. Dong, J. Zhao, D. S. Li and J. Zhang, *Inorg. Chem.*, 2016, **55**, 10114–10117.
- 49 K. Fan, S. S. Bao, W. X. Nie, C. H. Liao and L. M. Zheng, *Inorg. Chem.*, 2018, **57**, 1079–1089.
- 50 Z. F. Wu, L. K. Gong and X. Y. Huang, *Inorg. Chem.*, 2017, **56**, 7397–7403.
- 51 G. Ji, Z. Yang, H. Zhang, Y. Zhao, B. Yu, Z. Ma and Z. Liu, *Angew. Chem., Int. Ed.*, 2016, **55**, 9685–9689.
- 52 A. Shylaja, S. S. Roja, R. V. Priya and R. R. Kumar, *J. Org. Chem.*, 2018, **83**, 14084–14090.
- 53 G. X. Wen, Y. P. Wu, W. W. Dong, J. Zhao, D. S. Li and J. Zhang, *Inorg. Chem.*, 2016, **55**, 10114–10117.
- 54 L. N. Neupane, E. T. Oh, H. J. Park and K. H. Lee, *Anal. Chem.*, 2016, **88**, 3333–3340.
- 55 B. Gole, A. K. Bar and P. S. Mukherjee, *Chem.–Eur. J.*, 2014, **20**, 2276–2291.

