View Article Online View Journal

# CrystEngComm

### Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Wang, H. Yang, G. Cheng, Y. Wu and S. Lin, *CrystEngComm*, 2017, DOI: 10.1039/C7CE01795B.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/crystengcomm

Published on 16 November 2017. Downloaded by University of Florida Libraries on 16/11/2017 03:49:20

## Journal Name



## ARTICLE

Tb(III)-Functionalized a new layer-like Cd MOF as luminescent probe for highly selectively Sensing Cr<sup>3+</sup>

Wang Yi<sup>2a</sup>, Yang Huan<sup>1a</sup>\*, Gang Cheng<sup>2</sup>, Yunying Wu<sup>1</sup>, Shaomin Lin<sup>1</sup>

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A new layer-like metal-organic framework  $\{[Cd_4(NDIC)_4 \cdot 5DMF \cdot H_2O]DMF\}n$  (NDIC = 5-(5-Norbonene-2,3-dicarboximide)Isophthalic acid) has been synthesized with solvothermal method. It was used as a parent framework to sensitize via encapsulating  $Tb^{3+}$  cations in Cd-MOF. The obtained composite Tb(3+)@Cd-MOF shows excellent luminescence which performs a remarkable quenching effect in the luminescence emission of  $Tb^{3+}$  upon the introduction of  $Cr^{3+}$ . Subsequently, Tb(3+)@Cd-MOF was developed as a highly selective and sensitive probe for detection of  $Cr^{3+}$ . Most importantly, the luminescence probe of  $Cr^{3+}$  shows a low detection limit  $(7.5 \times 10^{-8}M)$ , a broad linear range  $(1 \times 10^{-7} - x5 \times 10^{-6}M)$ . A paper strip coated with Tb(3+)@Cd-MOF was also shown to be highly selective for  $Cr^{3+}$  under the irradiation of UV light of 254 nm by the naked eyes. This is first example for detecting metal ions based on a lanthanide functionalized a new metal-organic framework (MOF).

#### Introduction

Metal-organic frameworks (MOFs) have emerged a crystalline hybrid materials builting from an assembly of metal ions and organic linkers, have been extensively studied in a variety of applications in the past few years, such as catalysis.<sup>1,2</sup> magnetism,<sup>3,4</sup> gas storage and separation,<sup>5,6</sup> energy storge.<sup>7,8,9</sup> Among the large number of MOFs, LnMOFs have been receiving increasing attention due to their unique luminescence properties such as high luminescence quantum yield, long-lived emission, large Stokes shifts, and sharp line emissions.<sup>10-14</sup> The combination of these intrinsic luminescent features together with the inherent porosity of MOFs provides an effective platform for chemical sensing.<sup>15,16</sup> In the past decade, studies on luminescent Ln-MOFs for sensing metal ions,<sup>17,18</sup> anions,<sup>19,20</sup> small molecules<sup>21-25</sup> and temperature<sup>26-28</sup> have been reported. However, it also remains a great challenge to design and synthesis of the desired Ln-MOFs through direct synthesis due to the high coordination number and flexible coordination mode of lanthanide ions. 29,30

<sup>1</sup>School of Material science and Engineering Han Shan Normal University, Chaozhou, 521041, P.R. China

<sup>2</sup>College of chemistry and Material Engineering, Gui Yang University, 550005, Guiyang, P.R. China

E-mail:yanghuanjx@163.com

<sup>+</sup> Footnotes relating to the title and/or authors should appear here.

Fortunately, the incorporation of lanthanide ions within MOF using postsynthetic modification method should be expected to perform the similar luminescent sensing function of lanthanide MOFs<sup>-31,32</sup>

Cr<sup>3+</sup> and Cr<sup>3+</sup>-containing proteins is identified as an essential trace element of the human body for maintaining proper functioning of biological processes. Deficient or excessive intake may cause the loss of some physiological functions and diseases including ovulatory infertility.33-36 Recent scientific studies show that low concentrations of Cr<sup>3+</sup> could cause alterations in cell signaling, while high concentrations may lead to genotoxic DNA lesions, sewage from the industrial waste water forms one of the major sources of Cr<sup>3+</sup>. Most chromium reacts with the hides during the industrial process, while the rest chromium remains in the solid and waste water, and these are considered to be major sources of chromium environment pollutant. Therefore, it is necessary to detect Cr<sup>3+</sup> at trace levels. Some detection methods for chromium ions have been developed for Cr<sup>3+</sup>, such as inductively coupled plasma massspectroscopy (ICP-MS), atomic adsorption spectrometry (AFS), and synchrotron radiation X-rayspectrometry. <sup>37-39</sup> However, disadvantages such as time-consuming, sophisticated instruments and complicated preparation process have restricted the development of the techniques. Therefore, it is necessary to develop simple, rapid, sensitive and cost-effective approaches for this purpose. The wide variety of luminescent LnMOFs and their inherent synthetic versatility seems to make them ideal for metal ions recognition.

In our context, a new layer like Cd-MOF{[Cd<sub>4</sub>(NDIC)<sub>4</sub> $\cdot$ 5DMF $\cdot$  H<sub>2</sub>O]DMF}n was designed and synthesized based on 5-(5-Norbonene-2,3-dicarboximide)Isophthalic acid (NDIC) ligand

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Page 2 of 8

Journal Name	ARTICLE

through a facile **solvothermal** approach. Subsequently, novel luminescence material of lanthanide-doped Cd-MOF was obtained through encapsulating  $Tb^{3+}$  cations in Cd-MOF. What is more, Tb(3+)@Cd-MOF was developed as highly selective and sensitive luminescence probe targeting  $Cr^{3+}$  ions in ethanol solution. The possible sensing mechanisms toward to  $Cr^{3+}$  were also discussed in detail. As expected, Tb(3+)@Cd-MOF is suitable for becoming one luminescence probe with high selectivity and sensitivity.



Scheme 1. Selected organic ligands in the self-assembly of Cd-MOF.

#### **EXPERIMENTAL SECTION**

#### Materials

All the reagents and solvents were purchased from different companies, and directly used as received without further purication.

#### Single crystal X-ray crystallography

A block-like single crystal of Cd-MOF was sealed in a capillary tube under an optical microscope with some mother liquor inside in order to prevent desolvation of the sample. Single crystal X-ray diffraction data was collected on a Rigaku Oxford CCD diffractometer at 293 K using graphite monochromated Mo Ka radiation ( $\lambda$ =0.71073 A). All absorption corrections were performed by using the multiscan program, The structure were analyzed by direct methods and refined by full-matrix least squares on F^2 with the SHELXTL-97 program. Nonhydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Crystal data and other information on the structure determination are performed in Table S1.

IR absorption spectra of the MOF and HL ligand in KBr pellet were carried out in the range of 400-4000 cm<sup>-1</sup> on a IR Affinity-1 FT-IR spectrometer. Powder X-ray diffraction (PXRD) patterns were collected using a Rigaku Miniflex 600 X-ray diffractometer using Cu Ka radiation (1.5418°A) at room temperature. Thermogravimetric analysis (TGA) was performed with a Netzsch sta 449f3 at a heating rate of 5  $^{\circ}$ C min<sup>-1</sup>. Luminescence spectra were recorded on Horiba ihr320 fluorescence spectrophotometer at room temperature. The amounts of metal ions in Tb(3+)@Cd-MOF were measured by inductively coupled plasma mass spectrometry (ICP-MS, Icap Qc, Thermofisher, Germany)

# Synthesis of 5-(5-Norbonene-2,3-dicarboximide)Isophthalic acid (NDIC)

0.1 mol (16.4g) Norbonenedianhydrideand and 0.1mol (18.1g) 5-Aminoisophthalic acid were dissolved 200 mL acetic acid and allowed to react under reflux for 2 h, then slowly cooling to room temperature, the precipitate was filtered off and washed with acetic acid and distilled water, the product was dried under 100°C. The synthesis method is performed in FigS1

#### Synthesis of {[Cd<sub>4</sub>(NDIC)<sub>4</sub>·5DMF·H<sub>2</sub>O]DMF}n (Cd-MOF)

5-(5-Norbonene-2,3-dicarboximide) Isophthalic acid (NDIC) 0.0165g (0.05mmol) and 100 uL 1mol/L Cd(NO<sub>3</sub>)<sub>2</sub> dissolved in 3 mL DMF. The mixture was sealed in 15 mL Teflon -lined stainless autoclave. The autoclave was heated at 80°C for 3 days then slowly cooling to room temperature. The resulting colorless prism crystal were obtained in 65% yield based on NDIC .

#### Preparation of Tb(3+)@Cd-MOF

Cd-MOF (100 mg) is immersed in ethanol solution of Tb(NO<sub>3</sub>)<sub>3</sub>·  $6H_2O$  (10 mL, 2 mmol) for 2 days. After separating by centrifugation and washing with ethanol to remove redundant Tb<sup>3+</sup>, the samples was dried at 60  $^{\circ}$  C for 6 h.

#### Luminescence Sensing Experiment

The as-prepared Tb(3+)@Cd-MOF (2 mg) was dispersed into in ethanolic solution of MNO<sub>3</sub> (4 mL, 1  $\times$  10<sup>-3</sup> molL<sup>-1</sup>).(M<sup>n+</sup> =K<sup>+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>) to form a suspension at room temperature. The mixtures were used for luminescence measurements. The luminescence data were collected at the room temperature.

#### **Results and discussion**

#### 3.1 Description of crystal structure

Cd-L (1) crystallizes in the chiral space group  $P_{21}$ , and the asymmetric unit consist of three parts, one coordinated DMF(part 1), four Cd atoms and four ligands constitute part 2 and part 3(Fig.1a). The Cd<sup>2+</sup> adopt two similar coordination modes, the MOF form one enantiomer of a mesomeric chiral product after symmetric growth (Fig 1d). As shown in Fig 1b, in part 2, the Cd(1) atom displays a distorted octahedron geometry,the Cd(1) atom is six-coordinated by two pairs of chelating carboxylate oxygen atoms from two different L<sup>2-</sup> anion [Cd1-O1=2.356(1)Å,Cd1-O2=2.311(5)Å,Cd1-O5=2.433(8) Å, Cd1-O6=2.335(2)Å] and two carboxylate oxygen atoms from two ligands[Cd1-O3=2.196(6)Å,Cd1-O7=2.216(2)Å]. Different from Cd(1), the six-coordinated Cd(2) atom is bound to O by three carboxylate oxygen atoms from three ligands

This journal is © The Royal Society of Chemistry 20xxJ. Name., 2013, 00, 1-3 | 2

Published on 16 November 2017. Downloaded by University of Florida Libraries on 16/11/2017 03:49:20

#### Journal Name

ARTICLE

[Cd2–O4=2.242(6)Å, Cd2–O6=2.324(4)Å, Cd2–O8a=2.246(5)Å], two oxygen atoms from two coordinated DMF molecules[Cd2-O13=2.235(3)Å,Cd2-O14=2.280(5)Å]and one oxygen atom from one coordinated water molecule[Cd2-O15=2.338(6)Å]. In part 3, the coordination mode is the same except O15 from coordinated DMF. As shown in Fig.3c,  $HL^{2-}$  ligands adopted two kinds of coordination modes to connect to  $Cd^{2+}$  ions, giving a 1D polymeric chain. The linkers also bridge the  $Cd^{2+}$ ions to produce 2D layers (Fig.1d and Fig S2 in supporting information).The MOF was chosen as host to encapsulate Tb<sup>3+</sup> cations by one uncoordinated carbonyl group in its pores.





Figure 1 (a) Asymmetric unit of Cd-MOF (b) Coordination mode of metal ions (c) Two Coordination modes of ligand (d) Two-dimensional structure of Cd-MOF

#### 3.2 Purity and thermal stability

In order to explore application of Cd-MOF material, the purity and thermal stability of the material were investigated. Figure 2(a) shows the PXRD patterns of the Cd-MOF and Tb(3+)@Cd-MOF from 5° to 50°, the PXRD pattern of as prepared Cd-MOF is well matched with the simulated PXRD pattern based on single crystal X-ray diffraction data, which indicates a high purity of the Cd-MOF(CCDC: 1555655). The PXRD pattern of the synthesized Tb(3+)@Cd-MOF is in good agreement with the simulated Cd-MOF. The result shows that the preparation of the Tb(3+)@Cd-MOF is successful and the Cd-MOF could retain their crystallinity.

The thermal stability of Cd-MOF was studied as shown in Fig. 2(b). The first weight loss below 100°C is ascribed to the release of the surface water molecules. The second weight loss between 120 °C and 150 °C corresponds to the loss of coordinated DMF molecule . The third weight loss from 350 °C to 400 °C corresponds to the loss of ligand. Afterwards, The final plateau from 500 °C corresponds to cadmium oxide. The Tb(3+)@Cd-MOF was also monitored by TG analysis from 0 to 600 °C (Figure 1b). The TGA of Tb(3+)@Cd-MOF exhibits three events of weight losses and shows good thermal stability similar to Cd-MOF. The first step occurs in the range of 200–250 °C, which assigns to the partial decomposition of the linker. The second weight loss from 350 °C to 400 °C corresponds to the decomposition of the remaining organic ligand. The final plateau from 500 °C corresponds to oxide.

As shown in Figure 3,The absorption peak at 1705 cm<sup>-1</sup> is assigned to the  $v_{c=o}$  vibrations of free carboxyl grafted on the ligand, the absorption peak at 1564 cm<sup>-1</sup> belongs to coordinated  $v_{c=o}$  in Cd-MOF. Subsequently, Cd-MOF was immersed in ethanol solution of Tb(NO<sub>3</sub>)<sub>3</sub> for Tb<sup>3+</sup>-encapsulation by binding to the uncoordinated-COOH of Cd-MOF. the absorption band of Cd-MOF show a significant redshift (about 13 nm) after connecting to Tb<sup>3+</sup>, illustrating the interactions between the Tb<sup>3+</sup> and free-COOH of Cd-MOF. <sup>40</sup>After introducing Tb<sup>3+</sup> into the Cd-MOF, the compounds not affect the crystalline integrity, as shown by the PXRD patterns (Fig. 2a).





(b)

CrystEngComm Accepted Manuscript





Fig. 2 (a) Powder X-ray diffraction patterns of Tb(3+)@Cd-MOF. and single Xray simulated Cd-MOF. (b) TGA of Cd-MOF and Tb(3+)@Cd-MOF.





As expected, after postsynthetic functionalization of  $Tb^{3+}$ , the emission spectrum of the product exhibits characteristic emission of Tb<sup>3+</sup>. The sharp lines centered at 489, 545, 592 and 612 nm can be ascribed to  ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$  (J = 3–6) transitions of Tb<sup>3+</sup>. Under UV-light irradiation, Tb(3+)@Cd-MOF shows strong green luminescence which can be readily observed by naked eye, indicating the antenna effect occurs.



Fig. 4 The excitation (dashed) and emission (solid) spectra of the Tb(3+)@Cd-MOF

In light of the excellent luminescence of Tb(3+)@Cd-MOF, we examine the potential application of Tb(3+)@Cd-MOF for detecting metal ions. The as-prepared powder of Tb(3+)@Cd-MOF was dispersed in an ethanol solution of 0.001 mol L<sup>-1</sup>

 $M(NO_3)x$  (M = K<sup>+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup> respectively). The luminescent spectrum were recorded in Figure 5(a). The results revealed that various metal ions display markedly different effects on the luminescence of  $Tb^{3+}$  ions. For example, as shown in Figure 5(b), the luminescence intensity at 546 nm is decreased when Mg<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>,  $Cd^{2+}$ ,  $Co^{2+}$  are introduced. In the contrast, the luminescence intensity increased when  $K^{+}$  is introduced . The addition of  $Cr^{3+}$ induced the noticeable quench of luminescence intensity of  $Tb^{3+}$ , which contributes to probe Tb(3+)@Cd-MOF to be useful for selectively sensing  $Cr^{3+}$ . (a)





Fig. 5 (a) Diagrams of the  ${}^{5}D_{4}$ - ${}^{7}F_{5}$  transition intensities of the Tb(3+)@Cd-MOF. at 546 nm in various metal ions .(b) Emission spectra of the Tb(3+)@Cd-MOF. after being immersed in metal ions at room temperature (Aex= 303 nm).

To further prove that the fluorescence quenching by  $Cr^{3+}$ , concentration-dependent studies in the luminescence intensities of Tb(3+)@Cd-MOF when Cr<sup>3+</sup> ions were carried out. However, the PL intensity for Cr<sup>3+</sup>-induced samples are quite different for the Tb(3+)@Cd-MOF. As shown in Figure 6a, the luminescence intensity of the Tb(3+)@Cd-MOF decreases with the increase of  $Cr^{3+}$  concentration from  $1 \times 10^{-7}$  to  $5 \times 10^{-6}$  M. The linear correlation coefficient (R) in the Ksv curse of Tb(3+)@Cd-MOF with Cr<sup>3+</sup> is 0.9939, the relationship between the luminescence intensity of Tb(3+)@Cd-MOF and the concentration of Cr<sup>3+</sup> is well fitted by the Stern-Volmer equation:<sup>30</sup>

$$I_0/I = 1 + Ksv[M]$$

where the values  $I_0$  and I are the luminescence intensity of the Tb(3+)@Cd-MOF before and after addition of  $Cr^{3+}$ , respectively,

This journal is © The Royal Society of Chemistry 20xxJ. Name., 2013, 00, 1-3 | 4

(b)

Published on 16 November 2017. Downloaded by University of Florida Libraries on 16/11/2017 03:49:20

Tb(3+)@Cd-MOF.

-Please CrystEngCommargins

Journal Name

[M] is the Cr<sup>3+</sup>concentration. Ksv is the quenching constant,

the value is calculated as 1.81 imes 10<sup>5</sup>, which reveals a strong

quenching effect on the Tb(3+)@Cd-MOF luminescence. The

detection limit is about 7.5  $\times 10^{-8}$ M ( $\Delta$  S/N=3)<sup>41</sup>, the result suggests that Cr<sup>3+</sup> also can be detected quantitatively using

luminescence is completely quenched, indicating that the selectivity for  $Cr^{3+}$  is not interfered by the existence of other ions.

ARTICLE



Fig. 6 (a) Stern–Volmer plots describe the dependency of the luminescent intensities on the Cr<sup>3+</sup> concentration over the range of 5×10<sup>-6</sup>-1×10<sup>-7</sup> M in ethanol solution. (b) Luminescence emission spectra of Tb(3+)@Cd-MOF dispersed in ethanol upon incremental addition of Cr<sup>3+</sup> ethanol solution ( $\lambda$ ex= 303 nm)

The Tb(3+)@Cd-MOF is dispersed in the solution containing Cr<sup>3+</sup> and other metal ions, which include K<sup>+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>, Co<sup>2+</sup>, respectively. When excited at 303 nm, the luminescence intensity of the Tb(3+)@Cd-MOF dispersed in the ethanolic solution of other metal ions ( $1 \times 10^{-3}$  M, K<sup>+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>, Co<sup>2+</sup>, respectively) changes differently compared to the primitive one, as shown in Figure 7. However, when the Tb(3+)@Cd-MOF is immersed in the ethanolic solution of mixed ions ( $1 \times 10^{-3}$  M other metal ions +  $1 \times 10^{-3}$  M Cr<sup>3+</sup>), the measurement of the luminescence intensity shows that the



Fig. 7 The  ${}^{5}D_{4}{}^{-7}F_{5}$  transition intensities of the Tb(3+)@Cd-MOF upon the addition of different metal ions(1×10<sup>-3</sup> M) (blue) and subsequent addition of Cr<sup>3+</sup>(1×10<sup>-3</sup> M) (red) ( $\lambda$ ex= 303 nm).

To make the detection simple and portable, we fabricated a luminescence test paper for rapid detection of metal ions. Hence, the sensing of  $Cr^{3+}$  was carried out. The test paper was prepared by immersing a filter paper (2.  $0 \times 1.0 \text{ cm}^2$ ) in the ethanolic solution of Tb(3+)@Cd-MOF(0.5mg/mL) then drying it in air for 24h at room temperature. For the detection of  $Cr^{3+}$ , the test paper was immersed in the in ethanolic solution of metal ions( $1 \times 10^{-3}$  M, K<sup>+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>) and then dried in the air . In Figure 8, under the irradiation of UV light of 254 nm, the luminescent colors of the test paper changed from green to dark green and finally black with the different metal ions(left to right: K<sup>+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>, Cd<sup>2+</sup>, Ca<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>). Considering the results above, we can distinguish the colors of different metal ions by our naked eyes.



Fig. 8 Luminescent response of Tb(3+)@Cd-MOF coated paper strips to various metal ions(1×10<sup>-3</sup> M) under UV light (254nm) (left to right:  $K^*$ ,  $Mg^{2*}$ ,  $Pb^{2*}$ ,  $Zn^{2*}$ ,  $Ag^*$ ,  $Cd^{2*}$ ,  $Co^{2*}$ ,  $Cr^{3*}$ ).

#### 3.4 Quenching mechanism

Up to now, the quenching effect on luminescence of MOFs by metal ions is attributed to three reasons: (1) the interaction between metal ions and ligands; (2) the collapse of the crystal structure (3) the ions exchange between central metal ions of MOFs and the targeted metal ions.<sup>41</sup> Herein, the possible sensing mechanism for the luminescence quenching by the metal ions has been further studied. The powder XRD was employed to study on the structural data of the original and Tb(3+)@Cd-MOF treated with  $Cr^{3+}$ . As shown in Figure 9, the PXRD of is different from that of Tb(3+)@Cd-MOF, suggesting that the basic frameworks changed. We speculate that the remarkable quenching effect of Tb(3+)@Cd-MOF by  $Cr^{3+}$  results from the collapse of the crystal structure.

DOI: 10.1039/C7CE01795E



Fig.9 PXRD patterns of simulated Cd-MOF and Tb(3+)@Cd-MOF treated with  $Cr^{3*}$ .

#### Conclusions

In summary, a new layer like Cd-MOF({[Cd<sub>4</sub>(NDIC)<sub>4</sub> · 5DMF · H<sub>2</sub>O]DMF}n based on 5-(5-Norbonene-2,3dicarboximide)Isophthalic acid has been prepared which was used as host to sensitize Tb<sup>3+</sup> cations by one uncoordinated carbonyl group in its pores. The characters of PXRD, TGA and luminescent measurements demonstrate that this framework can be explored as potential luminescent material for sensing of  $Cr^{3+}$ . Studying of the luminescence properties reveals that Tb(3+)@Cd-MOF can develop as a highly selective and sensitive probe for detection of  $Cr^{3+}$  (detection limit, 7.5×10<sup>8</sup> M) via luminescence quenching of Tb<sup>3+</sup>. Under the irradiation of UV light, the colors of luminescence test paper treated with different metal ions can be observed changing from green to dark by naked eyes, respectively. Further study and speculation of the mechanism illustrate that the collapse of the crystal structure lead to the quenching effect of Tb(3+)@Cd-MOF. The present results may provide a facile route to design luminescence Ln-MOF for sensing and further studies are currently under way.

#### Conflicts of interest

<sup>a</sup>The authors contributes equally. There are no conflicts to declare.

#### Acknowledgements

The authors acknowledge the financial support of Chaozhou science and technology plan (2016GY22), Experimental Teaching Demonstrating Center of Guizhou province( science and education Experimental Teaching Demonstrating Center of Guiyang university) and Guiyang university(2017PT05).

#### Notes and references

**‡** Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

- S.J.Teat. G. Aromi, P.Gamez, J. Reedijk, Inorg. Chem., 2009, 48,
- 5. C. H. Wang, X. L Liu, N. K. Demir, J. P. Chen, K. Li, Chem. Soc.
- 6. M. P. Suh, H. J. Park, T. K. Prasad, D. W. Lim, Chem.
- 7. L. Wang, X. Feng, L. T. Ren, Q. H. Piao, J. Q. Zhong, Y. B. Wang, H. W. Li, Y. F. Chen, B. Wang, J. Am. Chem. Soc. 2015, 137. 4920.
- 8. X. X, Liu, C. D. Shi, C. W. Zhai, M. L. Cheng, Q. Liu, G. X. Wang, ACS Appl. Mater. Interfaces, 2016, 8, 4585.
- 9. C. Qu, Y. Jiao, B. T. Zhao, D. C. Chen, R.Q. Zou, K. S. Walton, M. L. Liu, Nano Energy. 2016, 26, 66.
- 10. L. V. Meyer, F. Schönfeld and K. Müller-Buschbaum. Chem. Commun., 2014, 50, 8093.
- 11. B. Li, H. M. Wen, Y. J. Cui, G. D. Qian, B.L. Chen, Prog. Polym. Sci., 2015, 48, 40.
- 12. J. Rocha, L. D. Carlos, F.A.A. Paz, D. Ananias, Chem. Soc. Rev., 2011, 40, 926.
- 13. Q. Yao, A.B. Gomez, J. Su, V. Pascanu, Y.F. Yun, H.Q. Zheng, H. Chen, L.F. Liu, H.N. Abdelhamid, B. Martin-Matute, X. D. Zou, Chem. Mater., 2015, 27, 5332.
- 14. W. P. Lustig, S. Mukherjee, N. D. Rudd, A. V. Desai, J. Li, S. K. Ghosh, Chem. Soc. Rev., 2017, 46, 3242.
- 15. S. V. Eliseevaa, J. C. Bünzli, Chem. Soc. Rev., 2010,39, 189.
- 16. J. Rocha, L. D. Carlos, F. A. Paz, D. Ananias, Chem. Soc. Rev., 2011, 40, 926.
- 17. G. F. Ji, J. J. Liu, X. C. Gao, W. Sun, J. Z. Wang, S. L. Zhao, Z. L. Liu, J. Mater. Chem. A, 2017, 5, 10200.
- Z. Sun, M. Yang, Y. Ma, L.C. Li, Crystal Growth & 18. Design, 2017, 17, 4326.
- 19. R. Z. Wu, X. Yang, L. W. Zhang, P, P, Zhou, Dalton Trans., 20 17, **46**, 9859
- 20. Y. J. Cui, Y. Yue, G.D. Qian, B. L. Chen, Chem. Rev., 2012, 112, 1126
- 21. M. L. Han, G. X. Wen, W. W. Dong, Z. H. Zhou, Y. P. Wu, J. Zhao, D. S. Li, L. F. Ma, X. H. Bu, J. Mater. Chem. C, 2017, 5, 8469
- 22. D. M. Chen, N. N. Zhang, C. S. Liu, M. Du, ACS Appl. Mater. Interfaces, 2017, 9, 24671.
- 23. X.Y. Xu, X. Lian, J. N. Hao, C. Zhang, B. Yan, Adv. Mater. 2017, **29**, 1702298.
- 24. S. Dang, X. Min, W. T. Yang, F.Y. Yi, H. P. You , Z. M. Sun CHEMISTRY - A EUROPEAN JOURNAL, 2013, 19, 17172.
- 25. S. Y. Zhang, W. Shi, P. Cheng, M. J. Zaworotko, J. Am. Chem. Soc., 2015, 137, 12203.
- 26. T. F. Xia, Y. J. Cui, Y. Yang, G. D. Qian, J. Mater. Chem. C, 2017, 5, 5044.
- 27. X. Rao, T. Song, J. Gao, Y. J. Cui, Y. Yang, C. Wu, B. L. Chen and G.D. Qian, J. Am. Chem. Soc., 2013, 135, 15559.
- 28. X. T. Rao, T. Song, J. K. Gao, Y. J. Cui, Y. Yang, C. D. Wu, B. L. Chen, G. D. Qian, J. Am. Chem. Soc., 2013, 135, 15559.
- 29. Z. S. Dou, J. C. Yu, Y. J. Cui, Y. Yang, Z. Y. Wang, D. R. Yang, G. D. Qian J. Am. Chem. Soc., 2014, 136, 5527.
- 30. Y. Wang, F. Zhang, Z. S. Fang, M. H. Yu, Y. Y. Yang, K. L. Wong, J. Mater. Chem. C, 2016, 4, 8466.
- 31. X. Lian, T. F. Miao, X. Y. Xu, C. Zhang, B. Yan, Biosens. Bioelectron. 2017, 97, 299-304.
- 32. J. N. Hao, B. Yan, Chem. Commun. 2015, 51, 7737.
- 33. J. P. Metters, R. O. Kadara , C. E. Banks, Analyst, 2012, 137, 896.
- 34. F. Z. Hu, B. Z. Zheng, D. M. Wang, M. P Liu, J. Du, D.

This journal is © The Royal Society of Chemistry 20xxJ. Name., 2013, 00, 1-3 | 6

**SrystEngComm Accepted Manuscrip** 

Published on 16 November 2017. Downloaded by University of Florida Libraries on 16/11/2017 03:49:20.

ARTICLE

#### Journal Name

Xiao, Analyst, 2014,139, 3607.

- 35. S. Goswami, A. K. Das, A. K. Maity, A. Manna, K. Aich, S. Maity, P. Saha, T. K. Mandal *Dalton Trans.*, 2014, **43**, 231-239
- 36. S. R. Zhang, J. Li, D. Y. Du, J. S. Qin, S. L. Li, W. W. He, Z. M. Su, Y. Q. Lan, J. Mater. Chem. A, 2015, 3, 23426.
- 37. C. Dong, G. H. Wu, Z. Q. Wang, W. Z. Ren, Y. J. Zhang, Z. Y. Shen, T. H. Li, A. G. Wu, *Dalton Trans.*, 2016,**45**, 8347.
- W. W. Chen, F. J. Cao, W. S. Zheng, Y. Tian, Y. L. Xianyu, P. Xu, W. Zhang, Z. Wang, K. Deng, X.Y. Jiang, *Nanoscale*, 2015, 7, 2042.
- 39. M. Elavarasi, S. A. Alex , N. Chandrasekaran, A Mukherjee, Analytical Methods, 2014, 6, 9554.
- 40. J. N. Hao, B. Yan , Adv. Funct. Mater, 2017, 27,1603856.
- X. Y. Xu, B. Yan, ACS Appl. Mater. Interfaces, 2015, 7, 721.-M. Y. Zhu, C.H. Zeng, T. S. Chu, H. M. Wang, Y. Y.Yang, Y. X. Tong, C.Y. Su, W.T. Wong, J. Mater. Chem. A, 2013, 1, 11312.

**CrystEngComm Accepted Manuscript** 

# TOC

