Journal of Alloys and Compounds 509 (2011) 2552–2554

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

A metal–organic framework for selectively sensing of PO_4^{3-} anion in aqueous solution

Hui Xu[a], Yunqing Xiao[a], Xingtang Rao[a], Zhongshang Dou[a], Weifen Li[b], Yuanjing Cui[a,*], Zhiyu Wang[a], Guodong Qian[a,*]

[a] *State Key Laboratory of Silicon Materials, Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, China*
[b] *Department of Chemistry, Hebei Teacher's College for Nationalities, Chengde, 067000, China*

ARTICLE INFO

Article history:
Received 10 September 2010
Received in revised form 9 November 2010
Accepted 11 November 2010
Available online 19 November 2010

Keywords:
Metal–organic framework
Photoluminescence
Anion sensing

ABSTRACT

A Tb-based metal–organic framework TbNTA H_2O (TbNTA**1**, NTA = nitrilotriacetate) was synthesized and characterized. Photoluminescence (PL) properties of anion incorporated TbNTA**1** were investigated with the addition of the aqueous solution of different anions such as F^-, Cl^-, NO_2^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-}. The luminescence intensity of the anion-incorporated TbNTA**1** showed a different degree of changes, particularly for the PO_4^{3-} incorporated TbNTA**1,** which showed a significant quenching effect. The unique selective detection of PO_4^{3-} ions in water indicates that TbNTA**1** is promising to be employed as a novel luminescence probe for phosphate ions in biological system.

1. Introduction

Phosphate anions are nature ingredient of food, and act as an important additive. It is also one of most important constituents of living systems. Phosphate anions generate the primary part of genes, which is one of the elements in living system [1]. In addition, phosphate anions play crucial roles in signal transduction and energy storage in biological systems. Plenty of phosphate sensors have been designed, but most of them are limited in organic solvents. The detection of phosphate in water remains to be a challenge [2]. In this regard, a fluorescent sensor which can detect phosphate ions in aqueous solution is essential.

Due to the attractive photophysical properties of lanthanide ions, it is a popular strategy to utilize lanthanide ions to form a highly luminescent material [3–12]. Meanwhile metal–organic frameworks (MOFs) have rapidly gained growing attention due to the characteristics such as structure diversity, predictability and high porosity [13,14]. MOFs can be used on gas uptake and separation [15–19], catalysis [20–23], luminescent sensor [24–29] and etc. Lanthanide-based MOFs show significant potential to be used as chemical sensors [30–32]. However, the instability of MOFs when immersed in aqueous environment has limited their sensing functions mainly in organic solvents [33,34]. Recently our group reported $Eu_2(FMA)_2(OX)(H_2O)_4$ $4H_2O$ (**1**, FMA = fumarate; OX = oxalate) for highly selective and sensitive sensing of Cu^{2+} in aqueous solution [35]. Herein we introduce a luminescent MOF TbNTA H_2O [36,37] (TbNTA**1**, NTA = nitrilotriacetate) which shows a unique selectively sensing of PO_4^{3-} anion in aqueous solution.

2. Experimental details

All reagents employed were commercially available and used without further purification. Preparation of TbNTA**1** (TbNTA·H_2O): a mixture of $Tb(NO_3)_3 5H_2O$ (0.087 g, 0.20 mmol), nitrilotriacetic acid (0.0573 g, 0.3 mmol) and H_2O (12 ml) were sealed in a Teflon-lined stainless steel vessel (25 ml) and heated at 150 °C for 3 days. Crystals of TbNTA**1** were harvested after washed with water and dried in reduced pressure. The elemental analysis for TbNTA**1**, Calc: C 19.74%; H 2.21%; N 3.84%. Found: C 19.75%; H 2.14%; N 3.32%.

Thermal gravimetric analyses (TGA) data were collected on a Netzsch TG209F3 under N_2 atmosphere. Sample was heated at 10 °C/min. Powder X-ray diffraction was measured by RIGAKU D/MAX 2550/PC X-ray diffractometer with copper Kα line. Samples were loaded to a glass holder and leveled with a glass slide before mounting it on the sample chamber. The specimens were scanned between 4° and 70°. The scan step-width and rate were set to 0.01° and 0.01°/s, respectively.

The photoluminescent properties were investigated in the solid state at room temperature. Photoluminescence (PL) spectra were taken on a Hitachi F4500 fluorescence spectrometer. The photomultiplier tube (PMT) voltage was 700 V, the scan speed was 240 nm/min and the slit widths were ex 2.5 nm and em 2.5 nm. The anion incorporated TbNTA**1** were prepared by introducing 20 mg of TbNTA into 2.00 ml of anion aqueous solutions with different amounts of NaX (X = F^-, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) respectively, collected by filtration and drying under vacuum for 24 h at 60 °C.

3. Results and discussion

In TbNTA**1**, each Tb^{3+} ion is eight coordinated. The TbNTA subunits were linked through the carboxyl bridges to form a cube,

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* Corresponding authors. Tel.: +86 0571 87952334.
E-mail addresses: cuiyj@zju.edu.cn (Y. Cui), gdqian@zju.edu.cn (G. Qian).

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doi:10.1016/j.jallcom.2010.11.087

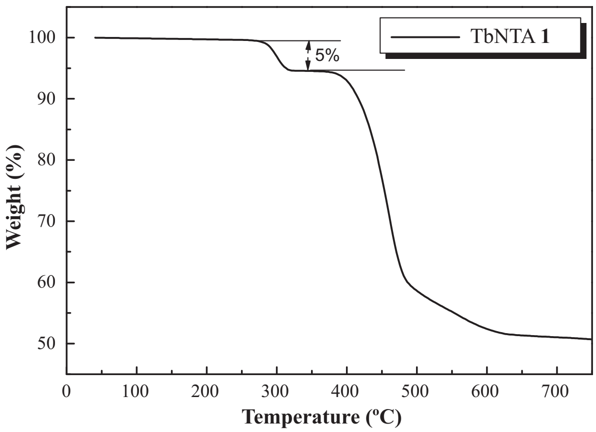

Fig. 1. TG curve of TbNTA**1**.

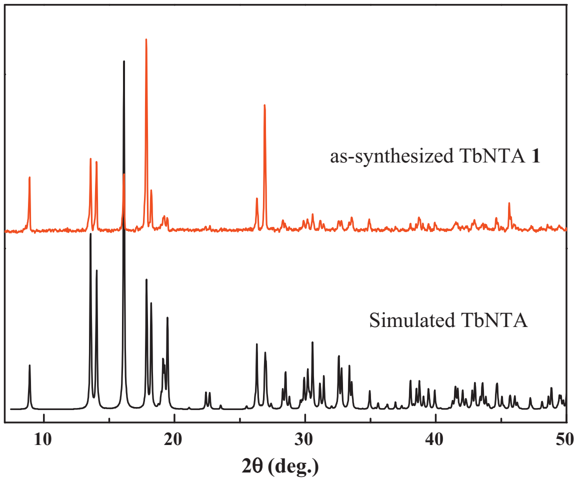

Fig. 2. Powder XRD patterns of as-synthesized TbNTA**1** (red) and simulated one (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

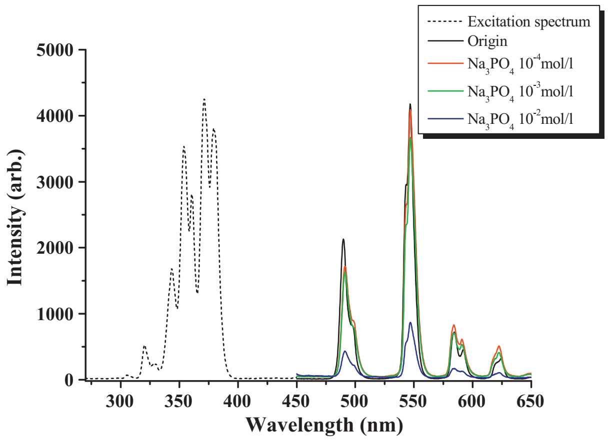

Fig. 3. The excitation (dotted) and PL spectra (solid) of TbNTA**1** solid activated in different concentration of Na_3PO_4 aqueous solution (excited and monitored at 371 nm and 547 nm, respectively).

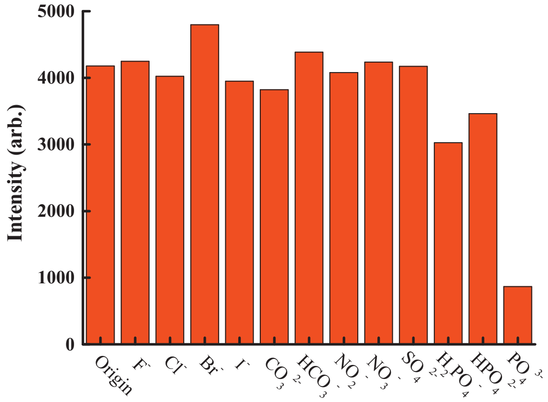

Fig. 4. Comparison of the $^5D_4 \rightarrow {}^7F_5$ transition intensities of TbNTA**1** solid activated in 10^{-2} M NaX aqueous solution.

and then further assembled into a 2D layer structure. The TG curve (Fig. 1) shows that the weight loss starts at 270 °C and the 5% loss is the corresponded one water molecule in TbNTA**1**. PXRD pattern (Fig. 2) of the as-synthesized TbNTA is the same with the simulated one, which indicated that they have the same structure.

The anion incorporated TbNTA**1** were prepared by introducing 20 mg of TbNTA**1** into 2.00 ml of anion aqueous solutions with different amounts of NaX (X = F^-, Cl^-, Br^-, I^-, $NO_3{}^-$, $NO_2{}^-$, $HCO_3{}^-$, $CO_3{}^{2-}$, $SO_4{}^{2-}$, $H_2PO_4{}^-$, $HPO_4{}^{2-}$ and $PO_4{}^{3-}$) respectively. The excitation and photoluminescence spectra of $PO_4{}^{3-}$ incorporated TbNTA**1** are shown in Fig. 3. The emission spectrum of TbNTA**1** excited at 371 nm is the feature of the f–f transitions of Tb^{3+} ions. It exhibits the characteristic transitions of the Tb^{3+} ion at 489 nm, 547 nm, 583 nm and 625 nm, which are ascribed to the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions, respectively. Among various anion-incorporated TbNTA**1**, only $PO_4{}^{3-}$ incorporated TbNTA**1** demonstrate a tremendous luminescence quench effect. The luminescent intensity of TbNTA**1** after immersed in 10^{-2} M Na_3PO_4 aqueous solution is more than 4 times weaker than as-synthesized TbNTA**1**, as shown in Fig. 4. This is the first reported MOF with highly selective sensing of $PO_4{}^{3-}$ anion in aqueous solution, and it gives us hope to trace small amount of $PO_4{}^{3-}$ anion in biological system.

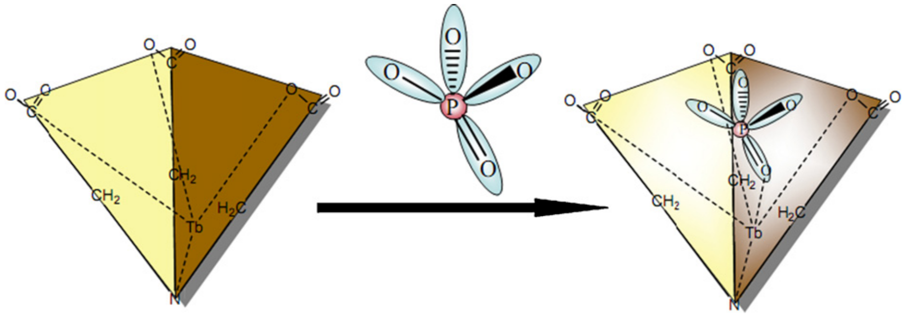

Fig. 5. A schematic representation of the phosphate anion sensor.

The quenching effect of PO_4^{3-} anion on the luminescence intensity of TbNTA**1** can be explained by the matching degree of TbNTA**1** with different anions. Anions have distinct shapes, sphere, prism, tetrahedron, etc. PO_4^{3-} anions have a shape of tetrahedron. The nitrilotriacetate ligand in TbNTA**1** has a lone pair on N atom which can repel three branches with carboxyl group to the same side. The generated cage is complementary to three faces of a tetrahedron. This is so called C_{3v} symmetric cavity, as shown in Fig. 5. The matching degree of TbNTA**1** with PO_4^{3-} anions may be determined by several factors, such as anion size and pH value. SO_4^{2-} anions which are also tetrahedron cannot quench Tb^{3+} luminescent. It may be caused by the irrational match between anion and MOF. Not like other anions, the pH value of aqueous solution containing PO_4^{3-} anions is larger than 7. This may enhance the effect of incorporation of PO_4^{3-} anions. After TbNTA1 incorporated with PO_4^{3-} anions, the Tb–O bond may dilute the energy that transferred to Tb^{3+} via non radioactive relaxation.

4. Conclusions

By incorporating a tripodal organic linker into a luminescent MOF, we developed a MOF which was highly sensitive and selective to PO_4^{3-} ions in aqueous solution. The MOF TbNTA**1** has a C_{3v} symmetric cavity which can be enclosed by tetrahedron shaped ions, thus decreasing the luminescent intensity of Tb. The detection of PO_4^{3-} ions in water has provided the foundation for the sensing of trace amount of phosphate ions in biological system.

Acknowledgements

The authors gratefully acknowledge the financial support for this work from the National Natural Science Foundation of China (Nos. 50625206, 50972127 and 51010002) and the Zhejiang Provincial Natural Science Foundation of China (Grant No. Z4080021).

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