Bull. Chem. Soc. Ethiop. **2017**, 31(2), 291-297. ISSN 1011-3924
© 2017 Chemical Society of Ethiopia and The Authors Printed in Ethiopia
DOI: http://dx.doi.org/10.4314/bcse.v31i2.10

A MICROPOROUS METAL–ORGANIC FRAMEWORK WITH OPEN METAL SITES FOR SELECTIVE SENSING Fe^{3+}, CrO_4^{2-} AND NITROBENZENE

Fu-Min Wang[1], Rui Wang[2], Yao-Yao Han[2], Sa-Ying Li[1], Jian-Hui Man[2], Yong-Xiang He[2] and Bao-Hong Li[2*]

[1]Department of Chemistry and Chemical Engineering, Shaanxi Xueqian Normal University, Xian, China; [2]Key Laboratory for Research and Development of New Medical Materials of Guangdong Medical University and School of Pharmacy, Guangdong Medical University, Dongguan, 523808, China

(Received March 19, 2017; revised September 14, 2017)

ABSTRACT. A 3D network with the ($4^2{\cdot}6{\cdot}8^3$) topology of metal-organic framework possessing an open 1D channel was synthesized by rigid and planar tetracarboxylic acid 5,5'-(1H-2,3,5-triazole-1,4-diyl)diisophthalic acid (H_4L). The luminescent properties of **1** shows highly sensitive response to nitrobenzene, Fe^{3+} and CrO_4^{2-} through luminescence quenching effects, making it a promising luminescent sensor for nitro aromatic compounds, Fe^{3+} and CrO_4^{2-}.

KEY WORDS: Metal-organic framework, Luminescence quenching, Iron(III), Chromate, Nitrobenzene

INTRODUCTION

During the last ten years, continuous endeavors have been devoted to the design and preparation of various luminescent metal-organic framework because they might have some potential applications [1-5]. Extensive studies on MOF-based sensors focused on immobilization of Lewis basic sites within porous MOFs. A few of examples of porous MOFs with Lewis basic sites have been reported, including $[Eu(btpca)(H_2O)]{\cdot}2DMF{\cdot}3H_2O$ [H_3btpca = 1,1′,1″-(benzene-1,3,5-triyl)tripiperidine-4-carboxylic acid] with multiple Lewis basic triazinyl nitrogen atoms for the sensing of Fe^{3+} ions [6], and $[Eu_3(bpydb)_3(HCOO)(\mu_3\text{-}OH)_2(DMF)]{\cdot}(DMF)_3(H_2O)_2$ [$bpydbH_2$ = 4,4′-(4,4′-bipyridine-2,6-diyl)dibenzoic acid] exhibits multi-responsive luminescence sensing of small organic molecules and inorganic ions [7]. These results highlight the significance of such Lewis basic sites within porous MOFs for their functional properties [8-13].

Recently, Hou and his co-workers have prepared a new MOF of $\{[Zn(H_2L)]{\cdot}H_2O\}_n$ (**1**), it has been constructed by a rigid and planar tetracarboxylic acid 5,5'-(1H-2,3,5-triazole-1,4-diyl)diisophthalic acid (H_4L) [14]. Moreover, **1** has five potential sensing sites and its sensing properties were not explored at all. Our group has also reported several interesting solvent-induced MOFs in recent works [15-19], and the results indicate that sensing feature are mainly controlled by solvent size and polarity, however, the mechanisms of solvent effects are still largely unexplored. Consequently, much research work in this area remains to be done [20].

Given the above concerns, we selected **1** as a luminescence material. As we expected, the luminescent properties of **1** shows highly sensitive response to small organic molecules (especially for nitro aromatic), Fe^{3+} and CrO_4^{2-} through luminescence quenching effects due to its more than sensing sites.

EXPERIMENTAL

Materials and methods

All reagents and solvents employed were commercially available and used as received without further purification. The powder X-ray diffraction (PXRD) patterns were measured using a

*Corresponding author. E-mail: gdmcli@126.com

Bruker D8 advance powder diffractometer at 40 kV and 40 mA for Cu Kα radiation (λ = 1.5418 Å), with a scan speed of 0.2 s/step and a step size of 0.02^o (2θ).

Synthesis of $\{[Zn(H_2L)]\cdot H_2O\}_n$ ***(1)***

A mixture of H_4L (19.8 mg, 0.05 mmol) and $Zn(NO_3)_2\cdot 4H_2O$ (18.9 mg, 0.1 mmol) were dissolved in DMF (5 mL) in a capped vial, then 0.1 mL HNO_3 were added into the mixture. The mixture was placed in a capped 15 mL vial and heated at 105 ^oC for 4 days [15].

Sensing method

The photoluminescence sensing were performed as follows: the photoluminescence properties of **1** were investigated in N,N-dimethylformamide (DMF) emulsions at room temperature using a RF-5301PC spectrofluorophotometer. The **1**@DMF inclusions were prepared by adding 5 mg of **1** powder into 3.00 mL of DMF and then ultrasonic agitation the mixture for 30 min before testing.

RESULTS AND DISCUSSION

1 shows 3D network possessing an open 1D channel with the free volume of 29.2% (707.6 out of the 2422.7 Å^3 unit cell volume) (Figure 1a-b) [13]. It should be noted that two carboxylate groups have not deprotonated. From the topological view, the whole 3D framework of **1** can be represented as a 4-connected net with $(4^2\cdot 6\cdot 8^3)$ topology. The phase purity of bulky samples was checked by powder X-ray diffraction (PXRD). For compound **1**, the measured PXRD patterns closely match the simulated ones generated from the single crystal X-ray diffraction data (Figure 1c), indicating the pure phase of the products [15].

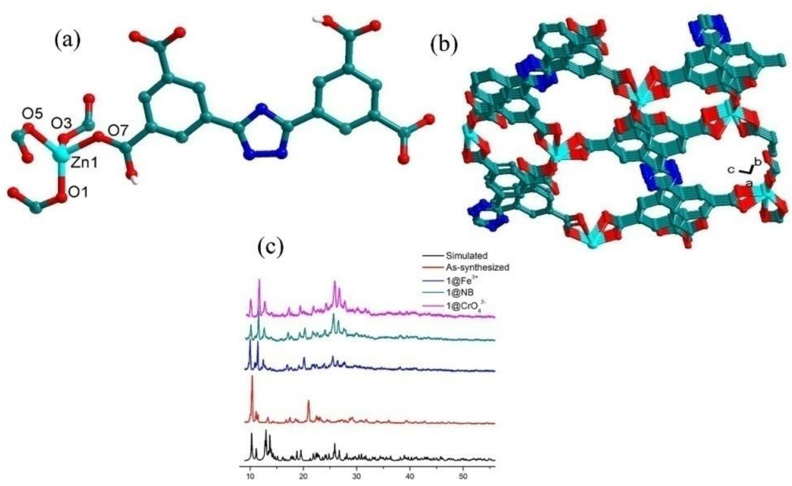

Figure 1. (a) View of the coordinative environment of metal center, (b) the 3D porous network and (c) the PXRD patterns of as-synthesized sample and its involving in different analytes in this work.

Based on the its structural feature [21], fluorescence detection experiments were carried out with the DMF suspension of **1**, which was carefully explored for sensing metal ions, anions and small organic molecules. Firstly, to investigate this potential application of **1** for heavy metal ions, **1** were ground and immersed in DMF solutions of $M(NO_3)_x$ (0.01 mol/L, M = Na^+, Ag^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and Cu^{2+}, respectively) for 24 h, and then oscillated for 30 min using ultrasonic waves to form uniform dispersion suspensions. The luminescent intensities of **1** are decreased sharply by Fe^{3+} ion, indicating its highly selective sensor [22-25]. To evaluate the sensing behavior for Fe^{3+} of **1**, the titration experiments were applied and the results showed that luminescent intensities were gradually weakened by increasing the concentrations of Fe^{3+} ions (Figure 2b-d). The luminescence titration results can be treated with the Stern-Volmer equation, $I_0\text{-}I/I_0 = 1 + K_{sv}[Q]$, where K_{sv} is the quenching constant, and Q is the quencher. The limit of detection (LOD) for Fe^{3+} was of 15.8 mg/L [25], which is relatively lower compared to reported examples. The results indicate that the different anions have a great influence on the luminescent intensity of **1**.

Furthermore, luminescent sensing for different solvent molecules was also employed carefully. It was found that luminescent intensities of **1** were dependent on the different solvents (Figure 3a). The luminescent intensity of **1** was completely quenched by nitrobenzene (NB) compared to other solvents (Figure 3b). Thus, **1** might be a potential luminescent probe for detection of NB molecule. Meanwhile, NB molecule was added slowly to the suspension of **1** in DMF solution to study the quantitative quenching effect, showing the distinctly gradual decrease of luminescent intensities at low concentrations. The quenching of luminescence intensity of **1** displays a good linear correlation with the increasing of the concentration of NB (from 0 to 150 mg/L). The limit of detection (LOD) for NB is of 20.5 mg/L [26].

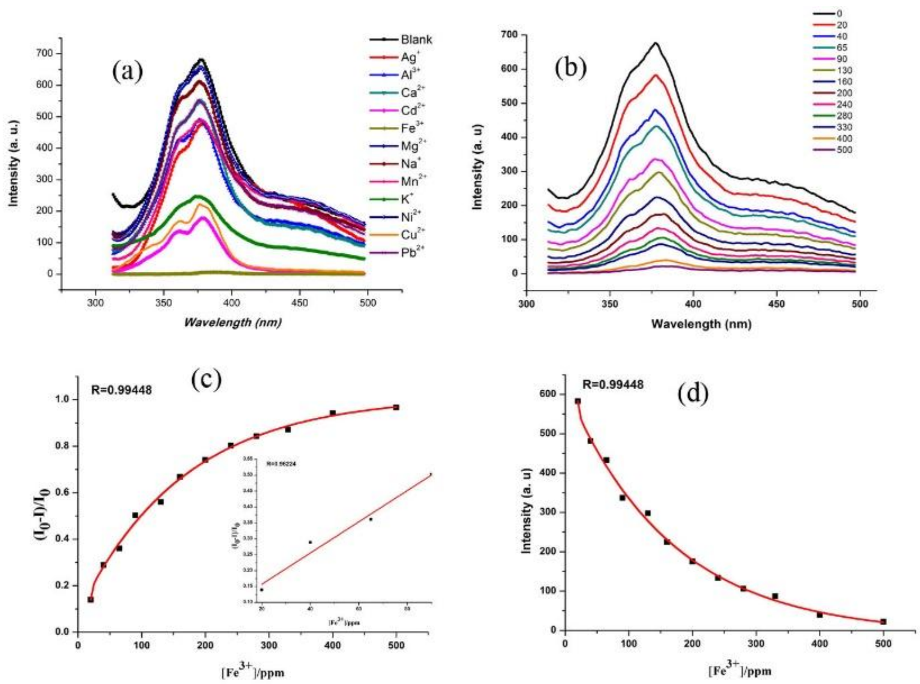

Figure 2. (a) Emission spectra of **1** in different anions, (b) emission spectra of **1** in different concentrations of Fe^{3+} in DMF, (c) Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of Fe^{3+}. Inset: Stern–Volmer plot at low Fe^{3+}concentrations and (d) view of the relationship of luminescent intensities and Fe^{3+}concentration.

Simultaneously, the potential detecting of different anions of **1** was also examined. Similar to the experiments of luminescent sensing for metal ions, we have analyzed luminescence properties of **1** after immersed in different selected anions in DMF solution. The results show that the luminescence intensities are significantly different for solutions containing different anions and only CrO_4^{2-} gave significant quenching effect on the fluorescence of **1**, indicating the high selectivity of **1** for the detection and specific recognition of CrO_4^{2-} in DMF solution (Figure 4a). CrO_4^{2-} as a toxic anion is badly harmful to human health and environment and can be accumulated in the living organisms leading to kinds of serious diseases [27]. To gain a better understanding of the ability of **1** to sense CrO_4^{2-}, PL quenching titrations were performed and the result indicated that the luminescent intensities were gradually weakened by increasing the amount of CrO_4^{2-} (Figure 4b). The luminescent intensity of **1** is almost completely quenched at a CrO_4^{2-} concentration of 500 mg/L. Furthermore, a nonlinear correlation for $(I_0\text{-}I)/I_0$ and the concentration of CrO_4^{2-} ions was obtained, the S–V curves deviate from the straight line (Figure 4c-d), and this phenomenon suggests that more than one quenching mechanism appear in the process, including dynamic quenching and static quenching [23]. However, the Stern–Volmer plots for CrO_4^{2-} are nearly linear at low concentrations (R^2 = 0.9755) with the K_{sv} value of 3.2 $\times 10^4$ M^{-1}. It has been reported that the CrO_4^{2-} ions may compete for the absorption of light with the organic molecules and thus reducing the efficiency of energy transfer from ligand to ions [28]. The powder X-ray diffraction (PXRD) (Figure 1c) patterns and IR indicated possible structural and/or symmetry changes within the crystal structure of **1** upon dispersion in the metal ion solutions, though notably these changes were consistent across all metal solutions, as well as when soaked in $Cr_2O_7^{2-}$ solutions.

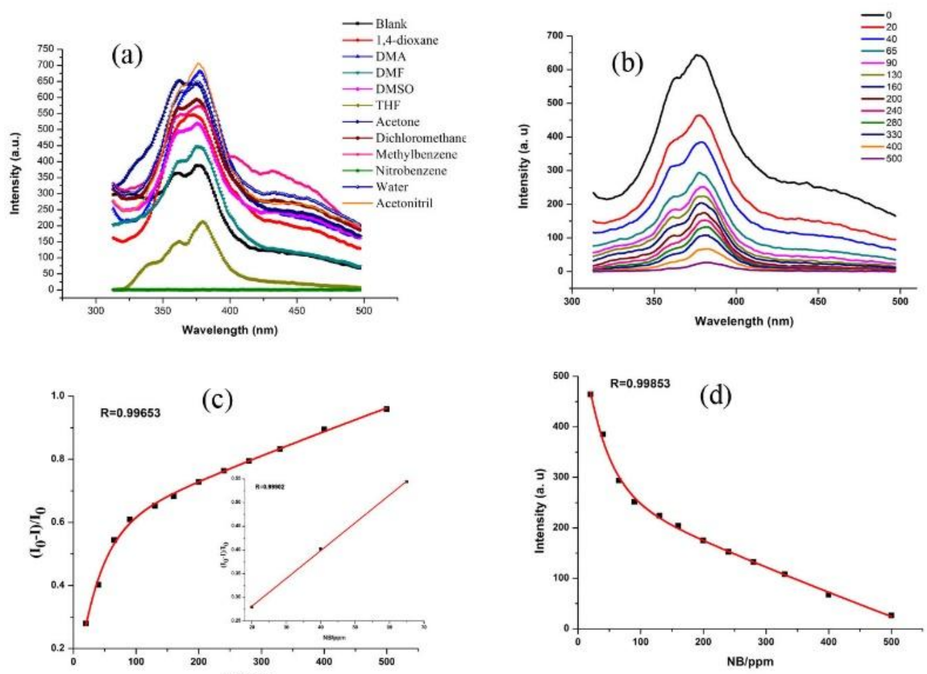

Figure 3. (a) Emission spectra of **1** in different small organic solvents, (b) emission spectra of **1** in different concentrations of NB in DMF, (c) Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of NB. Inset: Stern–Volmer plot at low NB

concentrations and (d) view of the relationship of luminescent intensities and NB concentration.

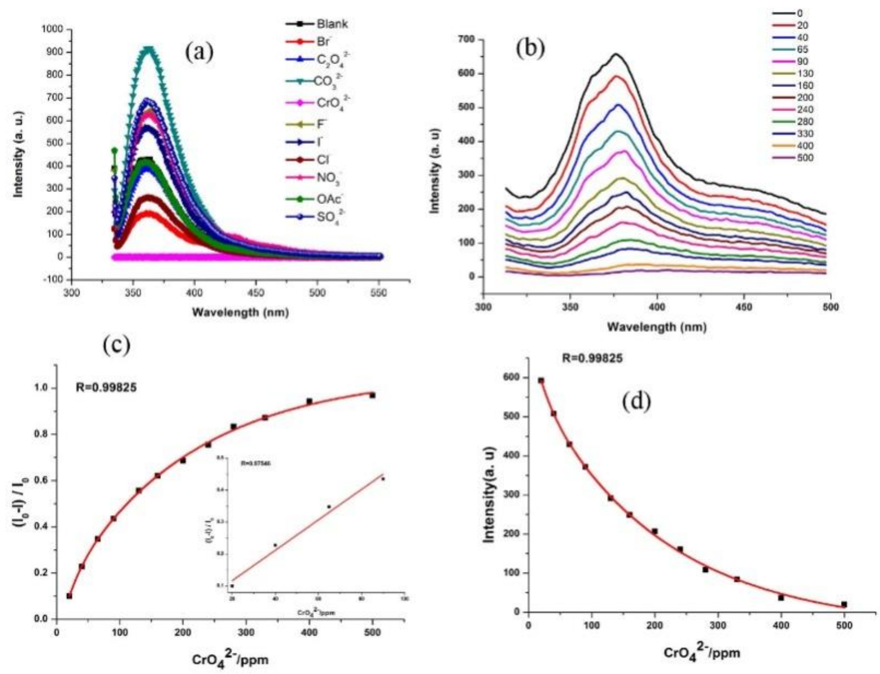

Figure 4. (a) Emission spectra of **1** in different anions, (b) emission spectra of **1** in different concentrations of CrO_4^{2-} in DMF, (c) Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of CrO_4^{2-}. Inset: Stern–Volmer plot at low CrO_4^{2-} concentrations and (d) view of the relationship of luminescent intensities and CrO_4^{2-} concentration.

CONCLUSION

This study shows that **1** could be a useful luminescent sensor for metal ions, anions and small organic molecules. In the subsequent study, wide applications of **1** in fluorescence test paper will be investigated. This opens up a way to use MOFs as hosts to build some highly sensitive sensors with multifunctional applications.

ACKNOWLEDGMENTS

The authors acknowledge Science Foundation funded project of Guangdong Medical University (M2016023) and Innovative Entrepreneurial Training Plan of undergraduates in Guangdong Province (201610571060; 201610571089; 201610571086; 201610571083; 201610571089 and 201610571066) and pecial Funds for Scientific and Technological Innovation of undergraduates in Guangdong Province (pdjh2017b0225) and Shaanxi Xueqian Normal University high-level talent introduction start-up fund scientific research projects (2014DS020).

REFERENCES

1. Qin, J.; Bao, S.; Li, P.; Xie, W.; Du, D.; Zhao, L.; Lan, Y.; Su, Z. A stable porous anionic metal-organic framework for luminescence sensing of Ln^{3+} ions and detection of nitrobenzene. *Chem. Asian J.* **2014**, 9, 749-753.
2. Cui, Y.; Yue, Y.; Qian, G.; Chen, B. Luminescent functional metal-organic frameworks. *Chem. Rev.***2012**, 112, 1126-1162.
3. Shan, X.; Jiang, F.; Yuan, D.; Zhang, H.; Wu, M.; Chen, L.; Wei, J.; Zhang, S.; Pan, J.; Hong, M. A multi-metal-cluster MOF with Cu_4I_4 and Cu_6S_6 as functional groups exhibiting dual emission with both thermochromic and near-IR character. *Chem. Rev.* **2013**, 4, 1484-1489.
4. Ablet, A.; Li, S.; Cao, W.; Zheng, X.; Wong, W.; Jin, L. Luminescence tuning and white-light emission of Co-doped Ln-Cd-organic frameworks. *Chem. Asian J.* **2013**, 8, 95-100.
5. Wang, J.; Li, M.; Li, D. A dynamic, luminescent and entangled MOF as a qualitative sensor for volatile organic solvents and a quantitative monitor for acetonitrile vapour. *Chem. Sci.* **2013**, 4, 1793-1801.
6. Tang, Q.; Liu, S.; Liu, Y.; Miao, J.; Li, S.; Zhang, L.; Shi, Z.; Zheng, Z. Cation sensing by a luminescent metal-organic framework with multiple Lewis basic sites. *Inorg. Chem.* **2013**, 52, 2799-2801.
7. Song, X.; Song, S.; Zhao, S.; Hao, Z.; Zhu, M.; Meng, X.; Wu, L.; Zhang, H. Single-crystal-to-single-crystal transformation of a europium(III) metal-organic framework producing a multi-responsive luminescent sensor. *Adv. Funct. Mater.* **2014**, 24, 4034-4041.
8. Liu, B.; Hou, L.; Wu, W.; Dou, A.; Wang, Y. Highly selective luminescence sensing for Cu^{2+} ions and selective CO_2 capture in a doubly interpenetrated MOF with Lewis basic pyridyl sites. *Dalton Trans.* **2015**, 44, 4423-4427.
9. Liu, J.; Wu, J.; Li, F.; Liu, W.; Li, B.; Wang, J.; Li, Q.; Yadave, R.; Kumar, A. Luminescent sensing from a new Zn(II) metal-organic framework. *RSC Advances* **2016**, 6, 31161-31166.
10. Li, B.; Wu, J.; Liu, J.; Gu, C.; Xu, J.; Luo, M.; Yadav, R.; Kumar, A.; Batten, S.R. A luminescent zinc(II) metal-organic framework for selective detection of nitroaromatics, Fe^{3+} and CrO_4^{2-}: A versatile threefold fluorescent sensor. *ChemPlusChem* **2016**, 81, 885-892.
11. Liu, J.; Li, G.; Liu, W.; Li, Q.; Li, B.; Gable, R.W.; Hou, L.; Batten, S.R. Two unusual nanocage-based Ln-MOFs with triazole sites: Highly fluorescent sensing for Fe^{3+} and $Cr_2O_7^{2-}$, and selective CO_2 capture. *ChemPlusChem* **2016**, 81, 1299-1304.
12. Roushani, M.; Baghelani, Y.M.; Abbasi, S.; Mohammadi, S.Z.; Mavaei, M. Solid phase extraction of trace amounts of zinc and cadmium ions using perlite as a supper sorbent. *Bull. Chem. Soc. Ethiop.* **2016**, 30, 175-184.
13. Chen, B.; Wang, L.; Zapata, F.; Qian, G.; Lobkovsky, E.B. A luminescent microporous metal-organic framework for the recognition and sensing of anions. *J. Am. Chem. Soc.* **2008**, 130, 6718-6719.
14. Wang, H.; Huang, C.; Han, Y.; Shao, Z.; Hou, H.; Fan, Y. Central-metal exchange, improved catalytic activity, photoluminescence properties of a new family of d^{10} coordination polymers based on the 5,5'-(1H-2,3,5-triazole-1,4-diyl)diisophthalic acid ligand. *Dalton Trans.* **2016**, 45, 7776-7785.
15. Esmaielzadeh, S.; Zare, Z.; Azimian, L. Synthesis, physical characterization, antibacterial activity and thermodynamic studies of five coodrdinate cobalt(III) Schiff base complexes. *Bull. Chem. Soc. Ethiop.* **2016**, 30, 209-220.
16. Assefa, Z.; Gore, S.B. Structural and spectroscopic studies of 2,9-dimethyl-1,10-phenanthrolinium cation (DPH) with chloride, triflate and gold dicyanide anions. The role of H-bonding in molecular recognition and enhancement of π-π stacking. *Bull. Chem. Soc. Ethiop.* **2016**, 30, 231-239.

17. Sadia, M.; Jan, M.R.; Shah, J.; ul-Haq, A.; Comparison of simple and chelated amberlite IR-120 for preconcentration and determination of Cu(II) from aqueous samples. *Bull. Chem. Soc. Ethiop.* **2016**, 30, 39-54.
18. Mahapatra, B.B.; Sarangi, A.K.; Mishra, R.R. Structural and theoretical study of six dinuclear Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes containing ON-NO donor azodye ligand, 4,4'-(1E,1'E)-(5,5'-(propane-2,2-diyl)bis(2-hydroxy-5,1-phenylene)-bis(diazene-2,1- diyl)dibenzenesulfonic acid. *Bull. Chem. Soc. Ethiop.* **2016**, 30, 87-100.
19. Kane, C.H.; Tinguiano, D.; Tamboura, F.B.; Thiam, I.E.; Barry, A.H.; Gaye, M.; Retailleau, P. Synthesis and characterization of novel M(II) (M = Mn(II), Ni(II), Cu(II) or Zn(II)) complexes with tridentate N2,O-donor ligand (E)-2-amino-N'-[1-(pyridin-2-yl)-ethylidene] benzohydrazide. *Bull. Chem. Soc. Ethiop.* **2016**, 30, 101-110.
20. Kreno, L.E.; Leong, K.; Farha, O.K.; Allendorf, M.; Van Duyne, R.P.; Hupp, J.T. Metal-organic framework materials as chemical sensors. *Chem. Rev.* **2012**, 112, 1105-1125.
21. Xi, C.; Zhang, B.Q.; Yu, Y.; Su, M.; Qin, W.M.; Li, B.; Zhuang, G.L.; Zhang, T.L. Synthesis, crystal structure and luminescence studies of zinc(II) and cadmium(II) complexes with 6-(1H-tetrazol-5-yl)-2-naphthoic acid. *CrystEngComm* **2016**, 18, 6396-6402.
22. Yang, J.S.; Swager, T.M. Fluorescent porous polymer films as TNT chemosensors: Electronic and structural effects. *J. Am. Chem. Soc.* **1998**, 120, 11864-11873.
23. Liang, Y.; Yang, G.; Liu, B.; Yan, Y.; Xi, Z.; Wang, Y., Four super water-stable lanthanide-organic frameworks with active uncoordinated carboxylic and pyridyl groups for selective luminescence sensing of Fe^{3+}. *Dalton Trans.* **2015**, 44, 13325-13330.
24. Singh, A.; Raj, T.; Aree, T.; Singh, N. Fluorescent organic nanoparticles of Biginelli-based molecules: recognition of Hg^{2+} and Cl^{-} in an aqueous medium. *Inorg. Chem.* **2013**, 52, 13830-13832.
25. Jayaramulu, K.; Narayanan, R.P.; George, S.J.; Maji, T.K., Luminescent microporous metal-organic framework with functional Lewis basic sites on the pore surface: Specific sensing and removal of metal ions. *Inorg. Chem.* **2012**, 51, 10089-10091.
26. Wang, C.; Li, J.; Lv, X.; Zhang, Y.; Guo, G., Photocatalytic organic pollutants degradation in metal-organic frameworks. *Energy Environ. Sci.* **2014**, 7, 2831-2867.
27. Liu, C.; Yan, B. Luminescent zinc metal-organic framework (ZIF-90) for sensing metal ions, anions and small molecules. *Photochem. Photobiol. Sci.* **2015**, 14, 1644-1650.
28. Lu, Y.; Yan, B., A ratiometric fluorescent pH sensor based on nanoscale metal-organic frameworks (MOFs) modified by europium(III) complexes. *Chem. Commun.* **2014**, 50, 13323-13326.