SYNTHESIZING AND CHARACTERIZING OPTICAL PROPERTY OF MOF-5 DOPED WITH TRIVALENT EUROPIUM

Bui Xuan Vuong

Ho Chi Minh City Industry and Trade College; vuongbx@yahoo.com

Abstract - In this study, we have successfully synthesized the metal organic framework MOF-5 and MOF-5 doped with the Eu rare earth element. Physical-Chemical analyses via SEM, FTIR and Elemental analysis showed the structure and the composition of synthetic materials. The analyses also confirmed that the effect of the additional Eu element changed the structural morphology of pure MOF-5. The implantation of europiumin in MOF-5 induced the modification of the MOF-5 original structure from the cubic shape into the diamond shape.The fluorescent spectroscopy results of MOF-5 doped with Eu were recorded at 617 nm in correspondence with the $^5D_o \rightarrow {}^7F_2$ transition of the transitional Eu^{3+} ion. The optical property of MOF-5 doped with Eu opens the applicability of this material in biosensor fabrication.

Key words - Metal organic frameworks; MOF; fluorescent; Eu; transition element; biosensor.

1. Introduction

Metal organic frameworks (MOFs) are considered as the hottest materials, expanding a large opportunity for the "green" industry, changing the face of solid material and material science. In recent years, MOFs have received much attention especially as newly developed porous materials. MOFs can generate stable, ordered and high surface areas, which are the advantages of both organic and inorganic porous materials. Therefore, they obtain a lot of potential applications. Among their applications suggested by the unusual properties of MOFs are gas storage [1], gas/vapor separation, size, shape, and enantion selective catalysis [2-3], luminescent and fluorescent materials, drug storage and drug delivery [4-5].

MOFs were discovered by Professor Omar Yaghi (from California University, Los Angeles), in the first years of 1990s [6]. After that, over 2,000 three-dimensional structures were developed and reported by researchers and scientists around the world.

In Vietnam, the Ho Chi Minh City University of Science and the Ho Chi Minh City University of Technology are the first two places researching MOFs [4]. These two universities have received lots of technical support from the experts of California University, Los Angeles (UCLA). In March 2011, the biggest conference on MOFs materials was organized. It is successful technical cooperation between Ho Chi Minh City University of Science and UCLA with MANAR (Molecular and Nano Architecture) (Knowledge Stream. June/2011).

With regard toMOF's structure, MOFs exist as infinite crystalline lattices comprising inorganic vertices (metal ions or clusters) and organic struts, connected by coordination bonds of moderate strength (Figure 1) [6].

The variety of metal ions, organic linkers, and structural motifs affords an infinite number of combinations [7]. From their diversity in terms of structural compositions and molecular level tunability, the flexibility of their chemical functionalization creates variety in the structure of MOFs. These subunits can be connected to form one dimensional (1D), 2 dimensional (2D), 3 dimensional (3D) MOFs by choosing appropriate polydentate organic ligands [8]. Some types of MOFs materials will be introduced as follows.

A fluorescent MOFs constructed by 2D infinite coordination polymers, $[Zn(BDC)(H_2O)]_n$ (BDC = 1,4-benzenedicarboxylate), was synthesized by the reaction of zinc acetate with H_2BDC in *N,N*-dimethylformamide (DMF) under ultrasonic irradiation at an ambient temperature and atmospheric pressure [9]. Whereas Peipei Long et al. studied a new MOFs material with an infinite 3D network, the MIL-96 structural type based on Crom and 1,3,5-benzenetricarboxylic acid (H_3BTC) ligand was first obtained by using H_2O and CH_3OH as a mixed solvent, which differs from the hydrothermal synthesis of MIL-96(Al), MIL-96(Ga), and MIL-96(In). MIL-100(Cr) [10]. Carlos Otero Areán et al. also synthesized MIL-100(Sc), $Sc_3O(OH)L_2(H_2O)_2$ (L = 1,3,5-benzenecarboxylate, trimesate) under solvothermal conditions at 423K, and studied hydrogen adsorption at low temperatures by variable temperature IR spectroscopy [11]. A series of MOFs-n materials with various structures were reported in 2000 by Yaghi and co-workers. Authors have been successfully in the preparation of MOF-n (n = 2, 3, 4, 5), using BDC, BTC as linkers, which offer important advantages due to their rigidity and consequent tendency to form rigid metal carboxylate clusters that ultimately act as SBUs in the extended solid [12]. A new isoreticular metal framework (IRMOF), IRMOF-0, having the same cubic topology as MOF-5, has been prepared by David J. Tranchemontagne et al [13] at room temperature, according to direct-mixing method. In this synthesis, acetylenedicarboxylic acid acts as linker and displaying double interpenetration. The pore apertures are too small to allow for the removal of trapped guest molecules or adsorption of gases but both Fourier transform infra-red spectroscopy (FTIR) and elemental analysis indicated that guest molecules were trapped within the pores [13]. While this material is nonporous, it is a demonstration of these new synthetic methods towards the design and synthesis of new MOFs.

Researching MOF-5, one member of the MOF-n family, Jinping Li et al. [1] indicate that it has a framework like a zeolite in which inorganic $[Zn_4O]^{6+}$ groups are joined to an octahedral array of BDC groups to form a robust and highly porous cubic framework of a space group.

From the previous research, we recognize that the synthesis of MOF-5 is simple, from precursors to

manipulations. In addition, MOF-5 also possesses common properties similar to MOF materials such as porous and ordered structures.

In this study, we focus on the fabrication of MOF-5 doped with the europium rare earth element,which can obtain fluorescent ability in suitable conditions.The synthetic material can be applied in biosensor fabrication.

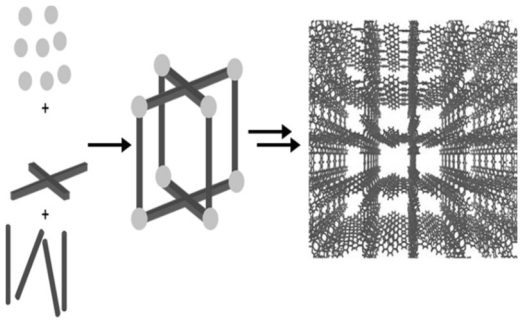

Figure 1. *General scheme of MOF synthesis*

2. Experimental procedure

2.1. Materials

The chemical reagents used in experiments were as follows: Zinc nitrate hexahydrate (Sigma-Aldrich); Europium (III) nitrate pentahydrate (Sigma-Aldrich); Benzene-1,4-dicarboxylic acid (Merk, 98%); Trimethylamine (99%, Merk); N,N-dimethylformamide (99%, Merk); Chloroform (99.0-99.4%, Merk).

2.2. Synthesis of MOF-5

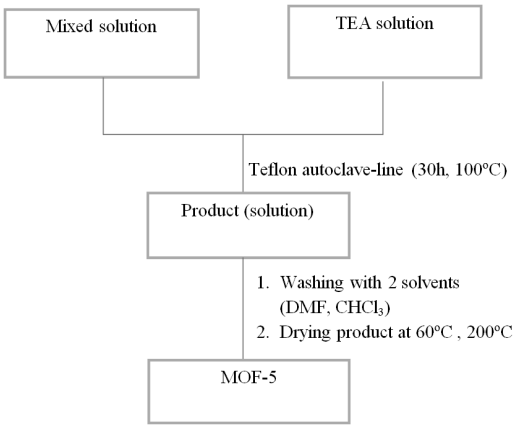

Figure 2. *Synthetic process of MOF-5*

The experimental steps in the detail are as follows: Zinc nitrate hexahydrate (1.071g, 3.6 mmol) was dissolved in 36 mL of N,N-dimethylformamide. Benzene-1,4-dicarboxylic acid (0.2988, 1.8 mmol) was dissolved in 36 mL of N,N-dimethylformamide. Mixing these 2 solutions was prepared on the agitated machine. Then 1.98 ml (1.6 mmol) of triethylamine was added (dropped gradually). This solution was stirred in 5 minutes. Then it was transferred into teflon autoclave-line. The resulting mixture was heated at 100°C, in 30 hours. After solvothermal reaction, we centrifugated the final solution with an N,N-dimethylformamide solvent (3 times), and a chloroform solvent (3 times). The volume for each time was 30 ml). The product was classified into 2 parts. One part was dried at 60°C and the other at 200°C. Then the products were preserved in vacuum bags (Figure 2).

2.3. Synthesis of MOF-5 doped europium

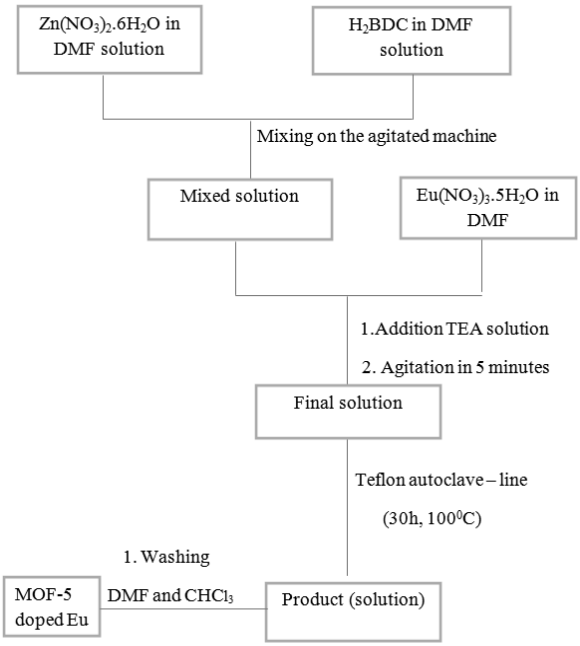

Figure 3. *Synthetic process of MOF-5 doped Europium*

The elaboration of MOF-5 doped Europium is designed in Figure 3. In detail, the experimental steps are as follows:

Experiment 1: Zinc nitrate hexahydrate (0.476 g, 1.6 mmol) was dissolved in 16 mL of N,N-dimethylformamide (a_1). Benzene-1,4-dicarboxylic acid (0.1328 g, 0.80 mmol) was dissolved in 16 mL of N,N-dimethylformamide (b_1). Europium (III) nitrate pentahydrate (0.1056 g, 0.25 mmol) was dissolved in 16 mL of N,N-dimethylformamide (c_1). The following step was mixing solution (a_1) with solution (b_1) and agitation on the agitated machine. The solution (c_1) was added into this mixture. Then, 0.88 mL of triethylamine was dropped gradually into the solution and stirred for 5 minutes. All this solution was transferred into a teflon autoclave-line. The resulting mixture was heated at 100°C, in 30 hours.

After solvothermal reaction, we centrifugated the final solution with an N,N-dimethylformamide solvent (3 times), and a chloroform solvent (3 times). The volume for each time was 30 mL). The final product was dried at 200°C and then preserved in a vacuum bag (sample 1).

Experiment 2: The quantity of the precursor materials decreased a half compared to the quantity of the materials in experiment 1; the volume of triethylamine also decreased a half. The details are as follow: Zinc nitrate hexahydrate (0.238 g, 0.8 mmol) was dissolved in 10 mL of N,N-dimethylformamide (a_2). Benzene-1,4-dicarboxylic acid (0.0664 g, 0.40 mmol) was dissolved in 10 mL of N,N-dimethylformamide (b_2). Europium (III) nitrate pentahydrate (0.0528 g, 0.12 mmol) was dissolved in 10 mL of N,N-dimethylformamide (c_2). The next steps were the same with experiment 1. The final product was dried at 60°C and was preserved in a vacuum bag (sample 2).

Experimental 3: Quantity of the precursor materials are the same experiment 2. But changing the volume of

catalytic reagent. Decreasing the volume of triethylamine solution equal 0.22ml. The following steps were the same with experiment 2. The final product was dried at 60°C and was preserved in a vacuum bag (sample 3).

2.4. Characterization

The morphology of synthetic materials was observed on Scanning Electron Microscope (SEM) by using the JEOL JSM-6490 program. The structures were characterized by Nexus 670 Fuorier Transform Infrared Spectroscopy (FT-IR). The spectra were registered from 400 cm^{-1} to 4000 cm^{-1}. Elemental analysis of MOF-5 doped Europium was measured on the 6490 (LA) quantitive analysis machine.Fluorescence spectroscopy was also used to analyze fluorescence from synthetic material.

3. Results and discussion

3.1. Characterization of MOF-5

The SEM image showed a three dimensional, cube shape with its diameter of approximately 10 micrometers as illustrated in Figure 4.

The infrared spectra of the MOF-5 exhibited the presence of strong peaks at 1574 cm^{-1}, 1389 cm^{-1},which were lower than the value for the C=O stretching vibration observed in the free carboxylic acids (regularity is 1850-1650cm^{-1}) as demonstrated in Figure 5. These strong peaks were the stretching vibration of the carboxylate anions present in the material. The absence of the strong absorption bands at 1850-1650cm^{-1}, where the –COOH group was, indicated the deprotonation of the –COOH group in the 1,4-benzenedicarboxylic acid upon the reaction with metal ions. The broad band at 3600-3000 cm^{-1} in both lines indicated the presence of the O-H group of water in the metal coordination sphere. It also demonstrated water adsorbed ability of MOF-5 and the preservation of products in a vacuum environment was important.

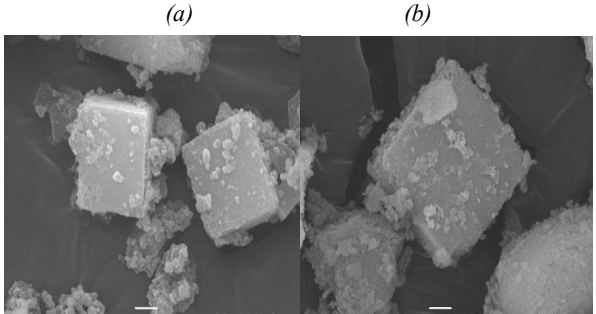

Figure 4. *SEM image of MOF-5 when dried at 60°C (a) and SEM image of MOF-5 when dried at 200°C (b)*

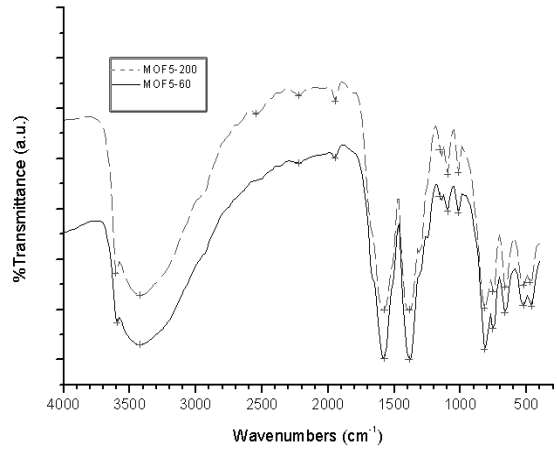

Figure 5. IR spectra of MOF-5 when products were dried at 60°C (dark line) and 200°C (red line)

3.2. Characterization of MOF-5 doped europium

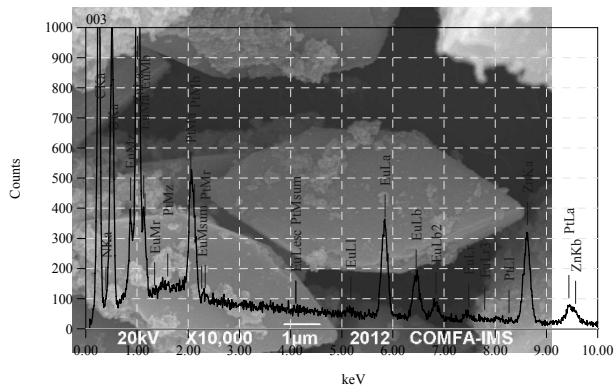

Figure 6. *SEM image of MOF-5 doped Europium*

From the SEM image of sample 1, the shape of MOF-5 deformed from the cubic shape into the diamond shape (Figure 6). Obtained results highlighted the effect of europium on the structure of pure MOF-5. It can be predicted that the presence of europium element disordered the crystal structure of MOF-5.

The elemental analysis of MOF-5 doped Europium was measured on the 6490 (LA) quantitive analysis machine as illustrated in Figure 7.

ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.4444

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	26.68	0.24	50.20				9.5438
N K*	0.392	0.20	1.44	0.32				0.2250
O K	0.525	26.86	0.50	37.94				26.6221
Zn K	8.630	23.69	1.84	8.19				32.0580
Eu L	5.842	22.56	1.55	3.35				31.5511
Total		100.00		100.00				

Figure 7*. Elemental analysis of MOF-5.Eu*

The fluorescent property of the sample was characterized by fluorescent spectroscopy. The emission spectra recorded in the range 400-800 nm showed the transition of Eu^{3+} ion with the hypersensitive $^5D_o \rightarrow {}^7F_2$ transition at 617 nm (red light), being the most prominent (Figure 8). It indicated an efficent intramolecular energy transfer from organic ligand to the Eu^{3+}.

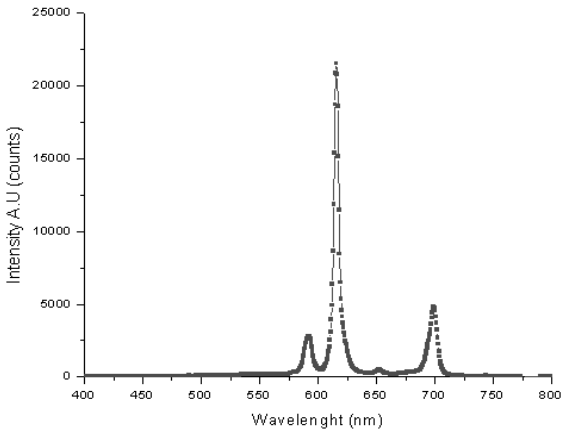

Figure 8.*Fluorescent spectra of MOF -5 doped Eu*

According to the SEM image and elemental analysis as well as fluorescent spectra, we can predict that europium can be penetrated into frameworks. Futhermore, we can completely dope europium element into MOF-5 to fabricate strongly fluorescent material in suitable conditions. This opens potential fabrication of porous materials containing fluorescent property.

4. Conclusion

In our study, we reached some achievements. We succeeded in synthesizing the MOF-5 material in a cubic shape via the solvothermal method. Moreover, MOF doped with Eu was also elaborated. SEM results highlighted the effect of Eu element on the morphology of pure MOF-5. The implantation of europium (rare earth element) in MOF-5 induced the modification of the MOF-5original structure of from a cubic shape into a diamond shape. MOF-5 doped with Eu also demonstraed the fluorescent property. This material can be applied in biosensor fabrication.

REFERENCES

[1] Jinping Li, Shaojuan Cheng, Qiang Zhao, Peipei Long, Jinxiang Dong. Synthesis and hydrogen-storage behavior of metal–organic framework MOF-5. 2009. *International journal of hydrogen energy*. 34 (2009).1377-1382.

[2] Nam T.S. Phan, Ky K.A. Le, Tuan D. Phan. MOF-5 as an efficient heterogeneous catalyst for Friedel–Crafts alkylation reactions. 2010. *Applied Catalysis A*: General 382 (2010) 246–253.

[3] Ugo Ravon, Marcelo.E Domine, Cyril Gaudillere, Arnold Desmartin-Chomel,David Farrusseng. MOF-5 as acid catalyst with shape selectivity properties. *Zeolites and Related Materials*: Trends, Targets and Challenges. Proceedings of 4th International FEZA ConferenceGédéon, P. Massiani and F. Babonneau (Editors). © 2008 Elsevier B.V.

[4] Ryan J. Kuppler, Daren J. Timmons, Qian-Rong Fang, Jian-Rong Li , Trevor A. Makal, Mark D. Young, Daqiang Yuan, Dan Zhao,Wenjuan Zhuang, Hong-Cai Zhou. Potential applications of metal-organic frameworks.2009. *Coordination Chemistry Reviews*. 253 (2009) 3042–3066.

[5] Rachel C Huxford, Joseph Della Rocca and Wenbin Lin. Metal–organic frameworks as potential drug carriers. 2010. *Current opinion in chemical biology*. 14:262–268.

[6] Omar K. Farha and Joseph T. Hupp. Rational Design, Synthesis, Purification, andActivation of Metal-Organic Framework Materials. 2010. *Accounts of chemical research*. 1166-1175 August 2010 Vol. 43, No. 8.

[7] Lauren E. Kreno,Kirsty Leong, Omar K. Farha, Mark Allendorf, Richard P. Van Duyne, and Joseph T. Hupp. Metal-Organic Framework Materials as Chemical Sensors. 2011. *Chemical Reviews*. Received August 18,2011.

[8] GUO Guangsheng , LIU Yangchun, ZHANG Jia, GUO Hongyou. A series of rare earth coordination polymer constructed from paddle-wheel building blocks. 2008. *Journal of rare earths*,. Vol. 26, No. 5, Oct. 2008, p. 633.

[9] Zong-Qun Li, Ling-Guang Qiu , Wei Wang, Tao Xu, Yun Wu, Xia Jiang. Fabrication of nanosheets of a fluorescent metal–organic framework $[Zn(BDC)(H_2O)]_n$ (BDC = 1,4-benzenedicarboxylate): Ultrasonic synthesis and sensing of ethylamine. 2008. *Inorganic Chemistry Communications*. 11 (2008) 1375–1377.

[10] Peipei Long , Huawei Wu, Qiang Zhao , Yingxia Wang , Jinxiang Dong , Jinping Li. Solvent effect on the synthesis of MIL-96(Cr) and MIL-100(Cr). 2011. *Microporous and Mesoporous Materials*. 142 (2011) 489–493.

[11] Carlos Otero Areán, Carlos Palomino Cabello, Gemma Turnes Palomino. Infrared spectroscopic and thermodynamic study on hydrogen adsorption on the metal organic framework MIL-100(Sc). 2012. *Chemical Physics Letters*. 521 (2012) 104–106.

[12] Mohamed Eddaoudi, Hailian Li, and O. M. Yaghi**.** Highly Porous and Stable Metal-Organic Frameworks: Structure Design and Sorption Properties. 2000. *J. Am. Chem. Soc.* 2000**,** 122, 1391-1397.

[13] David J. Tranchemontagne, Joseph R. Hunt, Omar M. Yaghi. Room temperature synthesis of metal-organic frameworks: MOF-5, MOF-74, MOF-177, MOF-199, and IRMOF-0. 2008. *Tetrahedron*. 64 (2008) 8553–8557.

(The Board of Editors received the paper on 09/9/2016, its review was completed on 03/10/2016)