Synthesis of alkaline earth metal-organic frameworks (MOF) based on benzene-1,2,4,5- tetracarboxylic acid

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ABSTRACT

In the past few decades, metal-organic frameworks (MOFs) have attracted much attention of chemists all over the world because of their esthetic topological architectures and potential applications in many fields such as gas storage and separation, catalysis, magnetism, optical, ion conductivity, luminescence and drug delivery. The structures of these crystalline materials consist of metal ion, organic ligand and solvents. Aromatic polycarboxylate ligands have been extensively employed in the preparation of such MOFs. A long and flexible ligand maybe a good candidate as a unique structural motif to produce interesting topologies and useful functions. In this work, a substance was synthesized by using calcium ion and benzene-1,2,4,5-tetracarboxylic acid in a mixture of water and alcohol by coprecipitation method; which was characterized by X-ray diffractometry, FTIR and photoluminescence spectroscopy.

Key words: MOF, Ca, benzene-1,2,4,5-tetracarboxylic acid

1. Introduction

Over the past two decades, metal-organic frameworks (MOFs) have attracted tremendous interests of many researchers as a new kind of porous materials. [1] MOFs have attracted much attention of chemists all over the world because of their esthetic topological architectures, potential applications, [2] their controllable pore sized and elaborately designed pore structure. [3] Metal organic frameworks are constructed by the coordination of metal cation or cluster and organic ligand, thus three dimensional network structure with high crystallinity and porosity is acquired. Porous materials are very useful in gas storage, adsorption based gas/vapor separation, shape/sized-selective catalysis, drug storage, [4] ion exchange, purification, sorption, remediation of radioactive cations, sensing, drug delivery and etc. [5]

In recent years MOFs have also been gradually explored as bio-immobilization platforms. Diverse biomolecules for instance, DNA, drug enzymes, other proteins have been successfully immobilized on MOFs for various applications. [1] Among many, alkali earth metal-organic frameworks have been of great interest attributable to their variable structural architectures and the subsequent properties. [5] In contrast with the extensive study over the transition metal-based MOFs, the MOFs based on alkaline earth metals have still been less investigated owing to their uncertain coordination number as well as geometry. [3] Alkaline earth metals are very reactive and show a wide range of coordination which makes them excellent candidates to construct a range of functional materials with specified structure and properties. [6] It is extremely important to select an appropriate organic linker to construct porous MOFs.

2. Experimental

2.1. Reagents and instrumentation

All the chemical agents are commercially available and employed without further purification. [1] The infrared spectra were recorded on SHIMADZU Transform IR, SHIMADZU spectrometer in the range of 4000-400 cm^{-1} using the KBr disk technique. X-ray powder diffraction (XRD) measurements were performed using a Bourevestnik Dron Poh-8 (V=40.00 KV, Current=20.08 mA) diffractometer with monochromated Cu-k_{α} radiation (λ=1.54056Å). The fluorescence experiments were performed at room temperature on a Shimadzu RF-6000 spectrometer (Kyoto, Japan) with a photomultiplier voltage of 700 V, scan speed of 60,000 nm min^{-1} excitation slit width of 900 nm, emission silt width of 200-800 nm, and 380 nm optical filter.

2.2. Preparation of compounds

A mixture of $Ca(NO_3)_2 \cdot 4H_2O$ (0.3g, 2mmol) dissolved in in distilled water and benzene-1,2,4,5-tetracarboxylic acid (0.25g, 1mmol) dissolved in ethanol:H_2O (1:1) were combined; After a while, a white precipitate was created. Then temperature is reached to 50°C and applied for about one hour to complete the reaction. Then the reaction is cooled down to RT in one hour.

3. Results and discussion

3.1. Synthesis and general characteristic

Under reaction conditions an MOF is synthesized by the reaction of benzene-1,2,4,5-tetracarboxylic acid and Ca(II) ion through coprecipitation method.

3.2. XRD

The phase purity of MOF showed by powder XRD in Fig. 1, the PXRD experimental pattern of new compound is shown, it is in good agreement with the simulated pattern generated from diffraction data, the differences in intensity may attribute to the preferred orientation of the powder sample. [7]

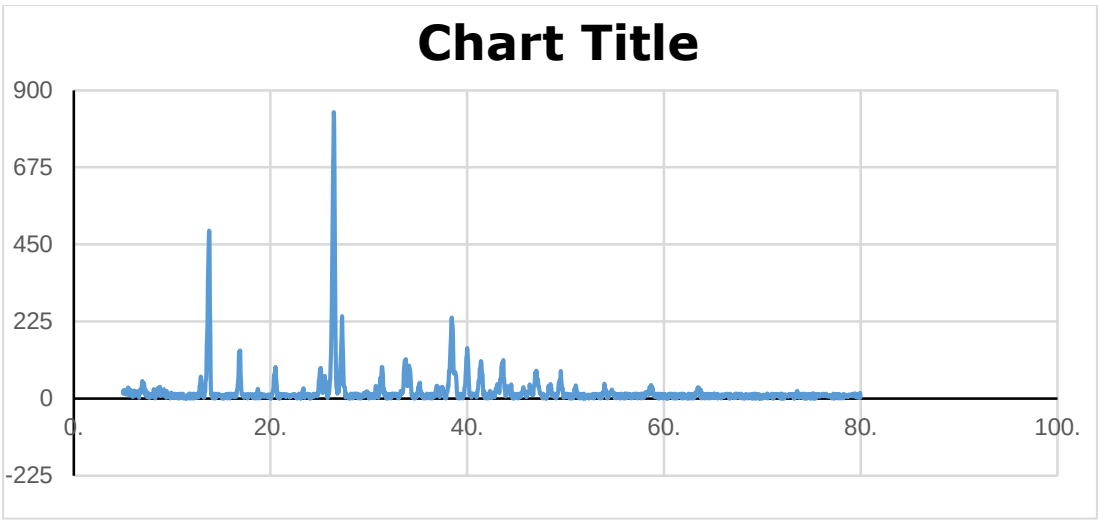

Fig. 1. The XRD pattern of the title MOF

3.3. FT IR

The FT-IR spectrum of new compound in the range of 4000-400 cm^{-1} is investigated. The peak centered at 3400 cm^{-1} can be observed which is attributed to the O–H stretching vibration of water molecules and the sharp peak in 1566 cm^{-1} showed O–H bonds of ligand in final MOF. Fig. 2

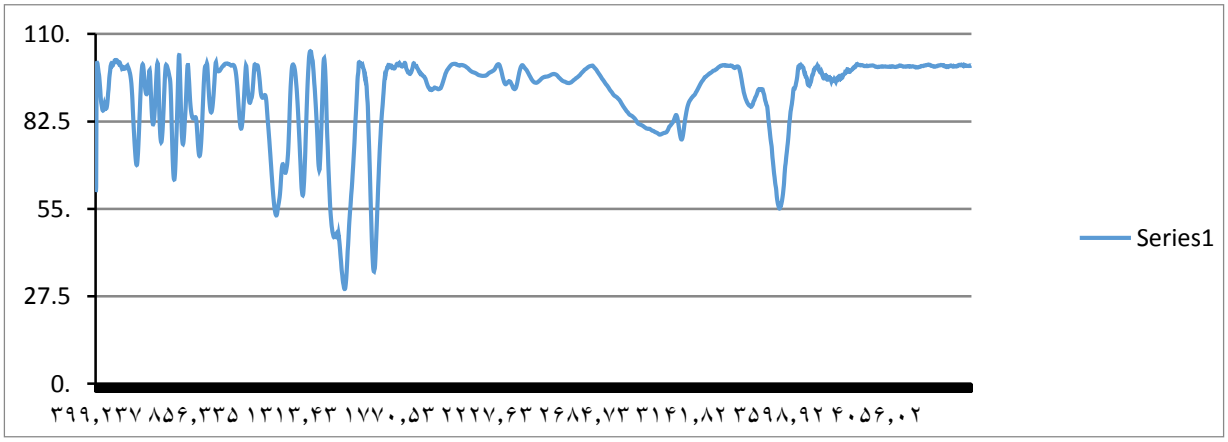

Fig. 2. The FTIR spectrum of the title MOF

3.4. Photoluminescence spectroscopy

To study the luminescence properties of the compound, the spectroscopy is performed at room temperature in solid state. The absorption of PL showed intensity at 300-800 (λ_{ex}=430 nm) and 330-800 nm (λ_{ex}=450 nm), which can be assigned to the $\pi^* \rightarrow$ n transitions as previously reported. [10]

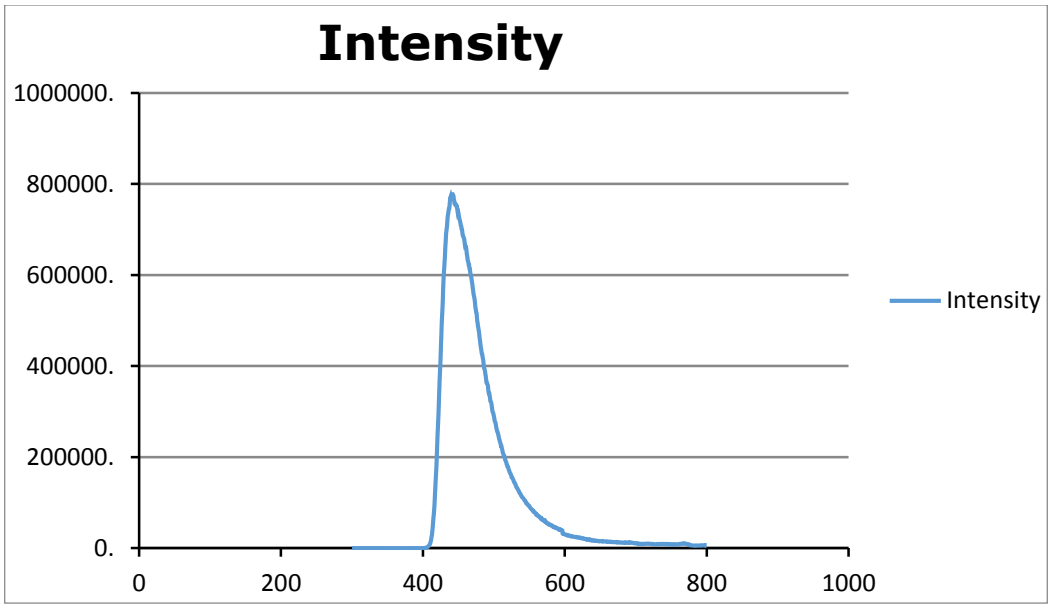

Fig. 3 (a)

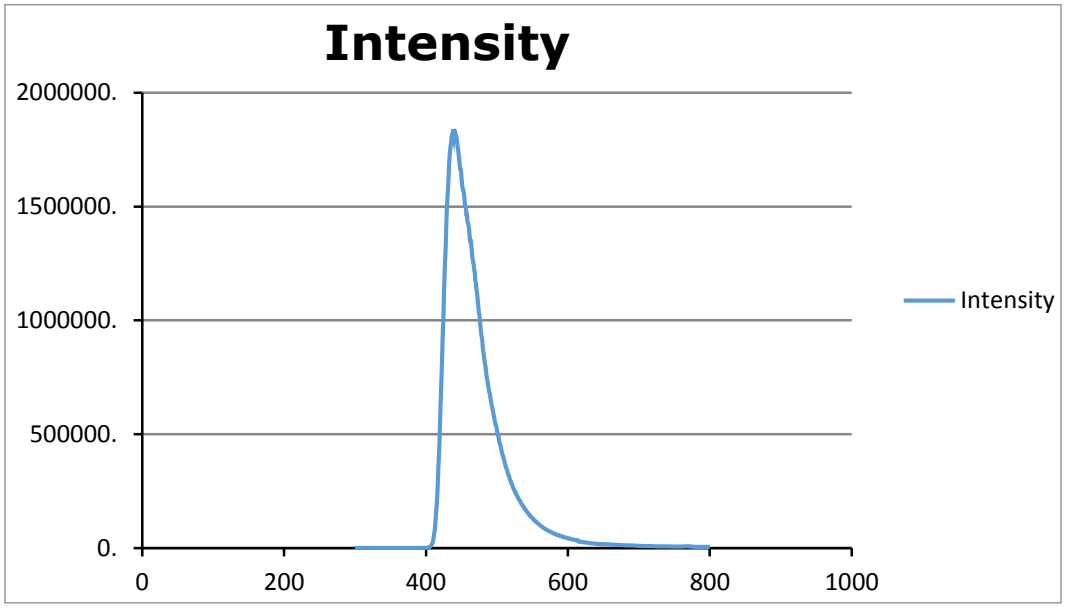

Fig. 3 (b)

Fig. 3. PL intensity at (a) 300 nm, (b) 330 nm

4. Conclusion

In summary, one new Ca MOF was synthesized based on benzene-1,2,4,5-tetracarboxylic acid through coprecipitation. XRD patterns and FTIR spectrum indicated the presence of a new substance and the intensity of peak expresses a long light emission that exists only in aromatic

compounds. In fact, the resonant ligand shows such a PL peak. Therefore, it can be concluded that the aromatic ligand is present in the MOF.

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