Synthesis of a novel porphyrin-based metal organic framework (Co-Por MOF)

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Abstract

In this study, a novel porphyrin-based metal–organic framework (Co-Por MOF) has been successfully synthesized by a simple one-step solvothermal method. we report a metal organic framework based on covalent interaction of an organic linker, 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (TCPP) with cobalt clusters. The properties of this material were analyzed by powder X-ray diffraction (XRD), ultraviolet visible adsorption spectroscopy (UV–Vis), Fourier-transform infrared spectroscopy (FTIR), differential reflectance spectroscopy (DRS).

Keywords: Porphyrin-based metal–organic framework, Co-Por MOF, Simple one-step solvothermal method, TCPP.

Introduction

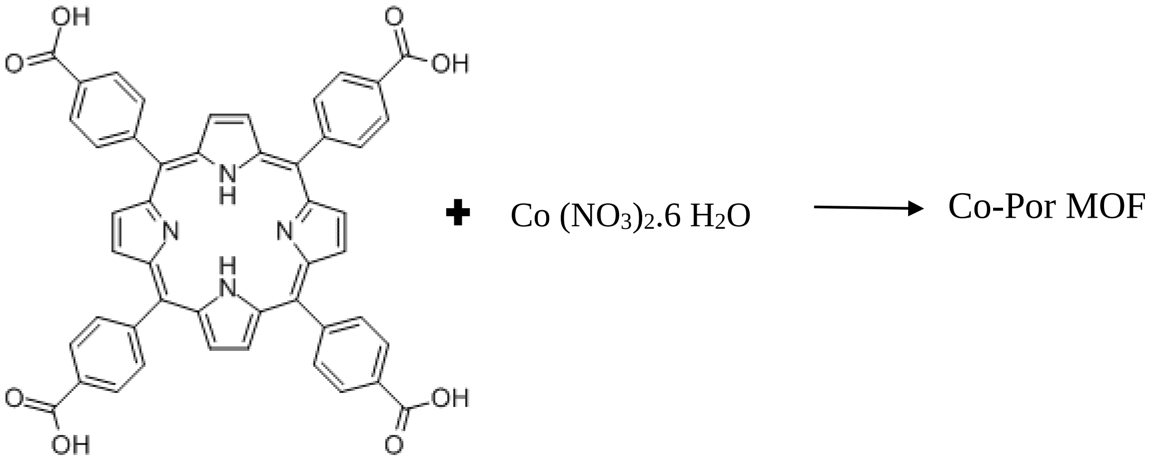
Metal-organic frameworks (MOFs) have attracted significant attention as a new class of porous materials, and developed in the last two decades. They have unique properties as permanently microporous materials. The ability to utilize a virtually unlimited range of organic struts [1-3], together with recent advances in purification and post synthesis manipulation, have facilitated the rational design of materials for many applications, such as gas storage [4], chemical separations [5], and catalysis [6], drug delivery [7], biomedical imaging, photosensitizer [8], sensors [9], etc.

Metal–organic frameworks (MOFs) are a class of hybrid materials assembled from organic linkers and metal ions or clusters [10,11]. In other words, MOFs are comprised of a central metal or metal complex that binds to organic ligands, creating patterned layers, which can be stacked with organic struts to create a three-dimensional porous structure.

Linker modification is one of the most direct methods for MOF functionalization. Porphyrinic ligand are such a category of versatile linkers that have been extensively explored [12,13].

Porphyrins and other pyrrolic systems are fairly widespread in nature and play vital roles in biological systems by contributing to the catalytic activity of many enzymes as cofactors in photosynthesis and respiration. Also porphyrin and metalloporphyrin molecules possess unique biological and chemical functionalities, so they can be used as anticancer drugs, catalysts, sensors, nonlinear optical materials, and DNA-binding or cleavage agents, photomedicine, and energy/electron-transfer systems [14]. Therefore, there are many metal–organic coordination networks assembled from porphyrin or metalloporphyrin building blocks, which present interesting topological network structures, great thermal and chemical stabilities [12].

Herein, we report the synthesis, and characterization of a new porphyrin-based MOF obtained from the reaction of 5,10,15,20-tetrakis(4-Carboxyphenyl) porphyrin with cobalt nitrate under solvothermal conditions. (Scheme 1).



Scheme 1- Synthesis of Co-PorMOF from TCPP ligand and $Co(NO_3)_2$. 6 H_2O.

This novel porous material can be applied as a heterogeneous photocatalyst which exhibit efficient CO_2 photochemical reduction under visible-light irradiation, by cooperating with porphyrin moiety photosensitizer.

Experimental section

General information. The commercial chemicals are used as purchased unless mentioned otherwise. Pyrrole and 4-carboxybenzaldehyde, ethanol, methanol, propionic acid, DMF and

$Co(NO_3)_2 .6H_2O$ were purchased from Sigma–Aldrich or Merck and were of analytical grade. All purchases materials were used without further purification.

Synthesis of TCPP

Porphyrin TCPP was prepared and purified by the methods reported previously [15]. First, 70 mL of propionic acid as solvent and catalyst was heated to refluxing temperature and 0.58 g of 4-carboxybenzaldehyde was added. Then 5 mL of pyrrole was dropwise added to the solution and refluxed for 2 h. The obtained solid was filtered, washed with distilled water and ethanol in order to remove the propionic acid and by products from porphyrin. The resulted purple porphyrin dried at room temperature.

Synthesis of Co-Por MOF

cobalt nitrate hexahydrate, TCPP and a mixed solvents of DMA (dimethylacetamide):MeOH:H_2O (v:v:v = 4:1:1) were ultrasonically dissolved in a 150 mL high pressure vessel. The mixture was sealed and heated at 115 °C for 24 h. After the vial cooled down to room temperature, dark green crystalline powder of Co-Por MOF was collected by filtration. Subsequently, they were washed using DMF and dried in air at room temperature.

Characterization

X-ray diffraction (XRD) patterns were collected on Bruker (AXS D8 Advance) X-ray diffractometer, with Cu Kα radiation. The accelerating voltage and the applied current were 40 KV and 40 mA, respectively. Data were recorded in the 2θ range of 5° to 40°. UV-visible absorption spectra of TCPP ligand were determined by a double beam UV-Vis spectrophotometer (Shimadzu UV-1700). The solid-state UV/Vis spectra (DRS) of the MOF was obtained for the dry-pressed disk samples using a Shimadzu (MPC- 2200) spectrophotometer. The IR experiments were carried out on a Shimadzu FTIR-8400S spectrophotometer, over a scan range from 4000 to 400 cm^{-1}.

Result and discussion

The UV-Vis absorption spectrum of TCPP porphyrin has been shown in figure 1. As can be seen TCPP spectrum exhibited a Soret band at 420 nm and four Q bands in the range of 500-700 nm.

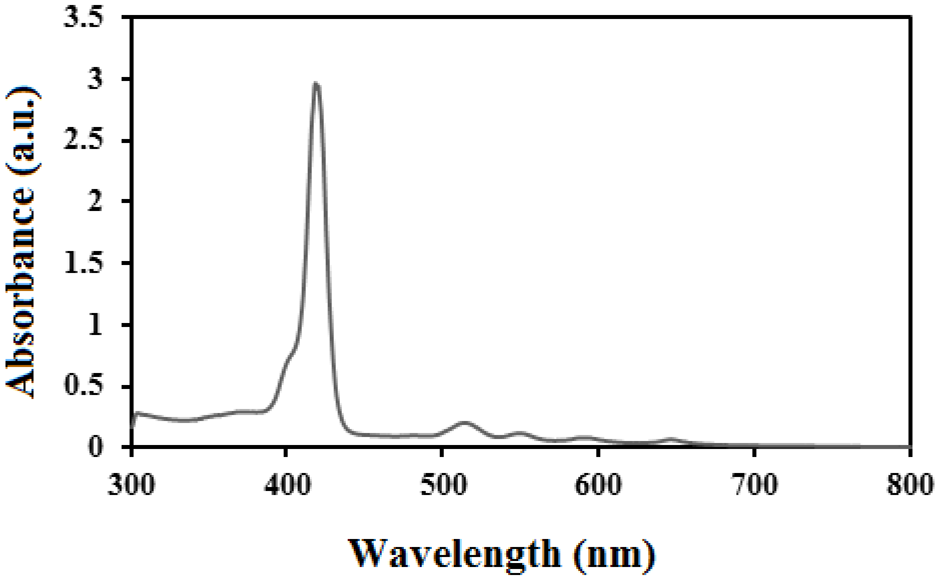


Fig. 1. The UV-Vis absorption spectrum of TCPP.

The UV-Vis-DRS of Co-Por MOF were investigated in Fig. 2, which represents the broad absorption bands in both UV and visible regions (200-800 nm). The characteristic Soret and Q bands of porphyrin MOF were observed at 408, 532 and 586 nm.

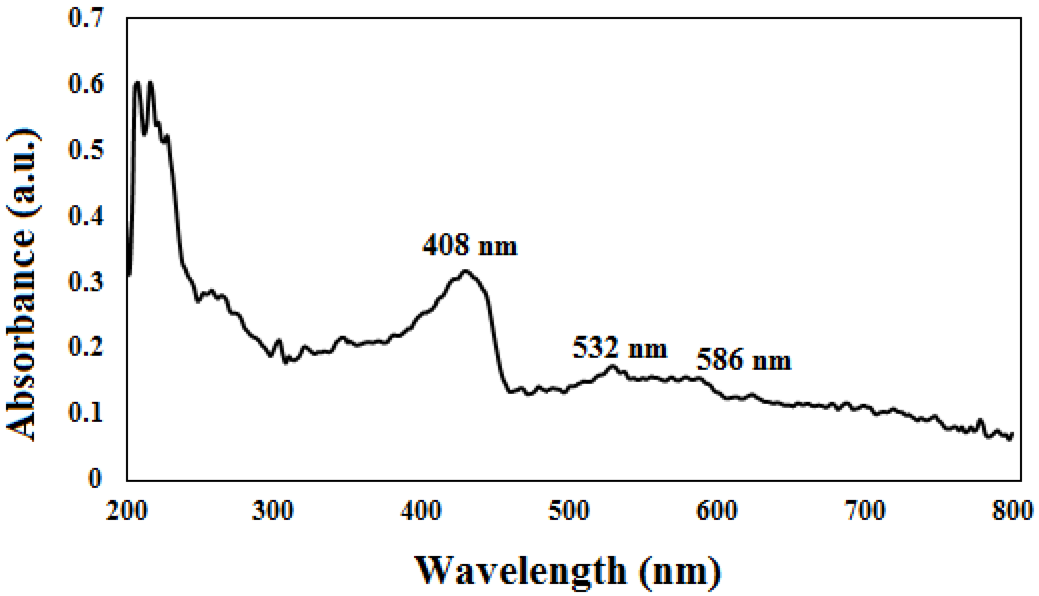


Fig. 2. The UV-Vis-DRS spectra of Co-Por MOF.

As it can be seen in Fig. 3, in FT-IR spectrum of Co-Por MOF the stretching vibration of =C-N and –C=N bands (pyrrole) appeared at 1373 cm^{-1} and 1720 cm^{-1}, respectively, and the stretching vibration of C=O at 1600 cm^{-1}. The stretching asymmetric and symmetric vibration bands attributed to the C-H (CH_2) band are discernible in 2846, 2918 and 2939 cm^{-1}.

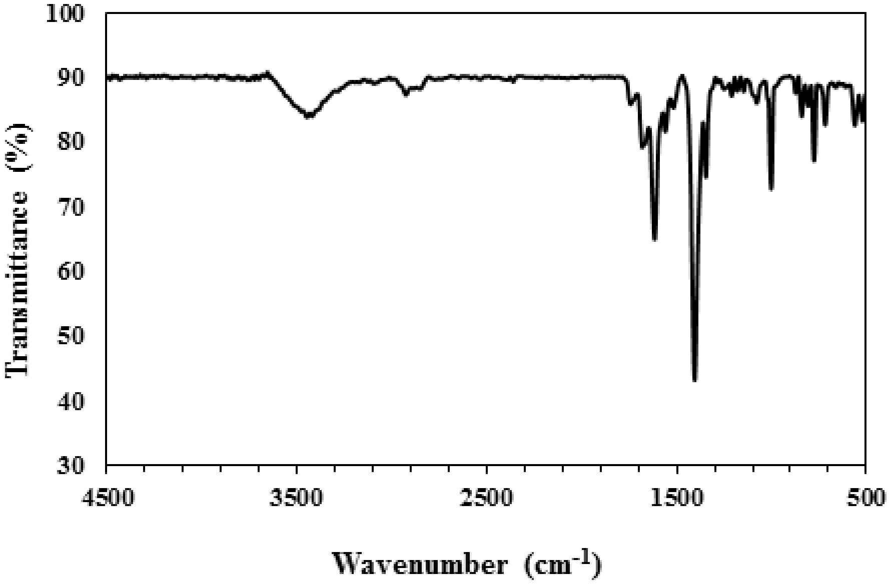


Fig. 3. The FT-IR spectra of Co-Por MOF.

The powder X-ray diffraction (PXRD) pattern of Co-Por MOF is in good agreement with the similar materials pattern (Fig. 4), and the phase purity of bulk Co-Por MOF verified by these studies shows a small contamination. It also indicates that the particles are well crystallized.

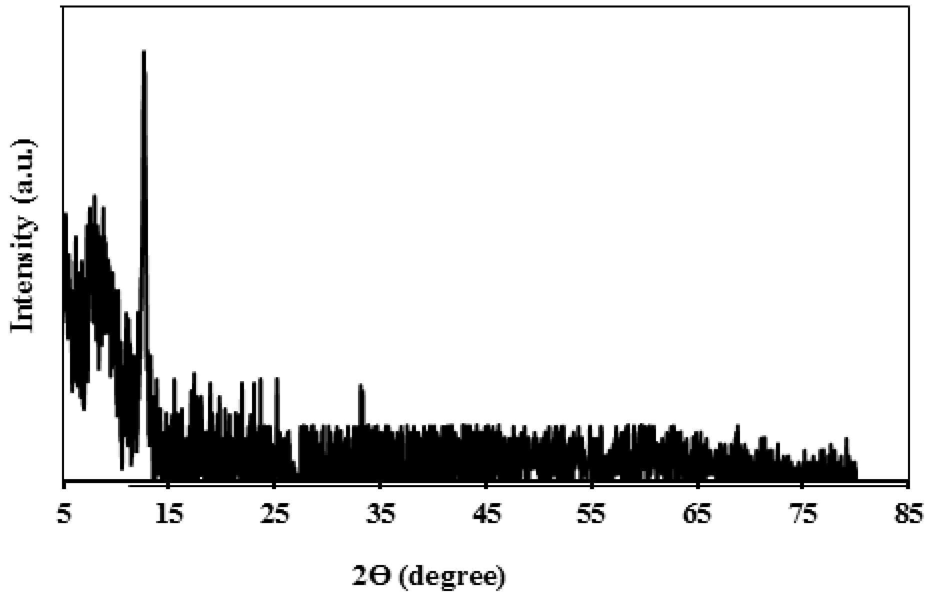


Fig. 4. The XRD pattern of Co-Por MOF.

conclusion

In conclusion, guided by a solvothermal condition, a porphyrin based MOF was constructed with TCPP porphyrin and $Co(NO_3)_2.6H_2O$. Then it characterized by XRD, FT-IR and UV-Vis techniques. This MOF material can be used in catalytic reaction for photocatalytic reduction of CO_2 under visible light irradiation.

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