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Newly synthesized Cu-MOF based on Schiff base linker: structure, properties, method of synthesis and characterization

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Abstract

Metal organic framework (MOF) represents a desirable material in our life because of array of nurturing features such as large surface area and porous structure. Herein, a newly synthesized Cu-MOF based on a novel Schiff base ligand (H_2L), as a linker, was developed under ultrasonic condition. The newly synthesized Schiff base was characterized via various characterization tools including Fourier-transform infrared (FT-IR), mass and ultraviolet-visible (UV-Vis) spectroscopy. The synthesized Cu-MOF structure was confirmed by many spectroscopic tools such as Fourier-transform infrared (FT-IR) and ultraviolet-visible (UV-Vis). The FT-IR and UV-Vis spectra confirmed the binding of the carboxylate group of the synthesized Schiff base in monodentate manner to Cu(II) ion.

Keywords: Metal-organic framework, Schiff base ligand, UV-Vis and FT-IR

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1. Introduction

Metal–organic framework (MOF), also known as porous coordination polymer (PCP), has been intensively studied by many research groups throughout the world since it was introduced in the late 1990s by Yaghi's group [1-8]. MOFs have emerged as an extensive class of crystalline materials with ultrahigh porosity up to 90% free volume and enormous internal surface areas, extending beyond 6 000 m^2/g [9]. MOFs are class of crystalline organic-inorganic hybrid compounds, in which the organic part such as N-containing aromatics or bivalent or trivalent aromatic carboxylic acids are commonly used as a linkers to form frameworks with the inorganic part which act as nodes [10-12]. So , a wide variety of inorganic and organic components could be used, and this elasticity has allowed the rational design and assembly of materials with newly topologies and exceptional properties [13, 14]. The synthetic-methods have been playing a major role in the properties of the synthesized MOFs such as surface area, degree of crystalinity and pore size [9]. MOFs can be synthesized through different methods such as solvothermal, hydrothermal, ultrasonic, mechanochemical and electrochemical methods. MOF as very novel material compared to other porous materials such as silica, zeolites or hyper cross-linked polymer particles [8].

The design, synthesis and the extraordinary degree of variability for both the organic and inorganic components of their structures, make metal-organic frameworks (MOFs) of interest and currently an active research area due to the potential applications in clean energy, most significantly as storage media for gases such as hydrogen and methane, sensors, gas separation, gas storage, heat transfer, catalysis or drug delivery [13, 15-20]. The common strategy for the construction of porous metal-organic networks is based primarily on the appropriate selection of long rigid organic ligands as linkers and inorganic building blocks as nodes [14, 21, 22]. So, for the preparation of MOF linker used in this study, a Schiff base ligand as along rigid organic ligand was prepared.

The perspective of Schiff bases for one of the groups most widely used in chemistry for metal coordination ligands and the chemistry of the Schiff bases was an area of increasing interest, which has gained paramount importance due to its versatility such as straight synthesis, multidentate existence and donor electron properties, resulting in very broad binding constants for f- and d –block metals [23]. Copper MOFs had considerable applications in different field such as removal of toxic sulfonamide antibiotics [24], oil [25], p-nitro-phenol [26], heavy metals [27], dye [28-32].

So due to the important of the Cu-MOF in our life because of the large surface area and pore size which made it used in different applications, therefore, this article deals with the synthesis of a newly metal-organic frameworks, Cu-MOF, via reaction of Cu(II) ion and novel Schiff base under the ultrasonic reaction conditions. Detailed characterization of the newly synthesized Schiff base was carried out by using FT-IR, mass spectrum and UV–visible spectroscopic tools. In addition, the synthesized Cu-MOF was characterized by FTIR and UV–visible spectroscopic tools.

2. Experimental

2.1. Materials and methods

All used chemicals were of analytical grade and distilled water was used throughout all experiments. Phthalaldehydic acid (2-formylbenzoic acid) (purity 97%), diaminodiphenyl ether (purity 98%) and copper(II) acetate dihydrate (purity 98%) were purchased from Sigma-Aldrich. Dimethyl formamide (DMF) and absolute ethyl alcohol organic solvents were spectroscopic pure from BDH [33].

FT-IR spectra were recorded using a Perkin-Elmer 1650 spectrometer (4000–400 cm^{-1}) as KBr pellets. Mass spectra were measured by the EI technique at 70 eV using MS-5988 GS-MS Hewlett-Packard instrument. Microanalyses of carbon, hydrogen and nitrogen were measured by using CHNS-932 (LECO) Vario Elemental Analyzer in the Microanalytical Center, Cairo University, Egypt. UV-Vis spectra were occurred on UVmini-1240, UV-Vis spectrophotometer, Shimadzu.

2.2. Synthesis of Schiff base ligand (H_2L)

Hot ethanolic solution of phthalaldehydic acid (6 g, 39.96 mmol) was mixed under stirring with DMF solution of diamino diphenyl ether (4 g, 19.97 mmol) by a ratio of 2:1. The reaction mixture was stirred under reflux for 5 -7 h. The resulting ligand was filtered and washed with hot ethanol / DMF and the solid ligand was dried over anhydrous calcium chloride in a desiccator. The yield percentage was 85%.

2.3. Synthesis of Cu-MOF

Hot dimethyl formamide solution of the Schiff base ligand (1g, 2.1 mmol) was mixed with hot ethanolic solution of the copper acetate dihydrate (0.287 g, 1.435 mmol) in 1:1.5 copper acetate dihydrate: The two solutions were placed into a container mounted in a water bath and then subjected to sonication for 60-75 min. The product has been isolated by centrifugation and the precipitate has been washed with water, DMF and ethanol and then dried at 130 °C for 12 h and then cooled for 15 min in air at room temperature.

3. Results and discussion

3.1. Characterization of Schiff base (H_2L) ligand

The Schiff base ligand was prepared as described in the experimental part and dried under vacuum and subjected to elemental analyses, mass, IR and Uv-vis spectral study.

The results of elemental analysis (C, H and N) showed carbon percent 72.21% (calcd. = 72.40%), nitrogen 5.98% (calcd. = 6.03%) and hydrogen 4.52% (calcd. = 4.31%). These results were consistent with the calculated values for the suggested formula ($C_{28}H_{20}N_2O_5$). It has a sharp melting point indicating the purity of the prepared Schiff base ligand. The Schiff base ligand was stable and has yellowish brown color.

The mass spectrum of the Schiff base ligand has a parent peak at m/z = 464.1 amu as indicated from elemental analyses corresponding to the ligand moiety $C_{28}H_{20}N_2O_5$ with atomic mass 464 amu. The series of peaks with values 65, 80, 108, 122, 171, 200, 288 and 376 amu, can be assigned to different fragments of the Schiff base ligand.

FT-IR spectrum of the Schiff base ligand showed that absorption peaks at 1759 and 1660 cm^{-1} were due to the (C=O) group of the ring form and the (C=O) group corresponding to the (COO^-) group, respectively [34]. Sharp absorption peaks at 3089 cm^{-1} and 2924 cm^{-1} were due to the NH group and NH^+ group, respectively [34, 35]. Absorption peak at 1620 cm^{-1} corresponding to the azomethine group confirmed the formation of the Schiff base ligand [36-39].

3.2. Characterization of Cu-MOF

The anticipated structure for Cu-MOF includes a Cu atom coordinated by four oxygen atoms from the carboxylate groups of four ligands and two oxygen atoms from the water molecule to form the structure of the Cu-MOF (Figure 1).

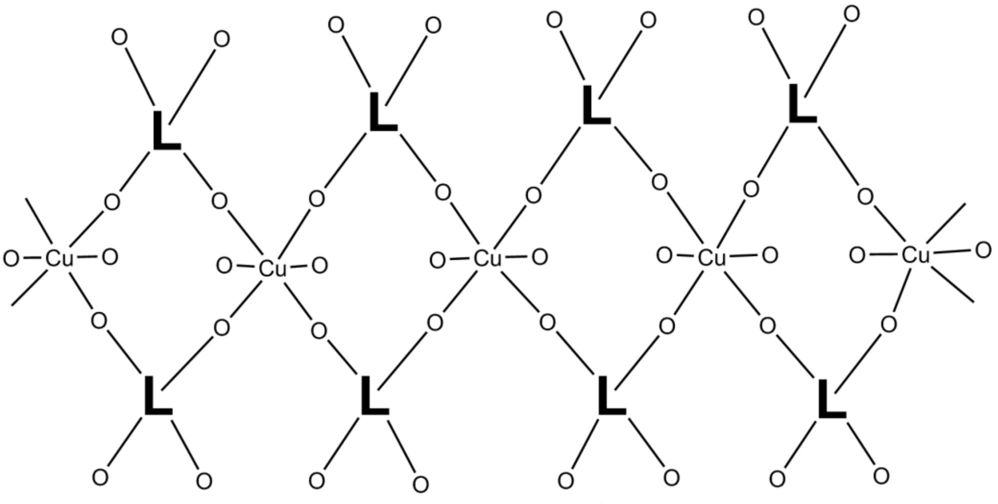

Fig (1): The proposed structure of the Cu-MOF.

FT-IR spectrum of Cu-MOF showed that the absorption peaks of NH^+ group and (C=O) group of carboxylate (COO^-) group at 2924 and 1660 cm^{-1} were disappeared, respectively. Appearance of a sharp absorption peak at 617 cm^{-1} due to the Cu–O bond [40, 41]. The absence of the characteristic bands from 1660–1800 cm^{-1} attributed to the protonated carboxylic groups indicating the monodentate coordination between the Cu(II) ion [15, 42]. The absorption peak at 755 cm^{-1} due to the Cu–O bond for coordinated water was confirmed by another broad band at 3400–3550 cm^{-1} for the OH group of coordinated water [40]. Finally, the disappearance of a sharp absorption peaks at 3089 and 1759 cm^{-1} assigned for NH and the another (C=O) group, respectively, indicated that the Cu(II) ion reacted with the ligand (H_2L) from the two carboxylate groups. So, the FT-IR supported the proposed structure of the Cu-MOF.

UV–visible spectra of H_2L and Cu-MOF were studied. H_2L ligand showed absorption peak at 297 nm which can assigned to the $\pi \rightarrow \pi^*$ transition for the chromophoric groups [43]. Cu-MOF showed two peaks at 307 and 346 nm which can assigned to π → π* and n → π* transitions, respectively. The n → π* transition refers to the carboxylic group where ligand to metal charge transfer (LMCT) transitions occur from oxygen atoms of the carboxylic group to octahedral Cu(II) atoms [43]. The shifting occur in the π → π* transition of the Schiff base from 297 to 307 and appearance of an absorption band at 346 nm for n → π* of the Cu-MOF referred to the binding of the synthesized Schiff base to the Cu(II) ion.

4. Conclusion

Metal organic frameworks have extensive properties such as large surface area and the pore size, which made them to be used in different application such as adsorbent, removal of different heavy metals, dyes, super capacitor and also as a sensor. So, this study discussed the preparation of new Cu-MOF by ultrasonic reaction between the Cu(II) ion and the newly synthesized Schiff base. Characterization of the newly synthesized Cu-MOF using FT-IR and UV-Vis spectroscopic tools confirmed its formation.

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