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Synthesis, Characterization, Optical and Luminescence Properties of Copper Based Metal Organic Frame Works

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Abstract. Herein, we report synthesis of two new copper metal organic frameworks. The organic linkers were terephthalic acid with 6-Dihydroimidazo[2,1-*b*]thiazole-2-carbaldehyde and terephthalic acid with 3-benzothiazol-2-yl-malonaldehyde used in the copper nano metal organic framework (MOF). Both the Cu-MOF's were characterized by XRD, UV-vis spectroscopy and FTIR. XRD crystallographic studies revealed the presence of copper metal at 2θ at 18.4°. Tauc plots were simulated to calculate the band gap of both Cu-MOF's and result indicated the band gap energy of Cu-MOF 1 at 3.31 eV and for Cu-MOF 2 was at 3.57 eV. The UV-Visible absorption studies indicated two bands for Cu-MOF 1 and Cu-MOF 2 at 326 nm. However, the second band in Cu MOF 1 at 509 nm was slightly shifted to higher wavelength at 516 nm in Cu-MOF 2 due to the extension of π-π^* transition. The photoluminescent properties of both Cu-MOF's indicated a strong band at 505 nm. Thus, the optical properties of both the Cu-MOF's infers that these can be a promising semiconductor material for various electronic applications.

Introduction

In recent years, material scientist are widely using the metal oxides as dopants to obtain desired optoelectronic properties. Various metals such as titanium oxide [1-2] doped with gadolinium [3-5], chromium oxide [6-7], strontium [8-10], zirconium doped along with yttrium [11-12], smarium oxide [13-14],chromium [15-16], titanate doped with strontium [17-19], yttrium on zinc oxide [20], titanium doped on nickel [21], titanium magnesium strontium [22], strontinum deposited on cadmium oxide [23], biosyntesised copper oxide [24], Tantalium oxide[25], tereliumoxide [26], yttrium doped on zirconium [27],smarium doped on terellium [28], zinc oxide [29-30] with copper oxide [31], iron oxide [32-34], copper oxide [34-37], were used as dopants. Metal organic frameworks (MOF's) [38] are hybrid crystalline porous materials synthesized by using organic linkers coordinated to metal ions that attain specific porosity [39]. Metals and its oxideshave diversified properties that includes electrical and magnetic properties whereas organic ligands do possess unique chemical and physical features [40]. Thus, when a unique combination of metal and organic linker are synthesized together results in materials with unique chemical, physical, electrical, and magnetic properties that can be used for various applications [41-44] such as field of electronics sensors [45], magnetism [46], adsorption of pollutants [47] medical research [48] and etc. Metal organic frameworks are widely used in various applications [49] due to their unique properties such as unique specific porous nature which are resulted as porous coordination polymers and leading to material that can easily bind or trap the other metals or organic molecules through either absorption or adsorption or through any weak force associated with elements present in the organic linkers. Their unique surface area ranging from 1000 to 10,000 m2/g [50] makes them as a material of choice for adsorption of gases such as

Co_2, ammonia, greenhouse gases etc., storage of gases such as hydrogen [51-52], methanol in various industries, also used in drug delivery system, also due to their antimicrobial property are widely used in surgical bandages etc., [53-56]. Further, fine tunability of electrochemical properties of MOF's by doping with suitable dopants, are widely used in semiconductor applications. Nevertheless, MOFs are also used as hybrid heterogenous catalyst for numerous oxidation [57-58], reduction [59] and coupling reactions [60]. The most common metal ions used in MOFs are Zinc, Copper [61-62], iron [63], Zirconium [64] , titanium [65], Scandium [66], vanadium [67], chromium [68], nickel [69], manganese [70], samarium [71], cobalt [72], while the common organic linkers can be classified into aromatic acids such as terephthalic acid [73], benzoic acid [74], trimeric acid [75], or 2-methylimidazole, benzene-1,3,5-tricarboxylic [76] acid, [1,1'-biphenyl]-4,4'-dicarboxylic acid,[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid [77], 4,4'-(ethyne-1,2-diyl)dibenzoic acid,pyrene-2,7-dicarboxylic acid [78] have been excessively used as organic linkers [79]. MOFs are synthesized [80-81] by Conventional electric (CE) heating, microwave (MW) heating, electrochemistry (EC), mechanochemistry (MC), and ultrasonic (US) methods and good crystallinity, porous size, control over morphology and thermally stable MOF are being obtained using this method. Yaghi et.al [82] discussed slow diffusion of $Zn(NO_3)_2$ reacted with H_2BDC in presence of triethylamine (TEA) for a week time that produced MOF-2, MOF-3, MOF-5. The present study deals with Cu based MOFs synthesized by solvothermal method and further, prepared Ag_2O and rGO (Reduced Graphene Oxide) were dispersed in MOFs-nanocomposite through stirring method and studied band gap variation.
Herein we have reported the two Cu-MOF's starting from 6-Dihydroimidazo[2,1-*b*]thiazole-2-carbaldehyde and terephthalic acid resulting in Cu-MOF 1 and 3-benzothiazol-2-yl-malonaldehyde and terephthalic acid resulting in Cu-MOF 2. Both the Cu-MOF's are characterized by FT-IR, XRD and UV-visible spectrophotometer. The optical and photoluminescence studies were carried out for the synthesized of Cu-MOF's.

Experimental

Materials: All the chemicals and reagents procured from Avra Synthesis Private Ltd, Spectro Chem Ltd., Sigma Aldrich, India and used without any further purifications. 1,1,3,3-tetramethoxy propane 99% (Sigma Aldrich), Imidazolidinethione, 99% (Sigma Aldrich), 2-Mercaptobenzothiazole, 99% (Spectro Chem), Terephthalic acid 98% (Avra Synthesis Private Ltd), $Cu(NO_3)_2.3H_2O$ 98% (Sigma-Aldrich Ltd).
Instrumentation: The morphological analysis for the synthesized MOFs were caried out by using powder X ray diffractometer (Bruker, Germany) fitted with D8-fine focus ceramic X-ray tube, Cu-Kα source radiation (λ =1.5406 Å) at room temperature. The presence of various organic functional group in the MOFs were studied using Fourier transformed infrared spectrometer (Bruker-Alpha, Germany). The optical properties of MOFs were studied by recording the maximum absorption using UV-Visible absorption Spectrometer (Spector 210 plus).
Preparation of 2-bromomalonaldehyde: Starting material 2-bromomalonaldehyde was prepared using the procedure given in literature. To a 100 ml of aqueous solution of 1, 1, 3, 3-tetramethoxypropane (100g, 0.12M), concentrated HCl (4.3mL) was added and stirred until it forms homogeneous solution, wherein temperature of the reaction mixture was maintained below 35 °C and later bromine (0.15M) solution was added drop wise slowly and stirring was continued for another 30 minutes. Then, reaction mixture was concentrated under vacuum maintaining temperature below 50 °C until thick slurry was obtained, and further washed using 200 mL cold water, 100 ml of cold dichloromethane and dried in vacuum. Yield: 65%, MP: 148 °C (Lit: 148 °C).
Preparation of 5,6-Dihydroimidazo[2,1-*b*]thiazole-2-carbaldehyde: To a stirred solution of imidazolidinethione (0.250g, 0.0024 mol) in ethanol was added an ethanol solution of 2-bromomalonaldehyde (0.370g, 0.0024 mol) dropwise over a period of 15 minutes and stirring continued for an hour at room temperature and then at 80ºC for two hours. The yellow color solid obtained was filtered and washed several times with acetone, then dried under vacuum. Reaction completion was monitored on TLC. Yield: 85% (0.320g).

Preparation of 3-benzothiazol-2-yl-malonaldehyde: To a stirred solution of 2-mercaptobenzothiazole (0.250 g, 0.0014 mol) in acetonitrile, 2-bromomalonaldehyde (0.225g, 0.0014 mol) was added drop wise for a period of 15 minutes. Kept for vigorous stirring at room temperature for an hour at room temperature and at 80 ° C for two hours in vacuum for the removal of solvent. Acetone was added and the pale colored solid was filtered, washed by acetone and further the compound obtained was dried in vacuum. Yield: 80% (0.283g). The synthesis of Cu-MOF's are as shown in Fig.1.

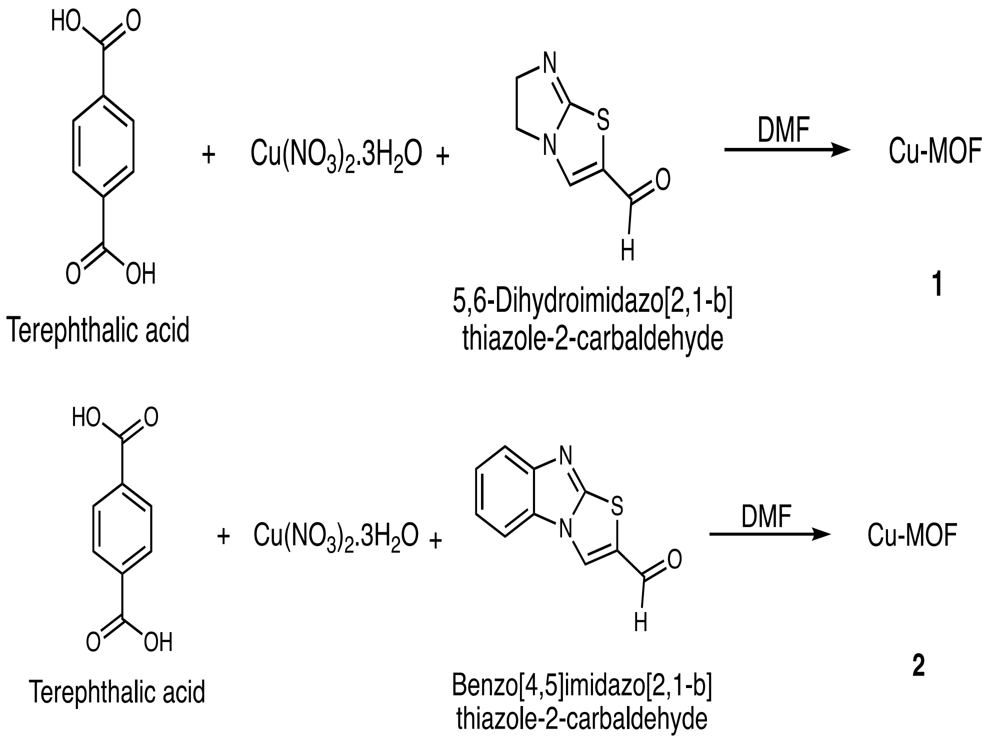

Figure 1. Preparation of Cu-MOF's: compound 1 and 2.

Result and Discussion

UV-Visible Spectral studies:

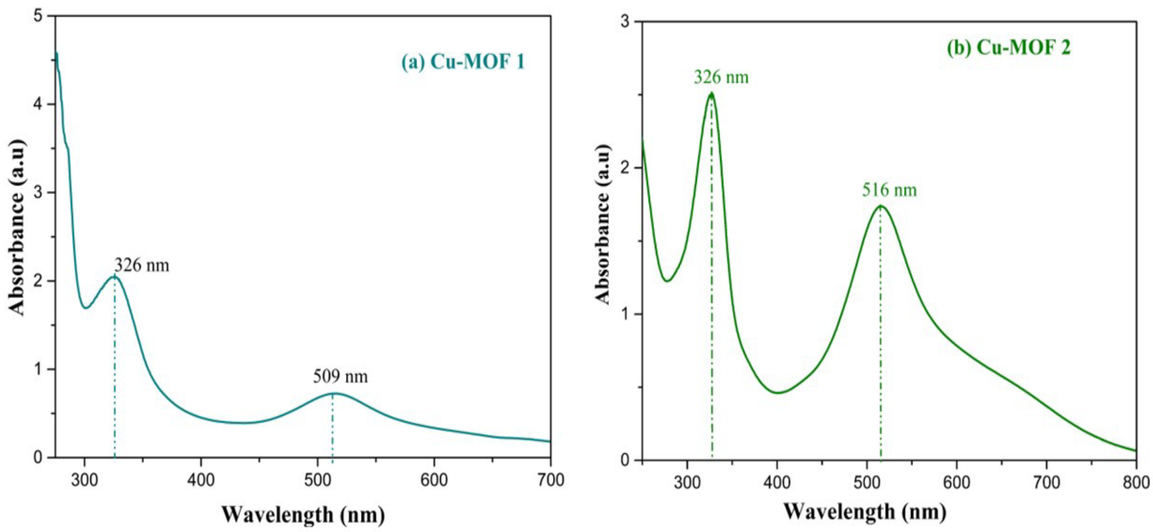

Fig. 2. UV-visible spectrum of Cu-MOF 1 and Cu-MOF 2.

Figure 2 indicates the UV-visible spectra of the synthesized Cu-MOF's. The Cu-MOF 1 showed two absorption bands at 326 nm and 509 nm whereas Cu-MOF 2 showed absorption bands at 326 nm and 516 nm. Both the absorption bands recorded may corresponds to the n-π* and π-π* excitation attributing the interaction between the oxygen of the organic framework [83] and apparently due to the optical transition of organic ligands to that of copper metal charge transfer. Increase in wavelength in Cu-MOF 2, attributed to the π-π* of phenyl ring thus decreasing the energy required between the two transition states [84].

FT-IR Spectral Analysis:

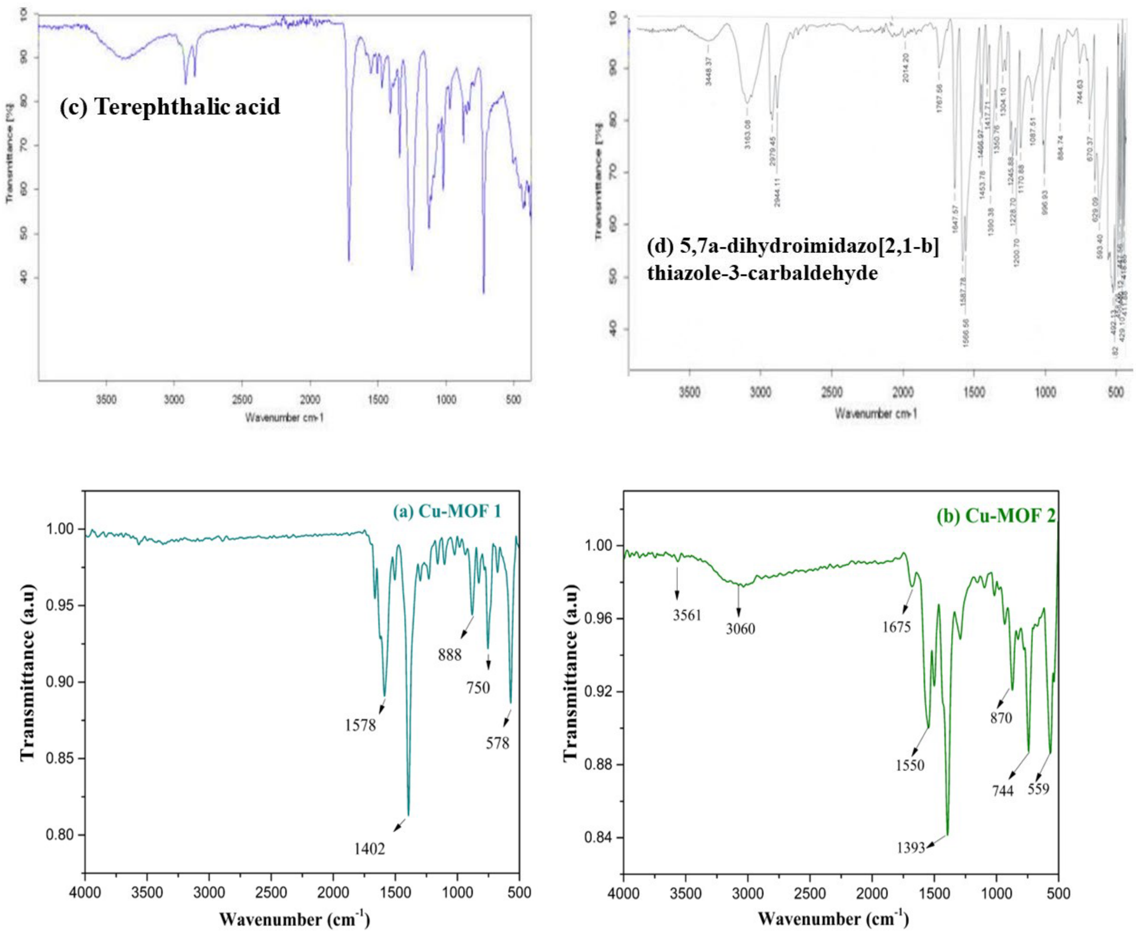

Figure 3: FT-IR spectrum of Cu-MOF 1, Cu-MOF 2, terephthalic acid and 5-7 dihyroimidazo [2,1-b]thiazole-3-carbaldehyde

Figure 3 shown the terephthalic acid, 5-7 dihyroimidazo [2,1-b]thiazole-3-carbaldehyde , Cu-MOF 1 and Cu MOF 2. The presence of O- H str band were observed in both terephthalic acid and 5-7 dihyroimidazo [2,1-b]thiazole-3-carbaldehyde [85]. A sharp carbonyl stretching was observed at 1767 cm^{-1} and Ald C-H stretching band at 2944 cm-1 for 5-7 dihyroimidazo [2,1-b]thiazole-3-carbaldehyde. However, in Cu-MOF 1 and Cu-MOF 2, all these characteristic bands i,e the O-H str band, carbonyl stretching band and Ald C-H stretching band disappeared upon formation of coordination bond with copper. In Cu-MOF 1 and Cu-MOF 2, the alkene C=C str was observed at 1564 cm^{-1}, C-H bending at 1412 cm^{-1}. In Cu-MOF 2, the presence of Ar C-H stretching was observed at 3060 cm^{-1}.

XRD diffraction studies

The phase purity and crystallinity of synthesized Cu-MOFs were identified with the XRD diffraction studies as shown in Fig 4. The A sharp arrow headed tripods with amorphous type of nature of peaks were observed due to the presence of pure copper with a cubic face centered structure. In both the

Cu-MOFs the peaks values i,e 2θ at 17.8°, 26.8°, 28.5° attributed to planes at (020), (040) (035) respectively for copper crystal planes which agrees with the JCPDS No.89-4897 [85]. Many such sharp peaks were observed between 2θ at 10° to 40°. Most of the peaks match with the literature reported as JCPDS card no. 89-2838 and 04-0836 for copper [86]. The crystallite size of Cu-MOFs were calculated using Scherrer equation.

$$D = \frac{k\lambda}{\beta \mathrm{Cos}\theta} \tag{1}$$

where K is crystallite shape constant (0.94), β is full width at half maximum, λ is wavelength of X-ray Cu-Kα radiation (1.5406 Å) and θ is glancing angle. The crystalline particle sizes were observed between 200-250 nm.

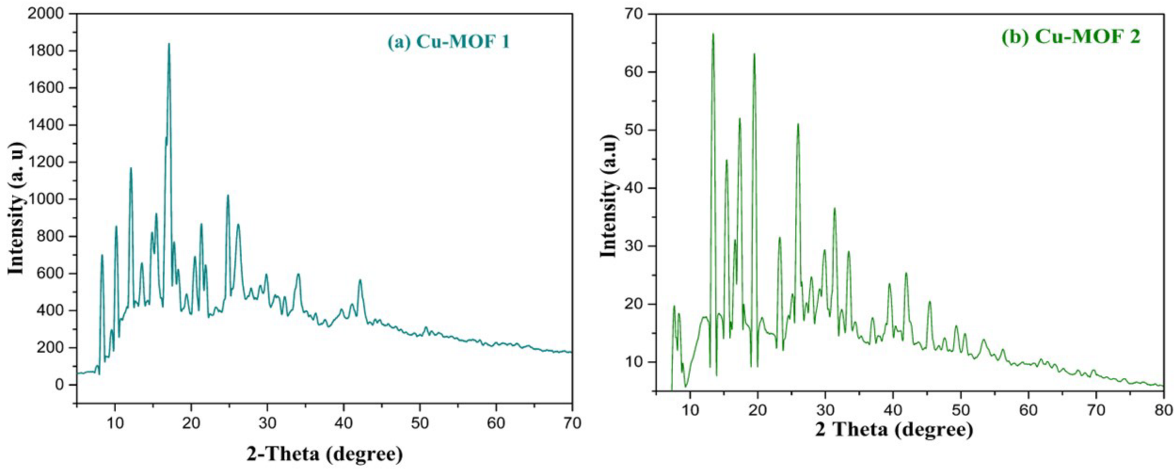

Figure 4. XRD patterns of Cu-MOF 1 and Cu-MOF 2.

Photoluminescence features of Cu-MOFs

Figure 5 infers the photoluminescence properties of Cu-MOFs. A sharp intense peak was observed at 504-505 nm was observed for both Cu-MOF 1 and Cu-MOF 2 contributing to the excitation of copper metals ions along with the ligands. A small shoulder peak was observed at 756 nm for both Cu-MOF 1 and Cu-MOF 2 respectively. The obtained photoluminescent properties are in accordance with the literature [87].

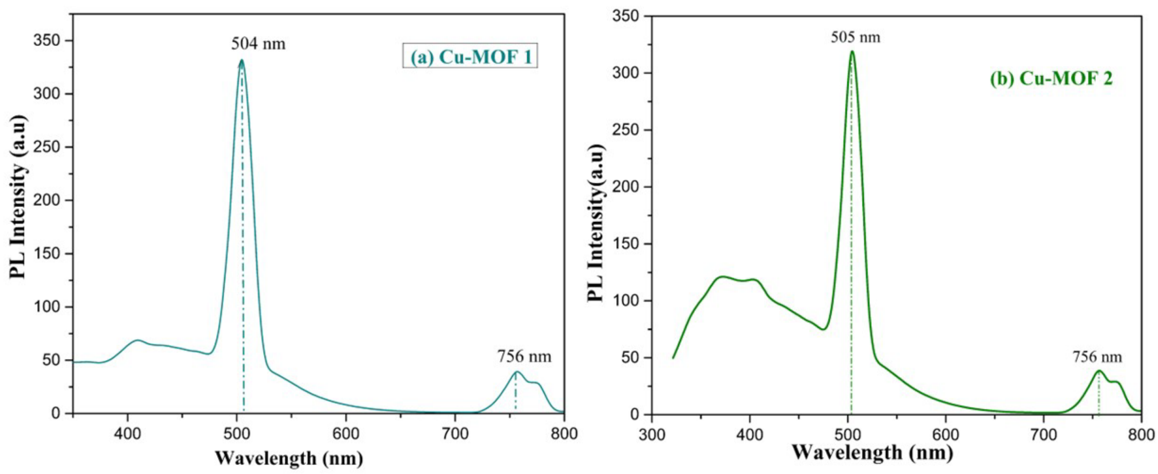

Figure 5: Photoluminescence spectrum of Cu-MOF1 and Cu-MOF2.

Optical properties

Band gap analysis: The UV-visible absorption spectra was carried out using 210 plus UV-Visible absorption Spectrometer. Tauc plots were obtained from simplifying equation 2 [88]. Graphically the bandgap energy was obtained by extrapolating the tangential line intersecting x axis at hγ = Eg as shown in Figure 6. The band gap energy for Cu-MOF 1 was recorded at 3.31 eV and that of Cu-MOF 2 at 3.57 eV. Structurally presence of phenyl ring didn't have impact on the band gap energy.

$$(\alpha h\nu) = A(h\gamma - E_g)^{1/2} \tag{2}$$

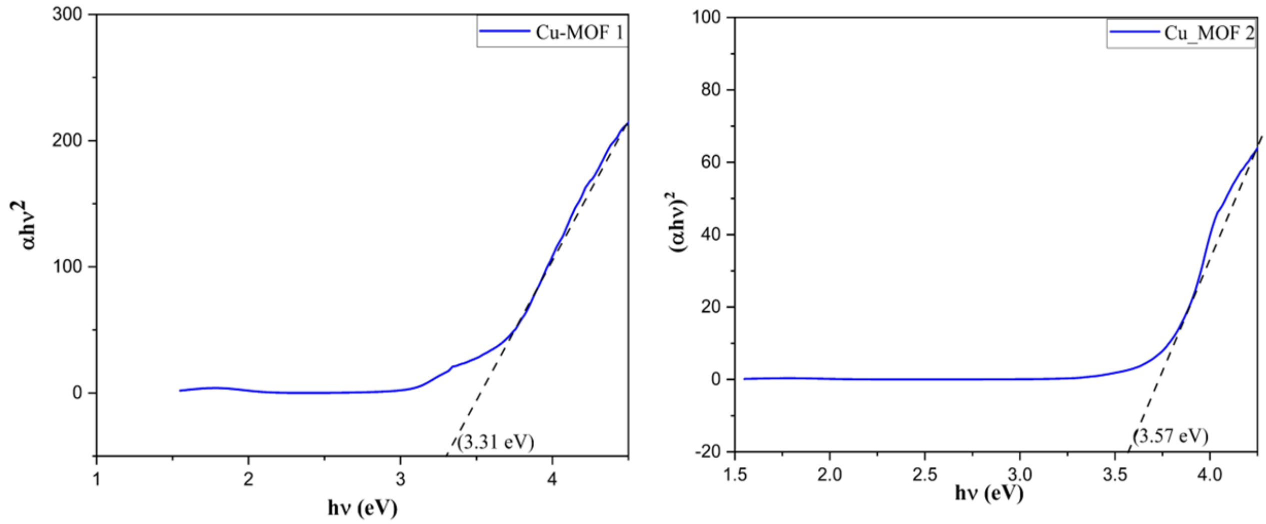

Figure 6. The energy band gaps of a) Cu-MOF 1 and Cu-MOF 2

Conclusion

This work reports the synthesis of copper based nano metal organic frame works starting from starting from terephthalic acid with 6-Dihydroimidazo[2,1-*b*]thiazole-2-carbaldehyde and 3-benzothiazol-2-yl-malonaldehyde. The synthesized Cu-MOF's were confirmed by a presence of sharp absorption band at 326 nm and broad shoulder band at 509 nm for Cu-MOF 1. A similar band was observed at 326 nm and 516 nm for Cu-MOF 2. An increase in 16 nm for the second band in Cu-MOF 2 was due to enhanced in π-π* transition. Further, the absence of Ald C-H stretching band and carbonyl stretching band in FT-IR spectroscopy of both Cu-MOF's resulted must be a co-ordination bond formed between the copper metal and the oxygen of aldehyde group. The XRD pattern of Cu-MOF's showed a sharp peak 2θ at 18. 4° for copper crystals with a cubic faced centered structure. The photoluminescent spectrum revealed a sharp band at 505 nm for both Cu-MOF's. Band gap energy of Cu-MOF's were calculated by using Tauc plots. The band gap energy for Cu-MOF 1 was calculated to be at 3.14 eV whereas for Cu-MOF 2 the band gap energy was 3.57 eV. This study results that the both Cu-MOF's are promising material for semiconductors, provided further optimization of band gap energy can be carried out to achieve a band gap energy of 1 to 0.5 eV for semiconductor applications. Further, to reduce the band gap, the synthesized Cu-MOF will be doped with metal oxides and screened for their sensory and photoluminescent applications.

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