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Development of hetero metal organic frameworks of transition metal ions

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Abstract

Heterometallic metal organic frameworks (MOFs) of transition metal ions have been hydrothermally synthesized with 1,4–benzenedicarboxylic acid as the organic linker in ethanol medium. The synthesized MOFs are found to be nanocrystalline and photoluminescent.

Keywords: MOF, hydrothermal synthesis, 1,4–benzenedicarboxylic acid, nano crystalline

1. INTRODUCTION

The discovery of MOFs in eighties created a revolution in chemistry. MOFs are hybrid crystalline materials with distinct structural properties and tuneable pore size, formed by the connectivity of metal ions and organic linkers [1]. MOFs find applications in gas storage, separation, photocatalysis, optoelectronics, sensors, bioimaging etc. Bimetallic MOFs find applications in gas storage and separation [2–4]. But the research in this area is still in its infancy. Hence we have synthesized bimetallic MOFs of transition metal ions such as zinc(II), copper(II) and manganese(II) and were characterised using FT–IR, SEM–EDS, PXRD and photoluminescent spectroscopy with a view to explore their applications in various fields.

2. EXPERIMENTAL

The heterometallic MOFs have been synthesized under solvothermal conditions by the reaction of 1,4–benzenedicarboxylic acid with corresponding metal salts. Heterobimetallic MOFs have been synthesised using various combination of transition metal ions such as Zn(II), Cu(II) and Mn(II) with 1,4–BDC in ethanol solvent. The reaction was carried out in an autoclave at 150^{o}C for 3 days under autogeneous pressure and cooled afterwards to get crystals. The crystals were filtered off, washed thoroughly with ethanol and dried at room temperature.

3. RESULTS AND DISCUSSIONS

3.1. IR spectral studies

In the IR spectrum of the ligand, there is a strong band at 1673cm^{-1}, due to COOH stretching of benzene ring. The presence of absorption around 3200–2800cm^{-1} is due to OH stretching of COOH bond. The band at 3200–2800cm^{-1}corresponding to OH is absent in various MOFs. The absorption band at 1673cm^{-1} in the ligand is shifted from 1673cm^{-1} to values between 1668cm^{1} to 1524cm^{-1} in all MOFs which indicates that the metal is bonded to carboxylic group.

3.2. Powder XRD Analysis

The PXRD data show the crystalline nature of MOFs. The particle sizes are calculated using Debye–Scherrer equation, D= Kλ/βcosθ. The calculated grain sizes in all the cases show that the frameworks are nanosized. The nature of the peaks indicates the crystalline nature of MOFs. In the PXRD patterns of heterobimetallic Zn/Cu –BDC MOF (Fig.1) and Cu/Mn–BDC MOF (Fig.2) the high intensity Bragg diffraction peaks are observed at 2θ = 14.77, 17.69, 24.17, 27.74, and 33.24° and at 2θ=18.35, 26.11, 28.06 and 36.48° respectively. The average grain sizes of these MOFs are calculated as 4.01 nm and 4.08nm respectively, from Debye – Scherrer formula and are found to be nano sized. The peaks indicate the crystalline nature of MOFs

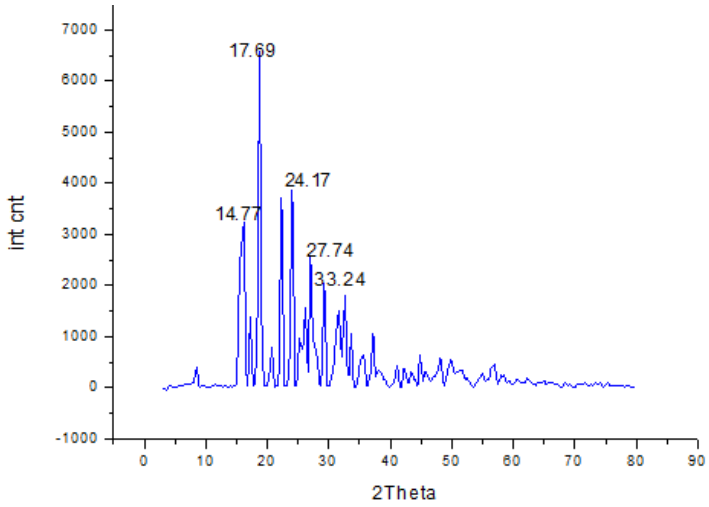

Fig.1: Powder XRD of heterobimetallic Zn/Cu-BDC MOF

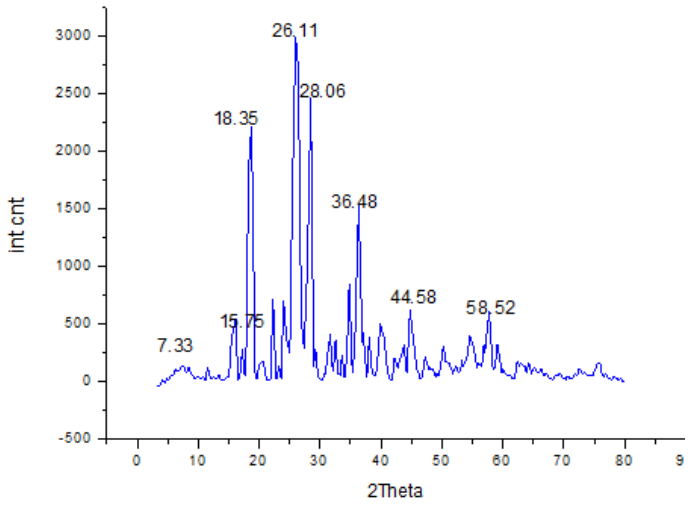

Fig. 2: Powder XRD of heterobimetallic Cu/Mn–BDC MOF

3.3. SEM–EDS Analysis

The morphology of MOF crystals were studied by SEM analysis. The SEM image of heterobimetallic Zn/Cu–BDC MOF (Fig.3) shows an agglomeration of particles. The SEM image of heterobimetallic Cu/Mn–BDC MOF (Fig.4) shows that the particles are crystalline in nature and has a structure similar to a cauliflower.

The elemental analyses of the newly synthesized MOFs of Zn/Cu & Cu/Mn with 1,4–Benzenedicarboxylic acid were carried out using EDS (Fig.5 & Fig.6). The results show that all the compounds contain the expected elements in their energy dispersive spectra. The EDS spectra confirm the successful synthesis of all these MOFs.

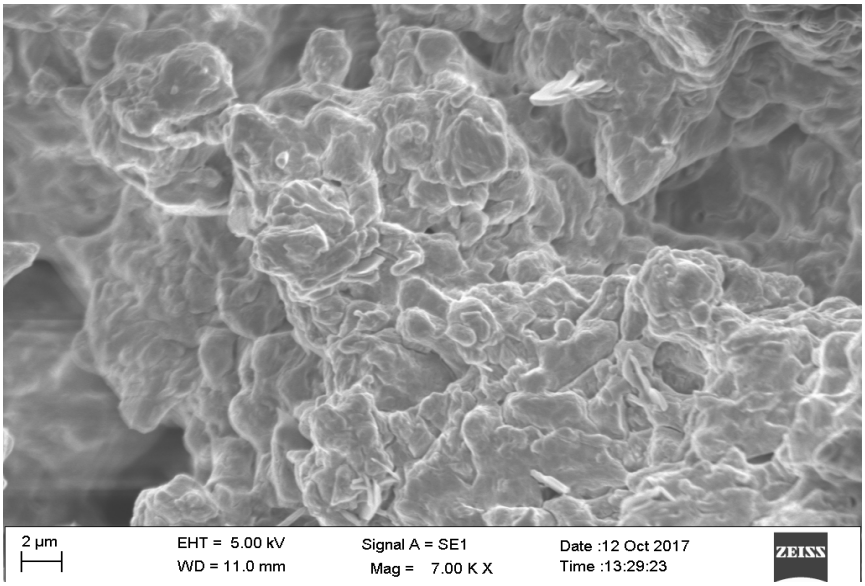

Fig. 3: SEM image of heterobimetallic Zn/Cu –BDC MOF

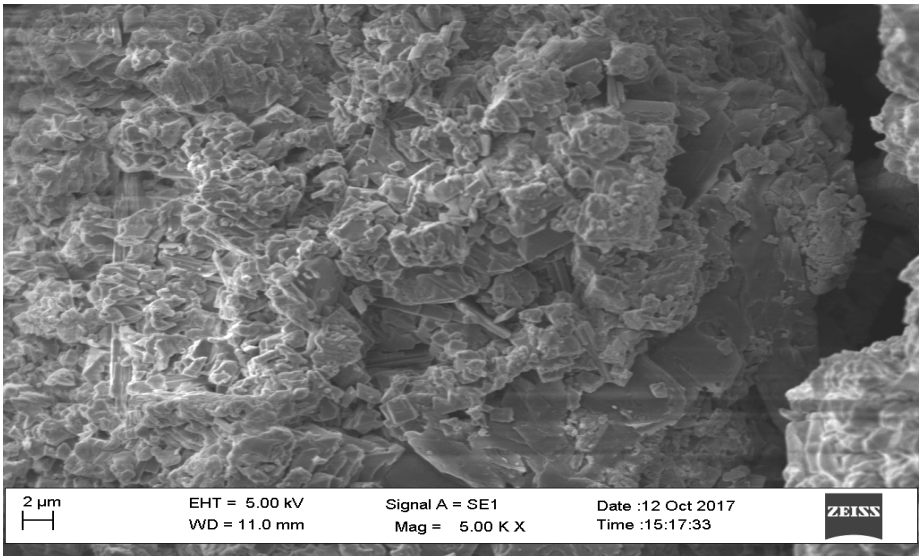

Fig. 4: SEM image of heterobimetallic Cu/Mn –BDC MOF

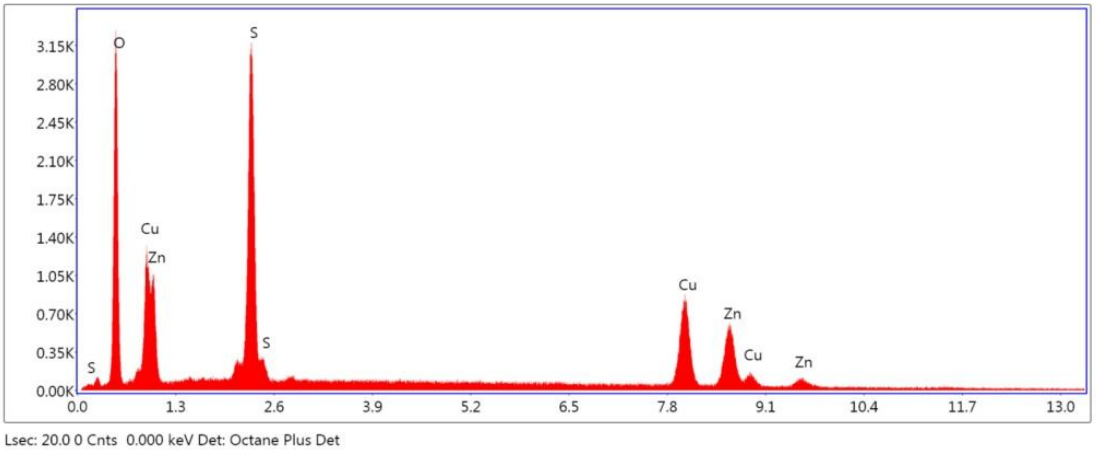

Fig. 5: EDS of heterobimetallic Zn/Cu –BDC MOF

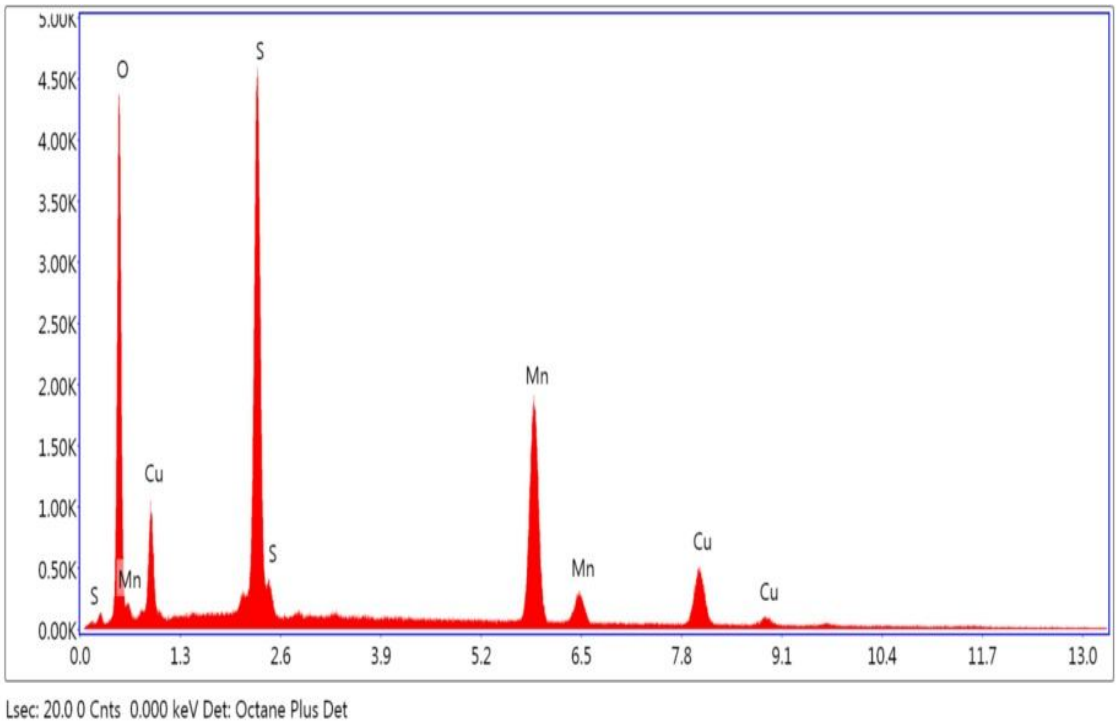

Fig. 6: EDS of heterobimetallic Cu/Mn –BDC MOF

3.4. Photoluminescent studies

The solution state photoluminescence properties of the ligand and the synthesized MOFs have been investigated in methanol at room temperature from 400 –750nm. The ligand shows emission maxima at 331 when excited at 300nm, corresponding to π–π* and n–π* transitions and also due to conjugation in the ligand.

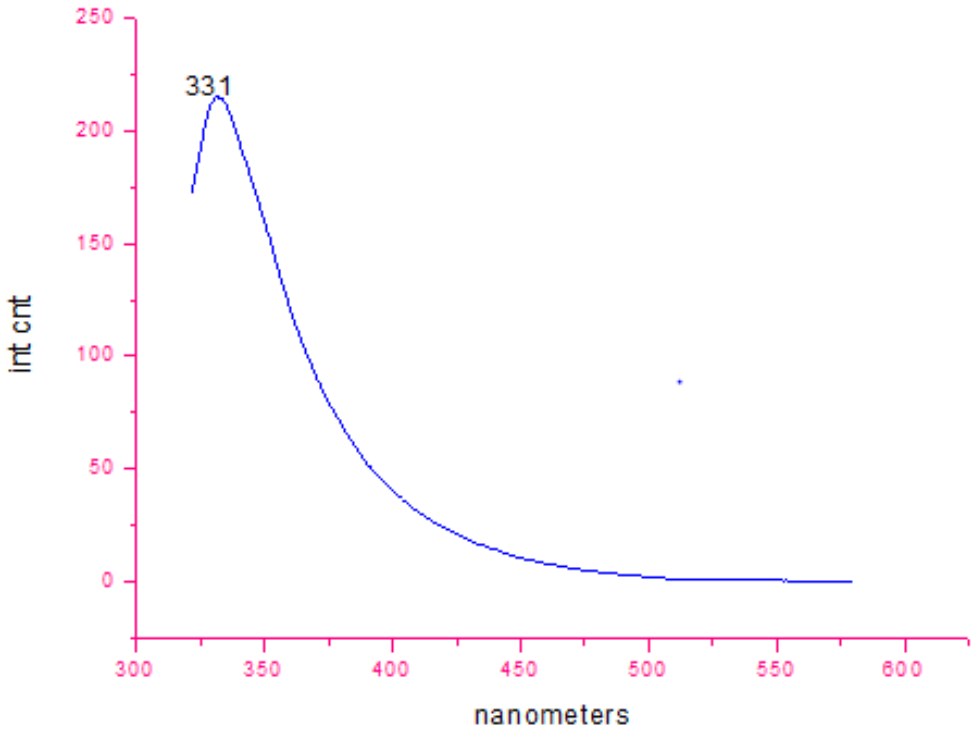

Fig. 7: PL of BDC excited at 300 nm

The emission maxima are observed at 404 nm, 426 nm for Zn/Cu MOF, when excited at 360nm. The emission maxima are observed at 476nm, 503nm and 540nm for Cu/Mn MOF, when excited at 360 nm.

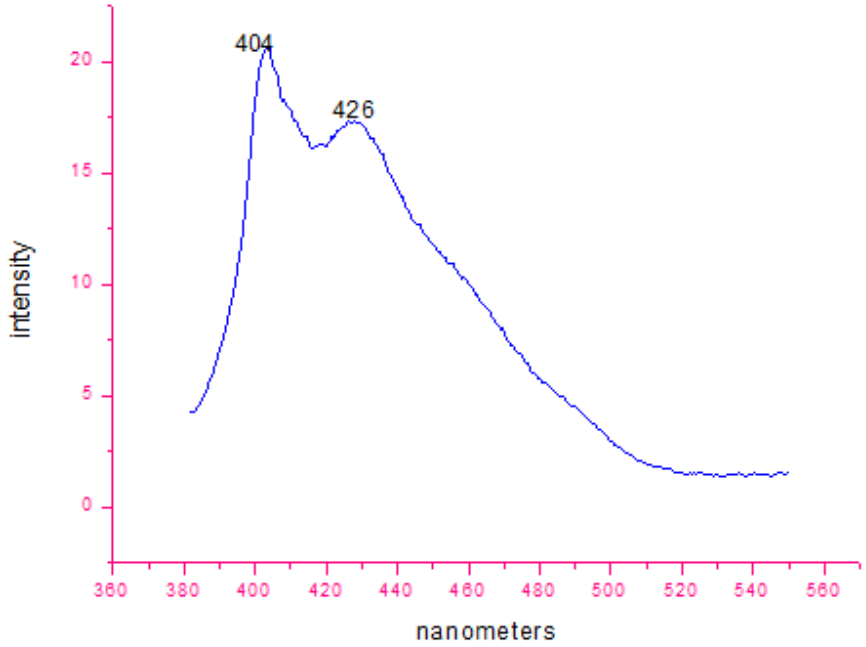

Fig. 8: PL of heterobimetallic Zn/Cu-BDC MOF (Excitation wavelength 360nm)

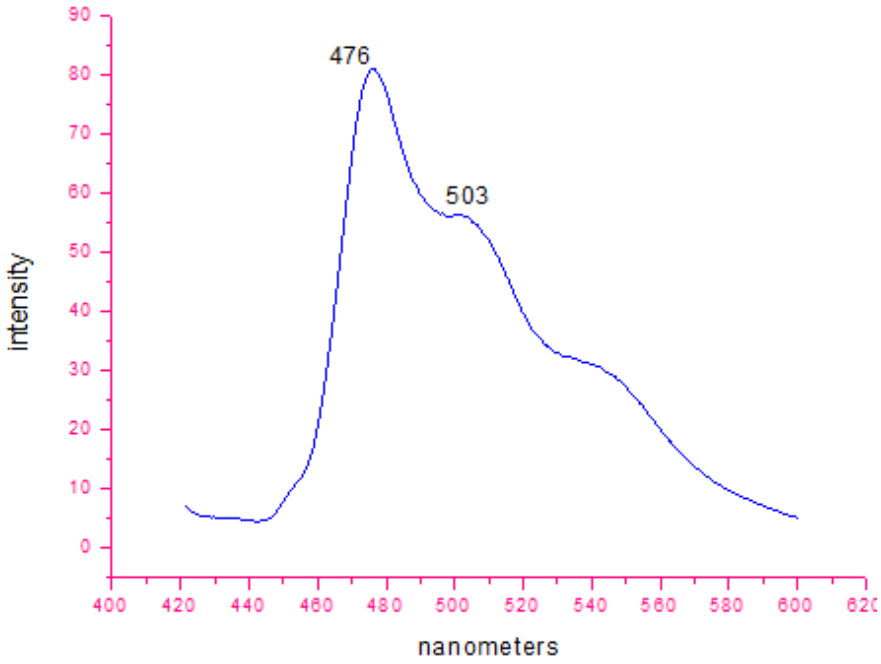

Fig. 9: PL of heterobimetallic Cu/Mn–BDC MOF (Excitation wavelength 360nm)

The PL spectra indicate that the synthesized MOFs are luminescent in nature due to ligand centred emissions. The emission spectra of transition metal complexes are due to ligand centred emissions and charge transfer spectra. The metal ion does not seem to have an effect on the shape of the emission spectra. Detailed investigations on the luminescence lifetimes and quantum yields may provide the missing insights on the luminescence properties of these compounds.

4. CONCLUSIONS

Photoluminescent and nanocrystalline heterobimetallic MOFs; Zn/Cu BDC MOF and Cu/Mn BDC MOF have been hydrothermally synthesized and characterized using FT–IR, PXRD, SEM–EDS and photoluminescent spectroscopy. The applicability of these MOFs as multifunctional materials may be explored in future research.

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