ZnO@MOF-5 as a Fluorescence “Turn-Off” Sensor for Ultrasensitive Detection as well as Probing of Copper(II) Ions

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ABSTRACT: Recently, the synthesis, characterization, and structural evaluation of metal−organic framework (MOF) nanocomposites gain more attention due to the versatility in their applications. In the present work, the fluorescent active ZnO@MOF-5 composite was synthesized by encapsulating ZnO nanoparticles into the zinc terephthalate metal−organic framework (MOF-5). ZnO nanoparticles were prepared by a green method using the leaf extract of Annona muricata. Incorporation of ZnO nanoparticles onto the framework structure (ZnO@MOF-5) was done by a solvothermal method. The new composite material was characterized by Fourier transform infrared spectroscopy, Powder X-ray diffraction, Ultraviolet–visible spectroscopy, Transmission Electron Microscopy, X-ray photoelectron spectroscopy, Brunauer–Emmett–Teller analysis, Dynamic light scattering, Thermogravimetry-Differential Thermal analysis, and Photoluminescence spectroscopy. The material displayed blue fluorescence with a peak at 402 nm upon excitation at 282.46 nm. ZnO@MOF-5 showed a good fluorescence sensing efficiency toward the detection as well as probing of Cu(II) ions in aqueous solution. Sensing experiments performed revealed that as the concentration of copper ions in the solution increases, the quenching efficiency of the composite also increases. A quenching efficiency of 96.20% was achieved on reaching a concentration of 5 μM. The limit of detection for the sensing of Cu²⁺ ions was calculated to be 0.185 μM.

INTRODUCTION

Metal−organic frameworks are the gateway to the era of molecular engineering and find impeccable significance in different fields like catalysis,1−3 gas storage,4 drug delivery systems,5 gas sensing,6 energy storage,7 etc. The tunable porosity and hybrid structure formed by the linkage of organic linkers and inorganic metal nodes make it more feasible for a versatile range of applications. MOFs are promising three-dimensional coordination polymers formed by the linkage of inorganic metal ions joined with organic multitopic ligands. The presence of both acidic as well as basic groups8 in the framework structures makes it a versatile architecture. Through postsynthetic methodologies, the porosity of MOFs can be tuned,9 and this makes these coordination polymers a better option than others. The better sensing capacity towards the inorganic metal moieties can be enhanced by tuning the porosity of the frameworks.9 By preserving structural integrity as well as robustness of metal−organic frameworks, the physicochemical properties can be enhanced by the incorporation of nanoparticles,10 polymers,11 perovskites,11 etc. The nanocomposites find a unique way to tune the porosity to our desired extent for applications such as drug delivery as well as adsorption or encapsulation of microlvel contaminants. Quantification of trace analytes is nevertheless a tedious process due to the lack of sensitivity of probes to a smaller

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extent. Preparation of MOF nanocomposites for environmental remediation purposes is an ongoing research area that needs much attention nowadays. The presence of inbuilt luminescent active sites like organic linkers as well as inorganic metal units makes the MOFs a better luminescent active material among others. The pores with an identical volume further extend the luminescence life by incorporating guest moieties within them. Integration of different moieties like nanoquantum dots, dyes, lanthanides, perovskites, etc. to the metal–organic framework structure will build photoactive sensors for probing chemicals at the nanolevel. Photoactive metallic MOF clusters will act as a better platform for the target-oriented sensing analysis of antibiotics, gases, inorganic metals, pesticides, and chemical explosives. MOFs have inherent luminescence centers, and their luminescence mechanisms include the photoinduced electron transfer (PET) process, ligand-to-metal charge transfer (LMCT), and metal-to-ligand charge transfer (MLCT).

The sensing as well as detection of various inorganic metal ions such as Fe³⁺ ions and Hg²⁺ ions is an emerging area of research. Moreover, sensing of biological molecules such as hemoglobin and lysozymes has dragged more attention since ancient times. The inorganic metal Cu²⁺ ion is one of the abundant species in the human body. The intake of 0.8–0.9 mg of copper per day is needed for the essential growth and development of human beings. However, a higher intake of copper may lead to kidney failure, liver damage, or even death of the person. The same situation gives enormous significance to the development of materials and methods for sensing copper ions. Nowadays, a lot of studies are ongoing for the synthesis of ultrasensitive fluorescence probes for the sensing as well as detection of inorganic metal ions such as copper ions. However, the development of semiconducting nanoparticles and MOF hybrid-based fluorescent ion sensors is an unexplored area of research. Traditional methods adopted for the screening as well as detection of metal ions are Inductively Coupled Plasma Mass Spectroscopy (ICPMS) and Atomic or molecular Absorption Spectroscopy (AAS). These methods are laboratory-based methods and are really helpful for subnanomolar-level analysis. While for analysis of a large number of water samples and real-time monitoring, the development of cheap and cost-effective systems and methods is needed. Thus, importance arises for the synthesis of fluorescent active materials such as MOF–nano hybrid materials that can selectively detect the presence of various inorganic metal ions present in smaller quantities through fluorescence spectroscopy.

Here, we present the synthesis and characterization of a metal–organic framework nanocomposite called ZnO@MOF-5 through a new synthetic strategy using a solvothermal method, and the study further investigates its effect as a better luminescent sensor for sensing of inorganic pollutants such as copper ions in drinking water. PL measurements show that these ZnO-based luminescent MOFs show a unique mechanism for the entrapment of copper ions from water even at a micromolar concentration.

**EXPERIMENTAL SECTION**

**Materials.** All the chemicals used for the synthesis were of AR grade. Zinc nitrate hexahydrate (Emplura, Merck Life Science Pvt. Ltd.), terephthalic acid (TCI Chemicals Pvt. Ltd., India), N,N-dimethyl formamide (Sisco Research Laboratories Pvt. Ltd., Mumbai, India), sodium hydroxide (Central Drug House Pvt. Ltd., New Delhi) were used for the synthesis.

**Instruments.** Fourier transform measurements were taken by using a Fourier transform infrared spectrophotometer (Thermo Scientific, Nicolet iS50 at CLIF, Kariavattom). Powder X-ray diffraction measurements were taken using an X-ray diffractometer (DST-SAIF Cochin). TEM images were recorded by using a JEOL/JEM 2100 (DST-SAIF Cochin). For understanding the effect of temperature dependence of the synthesized compounds, thermal analysis was carried out by using a thermogravimetric instrument called a simultaneous thermal analyzer (TGA/DTA/DSC) (PerkinElmer, STA8000, CLIF, Kariavattom). UV–visible absorption measurements were taken by a UV–VIS–NIR spectrophotometer (Agilent Technologies, Cary 5000, CLIF, Kariavattom). Photoluminescence spectra were taken by a Fluorolog TCSPC from Horiba Scientific (Dept. of Chemistry, Govt. College for Women, Trivandrum). X-ray photoelectron spectroscopy (XPS) was carried out by an X-ray photoelectron spectrometer (Thermo Scientific, ESCALAB Xi+, CLIF, Kariavattom). Surface area and porosity measurements were done by a BET surface area analyzer (Quantachrome Instruments, Nova Touch k4 Model, CLIF, Kariavattom). Particle size distribution and zeta potential measurements were done using a Horiba nanoparticle analyzer SZ-100 (Department of Chemistry, University of Kerala, Kariavattom).

**Methods. Synthesis of Zinc Oxide Nanoparticles.** Zinc oxide nanoparticles were synthesized by a green method with slight modifications. Zn(NO₃)₂·6H₂O (10 mL, 5 M) was homogeneously mixed with 40 mL of leaf extract of Annona muricata for 30 min. The precipitation of zinc hydroxide was done by the gentle addition of 5 M NaOH solution until the pH was 12. The resulting crude precipitate was filtered and washed with distilled water. After calcination at 550 °C for 3 h, the resulting powder of ZnO was collected.

**Preparation of MOF-5.** Equimolar concentrations (1.5 M) of zinc nitrate hexahydrate and terephthalic acid were dissolved separately in 20 mL of dimethyl formamide and mixed well. The transparent solutions thus obtained were taken in an autoclave and heated at 140 °C for 24 h. The precipitate thus obtained was washed with DMF two to five times, filtered, and dried.

**Preparation of ZnO@MOF-5.** Synthesized pure ZnO nanoparticles and MOF-5 were mixed in a 1:4 ratio and were dispersed in 40 mL of a dimethyl formamide solvent. The reaction mixture was stirred continuously for 30 min. The whole reaction mixture was taken inside an autoclave, sealed, and heated at 150 °C for 3 h. The remaining mixtures were collected, filtered, and washed with DMF. The resultant was dried under room temperature.

**Fluorimetric Estimation of Cu²⁺ Ions from CuCl₂·2H₂O.** A solution of ZnO@MOF-5 was prepared by dispersing 0.01 mg of the composite in 10 mL of water. Different micromolar concentrations of cupric chloride solutions were prepared separately in distilled water. A mixture of both solutions was vortexed for 20 min and kept undisturbed. The supernatant solution was decanted, and 3 mL of the same was taken in a cuvette of a fluorimeter. Upon excitation at a wavelength of 282.46 nm, the fluorescence spectrum was recorded. The same procedure was repeated for solutions of concentrations ranging from 0.1 to 5 μM, and FL spectra were recorded. The scheme for the fluorescence quenching of the prepared analyte by copper(II) ions is presented in Scheme 1.
RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy. FTIR spectra of pure MOF-5 as well as the composite ZnO@MOF-5 were characterized within the wavenumber range of 400–4000 cm\(^{-1}\) as shown in Figure 1. The sharp absorption band at 1573 cm\(^{-1}\) corresponds to the characteristic region of symmetric vibrations of the terephthalic group, which is less than that of the free carboxylic group present on the terephthalic acid group, which indicates the coordination with metal nodes.\(^2\) The absorption bands found between the wavenumbers of 600 and 1200 cm\(^{-1}\) are generally ascribed to the fingerprint region of terephthalate-based compounds.\(^1\) The peaks in the range of 1000–1200 cm\(^{-1}\) correspond to asymmetric stretching vibrations of CH groups present in the organic linkers. The range of 1680–1715 cm\(^{-1}\) shows no characteristic peaks in the spectrum and corresponds to the complete deprotonation of the 1,4-BDC linker. It is in good agreement with that of the work done by Song et al.\(^2\) Multiple peaks below 550 are attributed to the presence of the Zn–O bond of zinc oxide nanoparticles. The broader band at 3376 cm\(^{-1}\) is typically assigned to the O–H vibrations of the adsorbed atmospheric moisture. Effective incorporation of ZnO to the MOF was first suggested by the slight shift in the IR stretching frequencies in the composite compared with the pure MOF.

Powder X-ray Diffraction. The crystallinity and phase purity of the synthesized compounds were assessed by means of powder X-ray diffraction and are shown in Figure 2. The X-ray diffractogram reveals an ordered crystalline structure. The PXRD pattern of zincite is in good agreement with the JCPDS card entry number 96-900-8878 with the space group \(P\overline{6}_3mc\). The XRD pattern of synthesized MOF-5 matches with the JCPDS card entry number 96-432-6738. The Rietveld refined structure shows that the synthesized ZnO sample has unit cell lattice parameters \(a = 3.25271\) and \(b = 5.21063\). The final reduced \(\chi^2\) value of 9.8, which is less than 10, suggests good agreement of PXRD patterns with the Crystallography Open Database (COD) file. Refinement also suggests that the synthesized ZnO is in a single phase called zincite. The presence of the crystal planes (100), (002), (101), (012), (110), (013), (112), (201), (004), and (202) further confirms the formation of ZnO crystal planes corresponding to 2\(\theta\) values of 31.95, 34.62, 36.45, 47.60, 56.74, 63.11, 68.23, 69.31, 72.7, and 77.04°, respectively. The 2\(\theta\) values of 6.21, 8.92, 15.76, 17.79, and 18.59° obtained for MOF-5 correspond to the crystal plane indices (200), (220), (420), (333), and (440), respectively. It confirms the formation of the lattice of MOF-5.\(^3\) An additional peak at the peak position of 7.76° may be due to distortions that occurred in the lattice due to environmental exposure of the sample.\(^3\) The ligand-to-metal ratio and the addition of ZnO nanoparticles will greatly influence the XRD patterns of analytes. ZnO@MOF-5 shows slight variations in the peak positions as compared to the

![Infrared spectra of MOF-5, ZnO, and ZnO@MOF-5.](image1.png)

![Diagrammatic Representation for the Fluorescence Quenching of ZnO@MOF-5 by Copper Ions](image2.png)
MOF-5, which confirms the formation of new lattice planes within the composite. Almost all the peaks in the XRD patterns of ZnO were missing in the composite, which reveals the absence of distinct ZnO and MOF-5 particles. This also suggests the homogeneous distribution of ZnO nanoparticles either in the crystal surface or in the pore channels. The crystallite size of particles was deduced from the Debye–Scherrer equation:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

where \( \lambda \) is the wavelength of the X-ray used for the analysis, \( D \) is the crystalline size, \( \beta \) is the full width at half-maximum of each peak for calculation, and \( \theta \) is the Bragg’s angle in radians. Measurements done are shown in Table 1.

From Table 1, the crystallite size of ZnO@MOF-5 is 32.23 nm. It is evident that encapsulation of ZnO nanoparticles of 15.22 nm crystallite size to MOF-5 decreases the particle size of MOF-5 from 48.66 to 32.23 nm.

### Table 1. Crystallite Size Distribution of Analytes

| sample name | peak position (2θ) | FWHM | crystallite size (nm) | average crystallite size (nm) |
|-------------|-------------------|------|----------------------|-----------------------------|
| MOF-5       | 7.55525           | 4.08073 | 1.942552             |
|             | 7.76313           | 0.07759 | 102.1532             |
|             | 8.88005           | 0.16774 | 47.2186              |
|             | 10.95507          | 0.09722 | 81.34142             |
|             | 15.78203          | 0.27073 | 29.0661              |
|             | 17.77364          | 0.25929 | 30.27082             |
|             | 31.8861           | 0.34626 | 22.06063             |
|             | 34.5516           | 3.06 × 10⁻¹ | 24.7646             |
|             | 36.37493          | 0.36214 | 20.8411              |
| ZnO         | 47.67027          | 0.47209 | 15.39269             |
|             | 56.7176           | 0.46212 | 15.12788             |
|             | 62.98221          | 0.49731 | 13.62181             |
|             | 68.07277          | 0.52685 | 12.49557             |
|             | 69.19836          | 0.54498 | 11.99915             |
| ZnO@MOF-5   | 12.35936          | 0.15591 | 50.65824             |
|             | 18.81938          | 49.68076 | 0.157755             |

**UV–Visible Spectroscopy.** UV–visible spectra and Tauc plots of the synthesized compounds are shown in Figure 3. The MOF-5 and ZnO@MOF-5 show maximum absorption at wavelengths of 288.69 and 282.46 nm with bandgap values of 3.80 and 3.70 eV, respectively. The maximum absorption at 288.69 nm corresponds to the \( \pi-\pi^* \) transition exhibited by the \( \pi \) electrons of 1,4-benzene dicarboxylic acid (BDC) and corresponds to 1A_{1g} to 1B_{2u} excitations. The blueshift towards 282.46 nm is due to the incorporation of ZnO moieties.

**Photoluminescence Spectroscopy.** Photoluminescence spectra of samples were also recorded and are shown in Figure 4a. For MOF-5, excitation at 288.69 nm gave an emission at 414 nm, and for ZnO@MOF-5, the emission line was obtained at 402 nm at an excitation wavelength of 282.46 nm. The sharp peak at 414 nm corresponds to the ligand-to-metal charge transfer (LMCT) process. The hypsochromic shift in the wavelength occurs due to the incorporation of ZnO nanoparticles to MOF-5. Excitation of ZnO at 350 nm will give two emission peaks at 380 and 602 nm. The emission at 380 nm corresponds to the green emission, and red emission is observed at 602 nm. A higher number of surface oxygen vacancies may be the reason for a stronger PL band, and these defects make it a unique material to be a better photocatalyst among others. The blue emission value of ZnO is less than that of the corresponding MOF as well as the composite, and it may be due to the higher FL emission of ZnO as compared to the ZnO@MOF-5 and MOF-5.

**Dynamic Light Scattering Analysis.** DLS analysis gives the hydrodynamic diameter as well as the zeta potential of the synthesized samples, and spectra are shown in Figure 4b–e. Size distribution analysis of MOF-5 and ZnO@MOF-5 shows that the particles are polydisperse in nature. Mean diameters of the metal–organic framework as well as composites of the same are 773.6 and 1036.9 nm, respectively. The diameters obtained are far larger than the size obtained from XRD as well as TEM analysis. This may be due to the reason that the DLS instrument only detects the larger particles with higher diameters. The increase in the diameter when the MOF changes to the composite may be due to the agglomeration of particles or due to the adhesive nature of solvent molecules of water during analysis. The diameters obtained from the DLS analysis are not at all reliable due to the...
above-mentioned reasons. The zeta potential variation graphically presented in Figure 4c shows that values for MOF-5 and the nanocomposite are $-12.1$ and $-23$ mV with conductivity values of 0.085 and 0.092 ms/cm. A higher negative value of the zeta potential corresponds to deposition of ZnO onto the framework structure. The net negative value of the zeta potential may be due to the net negative charge localized on the MOF surface due to the presence of carboxylic groups on terephthalic acid.

**X-ray Photoelectron Spectroscopy.** To explain the binding energy distribution among different energy levels, XP spectra are taken, and the survey scan and deconvoluted spectra are shown in Figure 5a–e.

From the XP survey scan, spectral binding energies of different orbitals of zinc, carbon, and oxygen are noted. Intense peaks at binding energy values of 1043.88 and 1020.98 eV correspond to the terms 2p$_{1/2}$ and 2p$_{3/2}$, respectively$^{10}$ (Figure 5c). The sharp peak at 978.39 eV in the XP spectra of MOF-5 corresponds to the presence of free Zn$^{2+}$ ions on the framework topology. The absence of the same peak on the spectra of ZnO@MOF-5 is attributed to the absence of free metal ions on the surface topology that may be utilized for
bonding with the ZnO particles loaded. The intense peak at a BE value of 285.37 eV corresponds to the presence of 1s orbitals of carbon atoms of the terephthalate framework structure. The deconvoluted XP spectra of zinc show the shifting of binding energy values and a decrease in the intensity of peaks that may be due to the binding interactions of ZnO nanoparticles. The binding energy of O 1s is changed from 530.11 to 529.84 eV when encapsulation of ZnO occurs onto the framework structure, which further confirms the interaction of ZnO. More details of the bonding interactions can only be interpreted through Auger electron spectroscopy, which has to be done later.

**Transmission Electron Microscopy.** Transmission electron micrographs of the synthesized samples gave topographical as well as microcrystalline analysis of the synthesized samples and are shown in Figure 6A–D. In the micrograph

![Figure 5](https://example.com/figure5.png)

**Figure 5.** X-ray photoelectron survey spectra of (a) MOF-5 and (b) ZnO@MOF-5; deconvoluted XP spectra of (c) zinc 2p, (d) carbon 1s, and (e) oxygen 1s.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** (A,B) FETEM images of MOF-5, (C,D) FETEM images of ZnO@MOF-5, (E) thermograms of synthesized compounds, (F) DTA of analytes, (G,H) BET adsorption isotherms of the MOF and the MOF nanocomposite, and (I) pore radius-to-pore volume distribution of synthesized samples.
taken at a resolution of 2 nm, similar types of grains represent similar planes oriented in different directions. Hence, the MOF is polycrystalline in nature. At low magnification, TEM images will resemble SEM images, and the structure of the MOF resembles a thin flaky shape. TEM images of ZnO@MOF-5 are shown in Figure 6C,D. The images clearly indicate the deposition of particles onto the motif of MOF-5, and the pore size is found to be almost 0.23 nm, which is in good agreement with the data obtained from the BET analysis. The micrograph obtained at a resolution of 5 nm indicates the presence of different grain structural patterns, which resemble the different microcrystalline planes present in the MOF nanocomposite ZnO@MOF-5.

TG-DTA Analysis. Brunauer–Emmet–Teller surface area analysis was performed to investigate the surface topology, and BET adsorption isotherms of analytes are shown in Figure 6E,F. The thermal stability as well as phase purity of the analytes was studied by means of thermogravimetric analysis (TGA). The compounds were heated from a low temperature till 800 °C. Degradation temperatures were assessed, and corresponding decomposition temperatures were noted. The metal–organic framework shows one-stage decomposition at 474.55 °C with a weight loss of 34%, which is attributed to the destruction of the organic framework present. The MOF composite shows maximum weight due to the incorporation of ZnO onto the lattice surface. The surface area of MOF-5 is comparatively very low as compared to the reported one and may be due to exposure to a humid atmosphere.33 The Barrett–Joyner–Halenda (BJH) adsorption isotherm gives the distribution of the pore volume with the pore radius. The total pore volume of MOF-5 is $5.03 \times 10^{-3}$ cc/g at a relative pressure of 0.98869 atm, and that of the composite is $1.46 \times 10^{-2}$ cc/g at a relative pressure of 0.98590 atm. Evident from the BJH adsorption isotherm, ZnO@MOF-5 shows a better pore radius-to-pore diameter ratio than MOF-5 alone and suggests the possibility of formation of the crystalline nature of ZnO above 599 °C. The composite shows decompositions at temperatures of 192 and 457 °C with weight losses of 7 and 28% and suggests the extra thermal stability as compared to the pure organic framework.

BET Surface Area Analysis. Brunauer–Emmet–Teller surface area analysis was performed to investigate the surface topology, and BET adsorption isotherms of analytes are shown in Figure 6E,F. The pore size-to-pore volume distribution of different synthesized samples is shown in Figure 6G,H. The obtained graphs after the sorption measurements resemble a type 4 isotherm, which indicates that the samples are mesoporous in nature. Multipoint BET results shows that MOF-5 and ZnO@MOF-5 have surface areas of 3.050 and 9.335 m²/g, respectively. The increase in the surface area of the sample is attributed to the incorporation of ZnO onto the lattice surface. The surface area of MOF-5 is comparatively very low as compared to the reported one and may be due to exposure to a humid atmosphere.33 The Barrett–Joyner–Halenda (BJH) adsorption isotherm gives the distribution of the pore volume with the pore radius. The total pore volume of MOF-5 is $5.03 \times 10^{-3}$ cc/g at a relative pressure of 0.98869 atm, and that of the composite is $1.46 \times 10^{-2}$ cc/g at a relative pressure of 0.98590 atm. Evident from the BJH adsorption isotherm, ZnO@MOF-5 shows a better pore radius-to-pore diameter ratio than MOF-5 alone and suggests the surface
functionalization of ZnO nanoparticles rather than the encapsulation of nanoparticles due to a greater number of open channels in the composite.

**Sensing of Copper(II) Ions and Luminescence Quenching. Sensing of Divalent Metal Ions.** Sensing of the analyte ZnO@MOF-5 toward various metal ions was investigated. Equimolar concentrations of divalent metal ions such as Co²⁺, Ca²⁺, Ni²⁺, Zn²⁺, Sr²⁺, Mn²⁺, Ba²⁺, Mg²⁺, Cd²⁺, and Cu²⁺ were prepared for this purpose. The PL fluorescence intensity of the analyte before and after the addition of cupric chloride solution. 

The FL emission intensity of the analyte in various divalent cation solutions was recorded and is shown as a bar diagram (Figure 7a). The bar diagram of ZnO@MOF-5 showed good luminescence sensing activity toward different inorganic metal ions. The study further suggests the ultrasensitive ability of the porous analyte toward the detection of different inorganic metal ions in micromolar concentrations. The synthesized analyte showed the lowest sensing activity toward the Co²⁺ ion and a higher sensing activity toward the presence of Cu²⁺. For understanding the relative power of the analyte toward the ultrasensitive detection as well as to probing of metal ions, the quenching efficiency was calculated for each inorganic metal ion. The quenching efficiency of copper ions toward FL emission of ZnO@MOF-5 was again assessed by the Stern–Volmer equation, \( I_0/I = K_{sv}[Q] + 1 \). Here, \( I_0 \) and \( I \) represent the FL emission intensity of the analyte before and after the addition of cupric chloride solution. \( [Q] \) is the molar concentration at which the quenching process had been carried out, and \( K_{sv} \) is the quenching constant, which determines the efficiency of the MOF composite as a probe for sensing the presence of copper ions at the microscopic level. The higher the value of the constant \( K_{sv} \), the greater the quenching efficiency. The fluoroescence quenching efficiency was calculated by \( (I_0 - I)/I_0 \times 100 \). The quenching efficiencies of ZnO@MOF-5 toward various metal ions such as Co²⁺, Ca²⁺, Ni²⁺, Zn²⁺, Sr²⁺, Mn²⁺, Ba²⁺, Mg²⁺, Cd²⁺, and Cu²⁺ were obtained to be 98.44, 98.47, 98.70, 98.80, 99.0, 99.05, 99.14, 99.46, and 99.85%, respectively. The results suggest that the prepared analyte can be used as an effective tool for sensing different divalent cations with high accuracy.

**Effect of pH Values toward the Sensing Ability of Cu²⁺ Ions.** For optimizing the reaction conditions of sensing, solutions of copper having different pH values (range between 2 and 14) were prepared. The analyte showed different sensing properties as well as different quenching efficiencies toward the detection of the presence of copper ions in aqueous solutions. The variation in intensity of fluorescence with the change in pH values was recorded and is shown as a bar diagram (Figure 7b). Quenching efficiencies calculated were 98.44, 98.47, 98.70, 98.80, 99.0, 99.05, 99.14, 99.46, and 99.85%, respectively. It is clear that the analyte shows a quenching efficiency of more than 90% in the acidic range as well as in the basic range. It further suggests the better sensing efficiency of the analyte in both acidic as well as basic conditions. At a pH value of 14, ZnO@ MOF-5 shows better sensing with a quenching efficiency of 99.40%. Here, the quenching efficiency gradually increases with the increase in pH values of the medium.

**Effect of Concentration on Sensing of Cu²⁺ Ions.** The chemical environment at which fluorescence quenching occurs plays a significant role in the experimental part. The reaction is carried out in the presence of phosphate buffered saline (PBS), which is the best one suggested by Hu et al. for maintaining the pH value of the reaction medium. The PL spectra of the analytes after the successive addition of cupric chloride solutions in the concentration range of 0.1–5 μM are shown in Figure 7c. Excitation at 282.46 nm shows an emission at the range of 400–420 nm, which is in accordance with the emission values of the MOF as well as the ZnO@MOF-5 composite. The entrapment of copper ions onto the ZnO@MOF-5 framework may be due to the inherent porous nature of prepared composites. Occlusion or adsorption of Cu²⁺ within the crystal lattice of the porous composite framework leads to the decrease in intensity of the fluorescence spectrum. Mathematically, \( K_{sv} \) calculated from the Stern–Volmer equation, \( I_0/I = K_{sv}[Q] + 1 \), is found to be 5.09 × 10⁻⁴ M⁻¹, which is a far higher value than those of the conventional MOF composites that are used as sensors. It predicts the high degree of quenching and binding interaction of copper towards the ZnO@MOF-5 composite. The graph (Figure 7e) shows the relationship between \( I_0/I \) against the molar concentration, which is linear with a high degree of linear correlation with an R² value of 0.9878. The quenching efficiencies calculated are 88.95, 89.44, 90.23, 91.24, 91.35, 95.66, and 96.20% for concentrations of copper ions ranging from 0.1 to 5 μM. The higher the copper ion concentration, the higher the quenching efficiency; it predicts the possibility of the corresponding composite to act as a good sensing agent. The variation of fluorescence intensity with respect to time is shown as a bar diagram in Figure 7d. It is evident from the graph that as aging occurs, the fluorescence quenching power increases.

The Stern–Volmer plot (Figure 7e) shows a linear change of \( I_0/I \) with the concentration of the analyte Cu²⁺ ions. The limit of detection (LOD) and the limit of quantification (LOQ) in the sensing experiments were calculated by the same S–V plot (Stern–Volmer plot). The standard deviation of the intercept is given by the following:

\[
\text{standard deviation of the intercept} = (\text{standard error of the intercept}) \times n^{1/2}
\]

Here, “n” represents the number of measurements taken. The limit of detection (LOD) can be calculated by the following:

\[
\text{LOD} = 3.3 \times (\text{standard deviation of the intercept/slope})
\]

Here, slope represents the slope of the line obtained in the S–V plot. The LOD is calculated to be 0.185 μM. The value represents the lowest concentration of the analyte that can be calculated experimentally with a 95% accuracy. The value obtained is in good agreement with the experiments too. The value further suggests the better sensing power of the analyte toward the detection of the presence of Cu²⁺ ions in micromolar quantities.

**Sensing of Cu²⁺ Ions with Variation in Time.** Variation in the sensing activity of the analyte with time toward the sensing of copper ions in aqueous solution is analyzed. As the time progresses, the intensity of the fluorescence emission of ZnO@MOF-5 decreases. This may be due to the slow diffusion of copper ions into the vacant voids present in the hybrid structure of ZnO@MOF-5. Other plausible mechanisms have been suggested at the end of this manuscript. The quenching efficiency of the analyte toward the inorganic metal moieties increases with the increase in the time. Sensing experiments were done by varying time from 5 to 45 min with 5 min intervals, and the results obtained are shown in Figure 7d as a
bar diagram. The maximum quenching efficiency of 95.77% was obtained toward the detection of Cu$^{2+}$ ions.

**Plausible Binding Mechanism of the ZnO@Zn-MOF-5 Composite with Cu$^{2+}$ Ions Leading to a “Turn-Off Mechanism”**. We hereby suggest three possible mechanisms for the quenching of fluorescence after each successive addition of cupric chloride solutions of varying concentrations. First, the mechanism can be explained on the basis of the interaction of metal cations and ligands. The fluorescence emission peak at 413 nm may correspond to the ligand-to-metal charge transfer (LMCT) process from terephthalic linker to Zn$^{2+}$ metal nodes. The uncoordinated carboxylate groups on the terephthalate linker present in the channels of the MOF composite provide a binding site for copper ions. The electronic structure of the linker is perturbed due to the incorporation of Cu$^{2+}$, which may in turn effectively suppress the energy transfer from the ligand to the metal (LMCT) resulting in luminescence quenching. The FL intensity greatly depends upon the identity as well as the concentration of metal ions. Compared to alkali and alkaline-earth metals, the presence of d block elements plays a vital role in the fluorescence intensity maxima. Among the other transition metals, the presence of Cu$^{2+}$ has more significance. The fluorescence intensity of copper ion-incorporated ZnO@MOF-5 solution of 0.1 $\mu$M concentration is 8865 a.u., which is a far smaller value than that of the intensity of the blank of 80,243.35 a.u. This value itself suggests the higher quenching efficiency of the copper ion even at its micromolar-level presence.

The second mechanism that describes the FL intensity quenching deals with the probability of collapse of the metal–organic framework structure after the interaction of the terephthalic acid ligand with copper cations. The decrease in the fluorescence intensity can be explained on the basis of the electron transfer process occurring in the composite ZnO@MOF-5. The electrons present on the framework structure of the composite get excited on irradiation with light. These excited electrons may be transferred to the unoccupied energy levels of ZnO, which will further move down to the metal center zinc ions present in the framework, and the fluorescence will develop. Quenching of luminescence intensity during the addition of cupric chloride solution can be explained as suggested. When the cupric solution was added to the ZnO@MOF-5 composite, oxygen atoms present in the carboxyl group of 1,4-BDC linkers coordinate with Cu$^{2+}$ ions, which in turn results in the blocking of the electron transfer process (ET) occurring in the composite due to the collapse of the framework structure.

The third mechanism for the decrease in luminescence intensity in the composite may be due to the replacement of zinc atoms of ZnO@MOF-5 by copper ions of cupric chloride solutions. This mechanism may be more convincing and applicable in our ZnO@MOF-5 system due to the increase in the ratio of the pore radius to the pore volume as indicated from BET surface analysis and also from the decreasing XPS binding energy values of Zn (2p). The possibility of encapsulation or occlusion of copper(II) cations to ZnO nanoparticles present in the pores and further change to CuO can thus be discarded and there comes the possibility of isomorphous displacement of zinc of the framework by copper atoms, and this change in the luminescence center will result in the decrease in the fluorescence intensity of analytes. The explanation of the suggested binding mechanism of the analyte with copper(II) cations has to be further studied and confirmed through XPS, XRD, and FTIR measurements.

**CONCLUSIONS**

A luminescent MOF composite called ZnO@Zn-MOF-5 was prepared by means of a solvothermal method for the quantitative trace analysis of Cu$^{2+}$ ions in water medium. The extensive porous nature and the isoreticular framework structure of the nanocomposite make it a versatile fluorescent probe for the detection of copper ions from drinking water at the microscopic level. The feasibility of the same is tested from a level of 0.1 to 5 $\mu$M cupric chloride solution, and the intensity of FL emission is shown to be decreasing with increasing copper ion concentration. As the time proceeds, the quenching efficiency of the analyte toward the detection of Cu$^{2+}$ ions increases, which further suggests the nature of time-bound detection and elimination of Cu$^{2+}$ ions in aqueous media. As the pH value increases, the sensing ability of the analyte seems to be increasing, which also suggests the higher activity of the analyte toward the sensing at acidic as well as basic pH ranges. The FL turn-off mechanism is suggested due to the binding interaction of copper ions with the ZnO@MOF-5 composite. The quenching efficiency of ZnO@MOF-5 is 96.20% at a 5 $\mu$M cupric chloride concentration. The quenching of luminescence intensity in the composite may be due to the possibility of isomorphous displacement of Zn$^{2+}$ of the framework by copper(II) cations. This suggested mechanism may be more applicable in the synthesized ZnO@MOF-5 system, which has to be further complemented by XRD analysis and FTIR and XPS measurements. The property of the unique rate of adsorption can be extended to fabrication of nanosensing probes for the microlevel analysis as well as quantification of inorganic pollutants.

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