

Proceeding Paper

Facile Preparation of Nanostructures Copper-based Metal-organic Framework with Highly Selective and Sensitive Luminescent Sensing of THF Small Molecules and a Study of the Antibacterial Activity [†]

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[†] Presented at the 26th International Electronic Conference on Synthetic Organic Chemistry, 15–30 November 2022; Available online: <https://ecsoc-26.sciforum.net/>.

Abstract: Ultrasound-assisted has been provided a facile novel route synthesized nanostructures of $\text{Cu}_2(\text{bdc})_2(\text{bpy})$ compound by a sono-chemical irradiation process and characterized by XRD, FT-IR, TGA, and FE-SEM analysis. Herein, we report the recognition of fluorescent Cu-based three-dimensional nanostructures MOF, $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]$, (**1**; H_2bdc = 1,4-benzene dicarboxylate; bpy = 4,4'-bipyridine) for greatly sensing and selective of tetrahydrofuran (THF) small molecules in water aqueous solution. **1** shows a quick exploration of excellent solvent-relative luminescent spectra by emission intensity regarding quenched direction THF small molecule by a reply of time <1 min. As well as, the static quenching is calculated to be $11,181 \text{ M}^{-1}$ by the fluorescence titration experiments in low concentration of THF small molecules and with a detection limit of THF to be calculated at $0.0008 \mu\text{M}$. The antibacterial activities of $\text{Cu}_2(\text{bdc})_2\text{bpy}$ (**1**) were tested against gram-positive and gram-negative species. The as-synthesized **1** exhibited excellent antibacterial effectiveness against *Escherichia coli* and *Staphylococcus aureus*. This project is one of the first samples of a metal-organic framework based luminescent sensor as an efficacious multipurpose fluorescence component that can utilize for the selective detection of THF small molecules and antibacterial activity.

Keywords: Cu-based MOF; Ultrasound-assisted; Fluorescence sensor; THF small molecules; Antibacterial activity

Citation: Moradi, E.; Rahimi, R.; Azari, S. Facile Preparation of Nanostructures Copper-based Metal-organic Framework with Highly Selective and Sensitive Luminescent Sensing of THF Small Molecules and a Study of the Antibacterial Activity. 2022, 4, x. <https://doi.org/10.3390/xxxxx>

Academic Editor(s):

Published: 15 November 2022

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1. Introduction

Nanostructures ultrasound-assisted synthesized metal-organic frameworks (MOFs) have newly attracted powerful desirous during the last two decades due to their fascinating structures of tunable pore size with different network topologies, interesting characteristics of behavior with the ability of inner/outer surface decoration, high surface area feature of MOFs have been widely applied for several potential applications, [1,2] including chemical sensing, [3–5] gas storage and separation, [6,7] catalysis, [8,9] antibacterial activity [10,11] and drug delivery [12]. The immobilization of organic linker ligands to metal clusters or metal ions has boosted the fast sensing of luminescent MOFs materials. The taking benefit of the tunable porous structure material of luminescent MOFs, as an essential proceeding has been built in the various application of luminescent MOFs for, temperature, oxygen, metal ions, sensing explosives, and small molecules [13]. Some example works the same as Zang's group [14–17], as well as Li's group, which has reported high sensitivity of RDX (1,3,5-trinitroperhydro-1,3,5-triazine) from Zn-based luminescent

[18]. Qian's group has reported a high oxygen sensitivity and rapid recovery/response luminescent MOF (MIL-100-Tb³⁺) film [19]. Dinca's group has reported Zn₂(TCPE) and Mg(H₂DHBDC) MOFs, both displaying fascinating sensitivity to ammonia at 100 °C [20]. Chen and co-workers prepared a perylene-doped Eu-MOF reacting as a luminescent thermometer in the range of 20–80 °C [21]. MOFs contain metal ions that have antibacterial activity by forming coordinate bonds with carboxyl groups [22]. The three-dimensionality of MOFs creates a network-like structure around bacteria that leads to their antibacterial properties. MOF interactions with bacteria have two levels: the outer and inner membranes and the central atom of the MOF oxidizes and depolarizes the surface of the outer membrane of the bacteria and inhibits them [23]. The presence of metals such as Zn, Cu, Mn, Mg, Au, and Ag in the MOF structure can enter the bacterial cell wall and lead to their antibacterial behavior [24]. Until now, heavy metal ions, small molecule solvents, and other pollution exhibits make a lot of environmental subjects, and thus many struggles have been focused on their sensing, particularly in wastewater, soil, and plant [25]. The preparation and design of highly sensitive and selective chemosensors for environmentally and biologically important essential ionic species have attracted a major deal of attention [26]. Among different pollutants, THF small molecules are one of the most hazardous ions because of their high carcinogenicity and toxicity. It is widely used in many branches, like agriculture, industry, military affairs, and so on [27]. To date, The mechanisms have been explored for luminescent MOFs to sense THF small molecules. As well as, many studies on luminescent MOFs for sensing of THF, DMF, CH₂Cl₂, MeOH, and CH₃CN have been achieved based on metal-ligand coordination interaction, weak binding of metal ions to a heteroatom (O or N) within the ligands and intramolecular energy or electron transfer from the ligand to metal [13,28–30]. As a heterocyclic compound, tetrahydrofuran (THF), a dangerous and harmful volatile organic solvent, has been widely used in organic synthesis, high-power energy, and pharmaceutical preparation. It is very obvious the body to THF usually leads to chest distress, stomachache, keratitis, cough and even loss of fertility. Moreover, THF is very flammable and may contribute to the release of toxic gases and vapors in a fire. What else, as an industrial chemical for the generation of synths, diamars, plasthetics, and explosive peroxides can be formed comfortably [28,31]. For this reason, several studies emphasize the development of new analytical methods for sensing and reporting Various analytes. Luminescence is a forcible and comfortable method for the accurate, simple, and fast detection of ecological and different biological species [32,33]. Until now, many examples have been reported to determine cation and anion ions through fluorescence changes in materials. Although, not many reports have been explored on selective THF small molecule sensing using Cu-based MOF sensors. The coordination of Cu²⁺ metal ions with both 1,4-benzenedicarboxylate (H₂bdc) and the *N,N'*-bipyridine-type (bpy = 4,4'-bipyridine) rigid linker ligands produce MOF [Cu₂(bdc)₂(bpy)] (**1**), which is reported by Seki in 2002 [34]. In our preceding work [2], and this study, we reported the ultrasound-assisted facile novel route synthesis of nanostructures of a three-dimensional nano-porous MOF, [Cu₂(bdc)₂(bpy)] (**1**), which displayed highly examined fluorescent detection of THF solvent molecules with a response time <1 min. And in this regard, to examine the potential sensing of small molecule solvent, the fluorescence properties of **1** in various solvent emulsions were investigated and good shows performance for turn-off the THF solvent as a model system [35]. A literature review indicated that the sensing ability and antibacterial activity of the **1** were not investigated in detail. Herein, the **1** was performed at room temperature for sensing and antibacterial activity. As a result, the advantage of [Cu₂(bdc)₂(bpy)] (**1**) displays good performance for sensing THF small molecules in the concentration range of 50–250 μM. As well as, the static quenching is calculated to be 11181 M⁻¹ by the fluorescence titration experiments in low concentration of THF small molecule and with a detection limit of THF to be calculated 0.0008 μM. Finally, the antibacterial activity properties of the **1** was investigated using *Escherichia coli* (a gram-negative bacteria) and *Staphylococcus aureus* (a gram-positive bacteria) bacteria method.

2. Experimental Section

2.1. Chemicals, Reagents and Apparatus

Starting reagents for the preparation of **1** were purchased from Merck, Sigma-Aldrich, and others, and all materials were utilized without further purification. $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 1,4-benzenedicarboxylate (H_2bdc), and 4,4'-bipyridine (bpy) were used to synthesize **1**. *N,N*-dimethylformamide (DMF) was utilized as the solvent to purify **1**. The powder x-ray diffraction techniques were established by Philips x-pert diffractometer (PXRD) with monochromated $\text{Cu-K}\alpha$ radiation ($\lambda=1.54056\text{\AA}$). The powder XRD pattern was simulated and prepared by single-crystal data employing Mercury software [36]. The sonicator used in this study was a Misonix Sonicator 3500 with adjustable power output (maximum 600W at 50/60 kHz). The synthesized MOFs were determined using Fourier transform infrared spectroscopy (FT-IR) in the range of 400-4000 cm^{-1} , by the KBr pellet technique. Prepare material for the fluorescence experiments was accomplished at room temperature on a Shimadzu RF-6000 apparatus fluorescence spectrometer (Kyoto, Japan) with a scan rate of 60,000 nm min^{-1} and with 700 V photomultiplier voltage, an excitation split expanse of 458 nm, an emission split expanse of 200-700 nm, and a 350 nm optical filter. The fluorescent emission spectra were recorded in the wavelength range of 200-700 nm upon excitation at 350 nm. The size and shape of the nanostructure were analyzed by transmission failed electron microscopy operated at (FE-SEM) TESCAN VEGA II (Czech) with gold coating.

2.2. Solvothermal Synthesis of $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]$ (**1**)

Preparing of $\text{Cu}_2(\text{bdc})_2(\text{bpy})$ MOF was synthesized with the solvothermal method. In a typical experiment, solution of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0968 g, 0.4 mmol) in *N,N*-dimethylformamide (DMF) was dropwise added to a beaker (50 mL) containing solution of 1,4-benzenedicarboxylate (H_2bdc) (0.0664 g, 0.4 mmol) and 4,4'-bipyridine (0.0312 g, 0.2 mmol) in DMF (16 mL) under stirring condition at room temperature. Then, the mixture was placed in a Teflon reactor and heated at 120 °C for 24 h. After natural cooling dawn, green crystals were collected from the Teflon reactor and the solid product was filtered three times and washed with DMF.

2.3. Ultrasound-assisted Synthesis of $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]$ (**1**)

The ultrasound-assisted synthesis nanostructures of $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]$, by dissolving of 24 mL $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.47 mmol, 0.095 g; 0.02 M) in DMF was positioned in a high-density ultrasonic probe at ambient temperature and atmospheric pressure. In this mixture, 0.47 mmol (0.079 g) and 0.23 mmol (0.037 g) of the ligands H_2bdc and bpy, respectively, were added to the beaker and sonicated for 60 min. Also, the **1** was synthesized by various concentrations of initial reagents of 0.01, 0.02, and 0.04 M using constant ultrasound (US) generator power of 60 W for 60 min irradiation time. The obtained precipitates were filtered off, washed three times with DMF, and then dried in air.

2.4. The Solvent Sensing Experiments

The small organic molecules solvent sensing introduced 1 mg powder of **1** immersed into 4 mL of water under ultrasonic irradiation at 60 W for 5 min at room temperature. For selectivity various solvents of (Solvent = Water, EtOH, MeOH, DMF, CH_2Cl_2 , 1-Butanol, 1-Hexanol, CH_3CN , and THF), respectively. After the sonication solvent, the fluorescence spectra were measured.

3. Results and Discussion

3.1. Characterization of $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]$ (**1**)

The ultrasound-assisted synthesized of $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]$ (**1**) was by mixing copper acetate, 1,4-benzenedicarboxylate (H_2bdc), 4,4'-bipyridine (bpy), and DMF solvent for 1 h.

The compound of **1** possesses to afford a 3D network by porous that can be tuned by double interpenetration to have 1D channels. Interestingly, they are composed of two influencing, paddle-wheel-type and pillared networks. The 3D framework structure is comprised of dicopper paddle wheel nodes interconnected by two coordination modes; copper-bpy and copper-bdc (Figure 1b) [37]. The FT-IR spectra of **1** showed that the characteristic band of bdc (1678 cm^{-1}) turns into two strong peaks at 1620 cm^{-1} and 1388 cm^{-1} interaction with metal ions although corresponding to symmetric vibrations of coordinated carboxyl groups and asymmetric. The board's strong peak at 1620 cm^{-1} in the spectrum of **1** could also be allocated to the C=N bond in bipyridine. This change toward higher frequencies is apparent in the coordination of bpy to metal. The difference frequency between symmetric stretching and asymmetric vibration is more than 200 cm^{-1} displaying the bidentate-bridging coordination mode of the carboxylate group (Figure 1d) [38]. The x-ray diffraction pattern of the ultrasound-assisted as-prepared of **1** displaying was successfully prepared as reported in the literature (Figure 1c) [38,39].

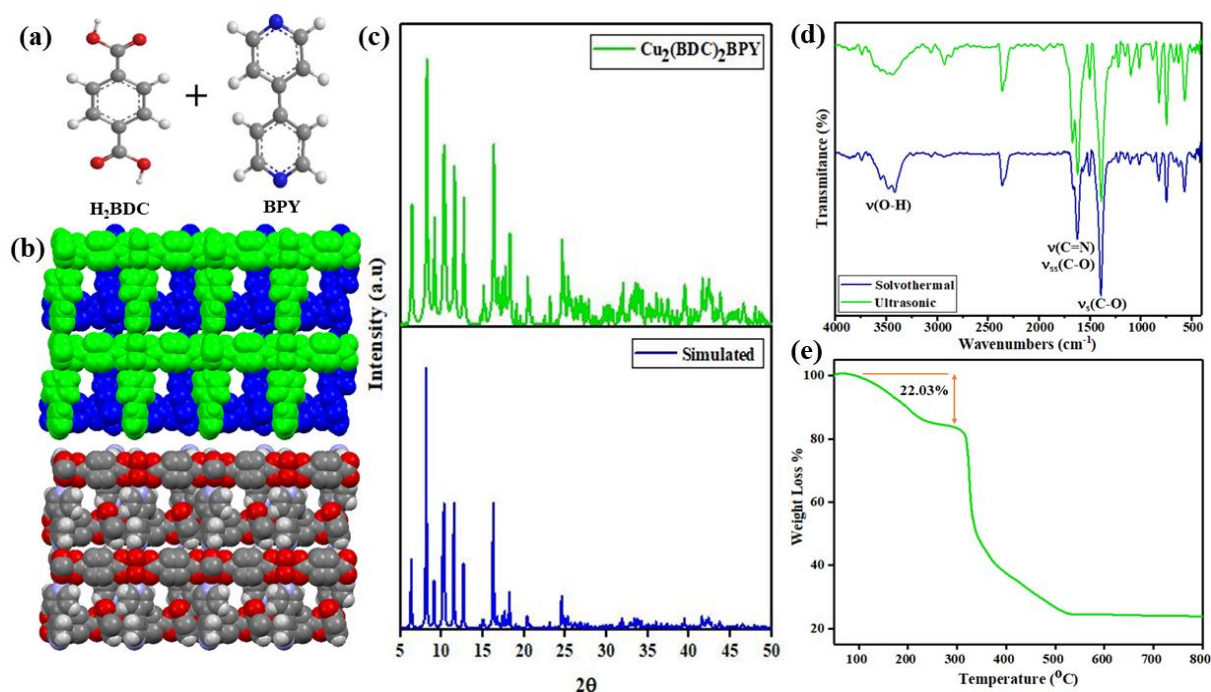


Figure 1. (a) Chemical structure ligands of H₂bdc and bpy (b) Crystal structure of the 3D framework [Cu₂(bdc)₂(bpy)] (**1**), showing the 1D channels running along the *a* axis (The disordered guest molecules are omitted for clarity). (c) PXRD pattern of **1** as-synthesized via the ultrasound-assisted method (green) and simulated (blue). (d) FT-IR spectra of ultrasound-assisted (green) and solvothermal method (blue) synthesized **1**. (e) The TGA activated of **1**.

In addition, The TGA curve of **1** exposes of weight loss of the trapped DMF in the porous. The elimination of guest molecule (DMF) started at 230 °C and the framework is thermally stable up to 350 °C , showing the good thermal stability of the framework. The weight loss of 22 wt% between 50 and 250 °C corresponds to the elimination of the trapped DMF in the pores (calcd.: ~22.03 %) (Figure 1e) [40].

The size and morphology of the nanostructure synthesized of **1** were obtained by the US procedure and nanostructures are identical to the solvothermal powder obtained by the conventional electric (CE) heating method. So, using US techniques is dependent on various parameters such as the concentration of initial reagents [2,41–43]. Moreover, the more important parameters on the size and morphology of the MOF, the powder synthesized of **1** with the US method using various reaction conditions were determined by field emission scanning electron microscopy (FE-SEM). The FE-SEM images (in Figure 2) display the shape of **1** synthesized in various concentrations of initial reagents of 0.01, 0.02,

and 0.04 M under US condition generator 60 W for 1 h irradiation time. The US irradiation samples with different concentrations (0.01, 0.02, and 0.04 M, Figure 2 a–d) compare by the solvothermal reaction method (Figure 2 e–f) display that different concentrations of US reagent made increased the smaller particle size uniform of MOF. Also, nanoflowers like sheets formed made by the solvothermal method, by modifying the synthetic-ultrasonic method, with varying concentrations, make a new regular geometry nanostructures morphology of MOF [44].

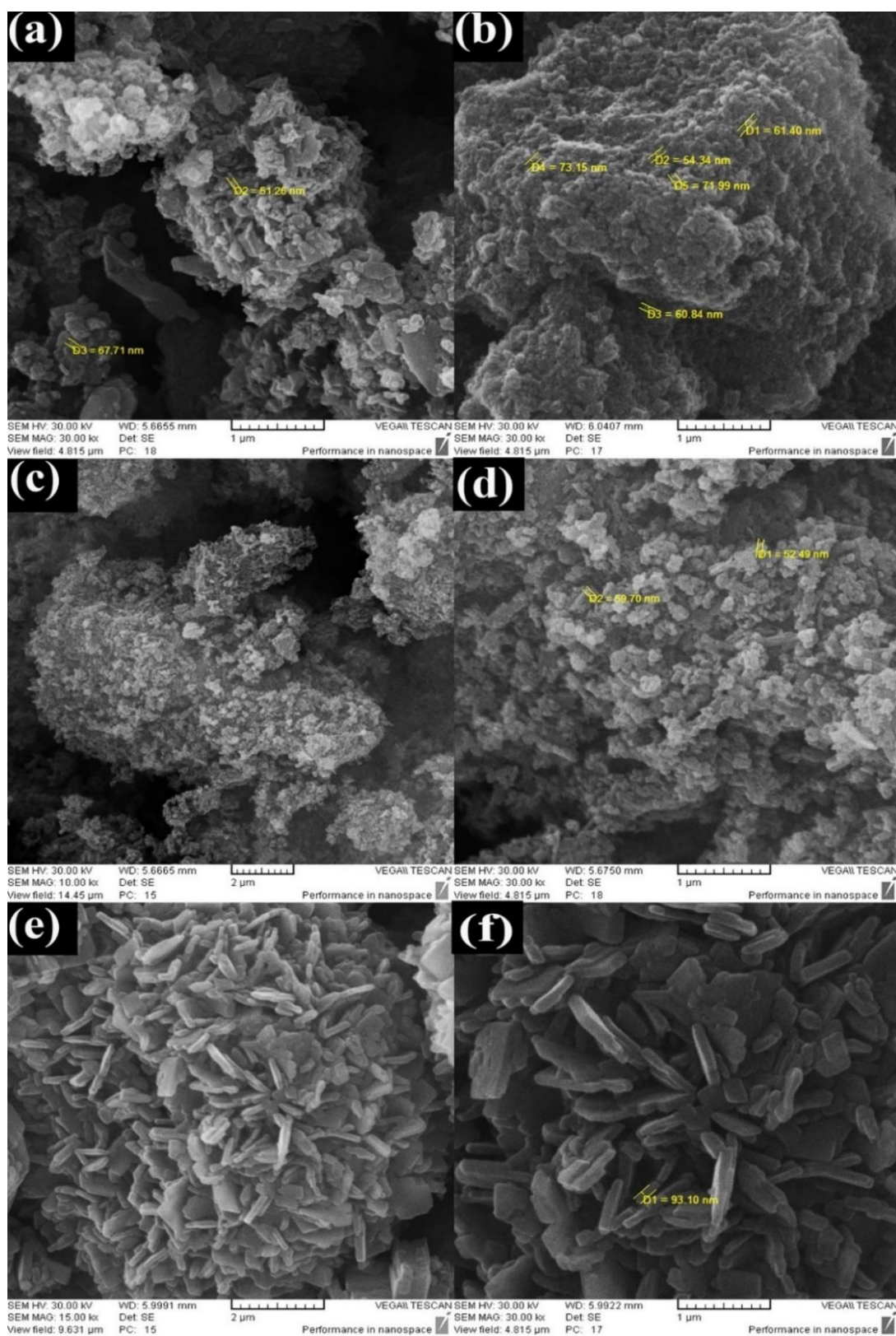


Figure 2. FE-SEM images nanostructures of [Cu₂(bdc)₂(bpy)] (1) prepared by US generator power of 60 W at 1 h irradiation time with different concentration of initial reagents (a) 0.01 M, (b) 0.02 M and (c,d) 0.04 M. (e,f) FE-SEM images bulk powder of 1 with nanoflowers like sheet formed via solvothermal method.

4. Fluorescent Properties of [Cu₂(bdc)₂(bpy)] (1)

The property of metal-organic coordination hybrids constructed by d^9 metal ions and conjugated organic with ligands are considered promising luminescent compounds. Therefore, the photoluminescent (PL) property was investigated in the sensing behavior of compound **1** towards cations and small molecules. Figure 3a shows the spectrum of **1** as an intensive band emission centered at 458 nm upon excitation at 350 nm is a good potential sensor for metal ions and small molecules detection. Moreover, the most significant structural feature luminescent intensity emission spectra of **1** and, the two organic ligands, H₂bdc and bpy, have been recorded in the PL solid-state at room temperature as shown in Figure 4a. Also, emission peaks were displayed in the bpy and H₂bdc ligands properties luminescent emission maxima at 458 nm. The solid-state PL spectrum of **1** appeared excellent and strong emission bands at $\lambda_{em} = 458$ nm upon excitation at 350 nm, as shown in Figure 4a, the red-shifts of the emission of the **1** compared to the pure ligands are most probably due to substantial electronic coupling between of bpy and H₂bdc are stronger than of the corresponding MOFs (Solvothermal and US), maybe because of the aggregation-induced enhancement or quenching impression in a solid-state. The mechanism of fluorescence for this phenomenon can be related to the change or collapse of the structure, the competitive photon absorption between the adsorbed ions and MOFs, and the ionic exchange. The UV absorption spectrum of the Cu-based nanostructure material and the competitive photon absorption between the adsorbed ions and MOFs its confirm this mechanism. In Figure 4b, the emission wavelength exhibited no shift while the excitation wavelength was changed from 260 nm to 390 nm, displaying that the **1** indicates the excitation-independent fluorescence properties. Upon excitation at 350 nm beam, the fluorescence spectrum of **1** shows an emission strong peak at 458 nm [45].

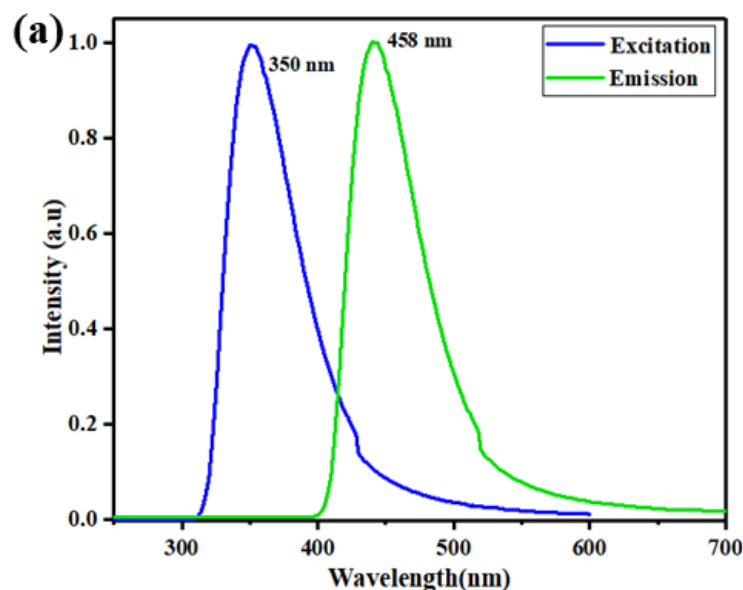


Figure 3. (a) The PL excitation ($\lambda_{em}=458$ nm) and emission ($\lambda_{ex}=350$ nm) spectra of **1**.

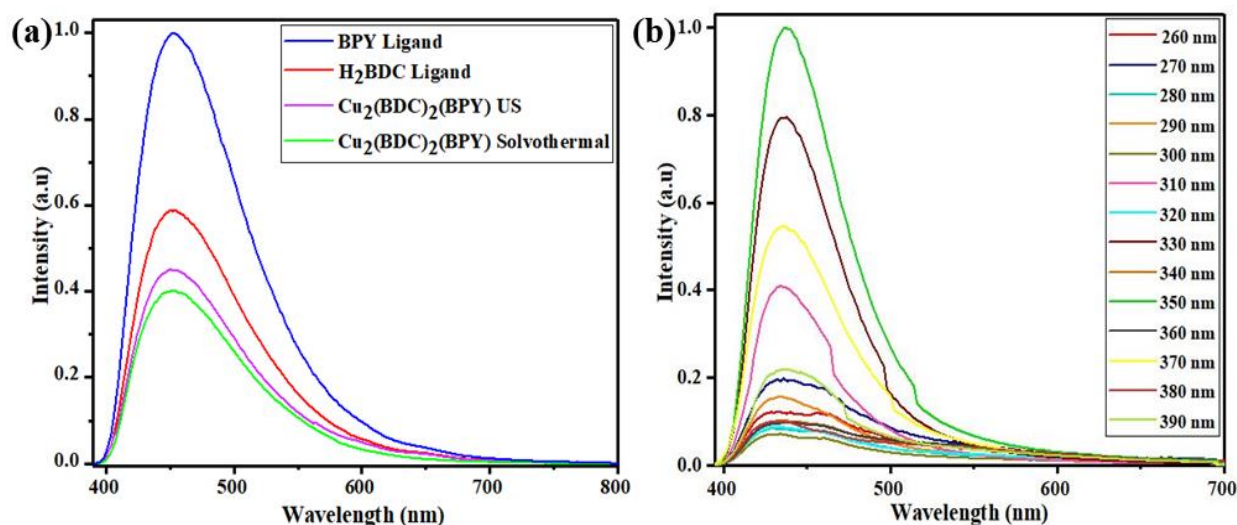


Figure 4. (a) The emission spectra ($\lambda_{\text{ex}}=350$ nm) of **1**, solvothermal MOF, H₂bdc and bpy ligands as solid samples. (b) Photoluminescence emission spectra with progressively longer excitation wavelengths from 260 nm to 390 nm of **1**.

4.1. Fluorescence Detection of Small Organic Molecules Based on [Cu₂(bdc)₂(bpy)] (**1**)

The properties luminescence of **1** to investigate the various solvent the same as DMF, MeOH, CH₃CN, Water, THF, EtOH, CH₂Cl₂, 1-Buthanol, and 1-Hexanol were also considered these suspensions were recorded in Figure 5a at $\lambda_{\text{ex}} = 350$ nm. The experiment sensing of organic molecules is a leader as follows: the gained Cu₂(bdc)₂(bpy) (1 mg) were weighed and soaked in 4 mL of different organic solvents (DMF, MeOH, CH₃CN, Water, THF, EtOH, CH₂Cl₂, 1-Buthanol, and 1-Hexanol). The main feature is that as shown in Figure 5a, its PL intensities are widely dependent on the solvent molecules, especially in the sample of THF, which showed the most quenching behavior effect. The histogram curves obviously display the decreasing emission effect of the following order: Water > EtOH > MeOH > DMF > CH₂Cl₂ > 1-Buthanol > 1-Hexanol > CH₃CN > THF, which exhibited the weaker emission intensity for THF (Figure 5b). Thus, to examine sensing sensitivity toward THF solvent in more detail. A gradual quenching of the fluorescence intensity appeared upon the titration of THF into **1** suspended in water. When the THF solvent was gradually added and increased to **1**@water standard suspension, the fluorescence intensity of the standard suspension gradually reduced with the addition of THF solvent (Figure 6a). As shown in Figure 6b, there is excellent linearity between $I_0/I-1$ and [THF] at a specific concentration range, which is indicative of the sensitive sensing characteristics of **1** towards THF in water solutions. The quenching efficiency was analyzed by fitting the experimental data to the Stern-Volmer equation, $I_0/I = 1 + K_{\text{sv}} [\text{THF}]$. The Stern-Volmer plot for THF in lower concentrations displayed linear correlation coefficients $R^2 = 0.9930$ for **1**. The quenching constants (K_{sv}) of **1** for tetrahydrofuran in water was calculated to be 11181 M^{-1} , and the detection limit was also found to be $0.0008 \mu\text{M}$. The luminescence quenching of **1** by the THF molecule could be attributed to the interaction of the analyte within the pores of **1**. The encouraging conclusions display that **1** could be a promising luminescent sensor for detecting small molecule tetrahydrofuran.

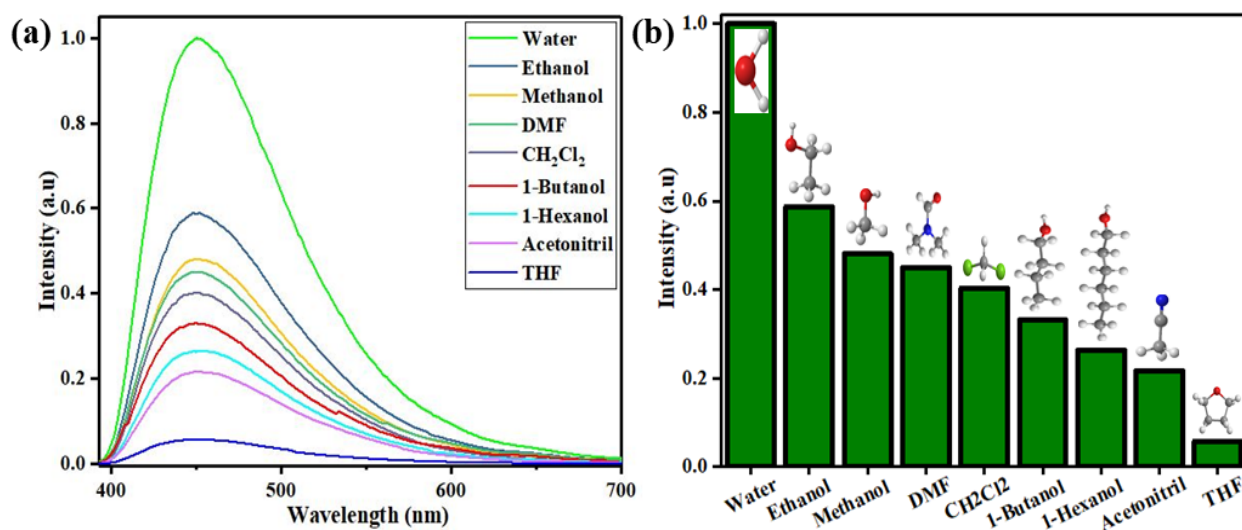


Figure 5. (a) The PL spectra of 1 display different solvent at room temperature. (b) Comparisons of the luminescence intensity of 1-solvent emulsions at room temperature (Solvent = Water, EtOH, MeOH, DMF, CH₂Cl₂, 1-Butanol, 1-Hexanol, CH₃CN, and THF).

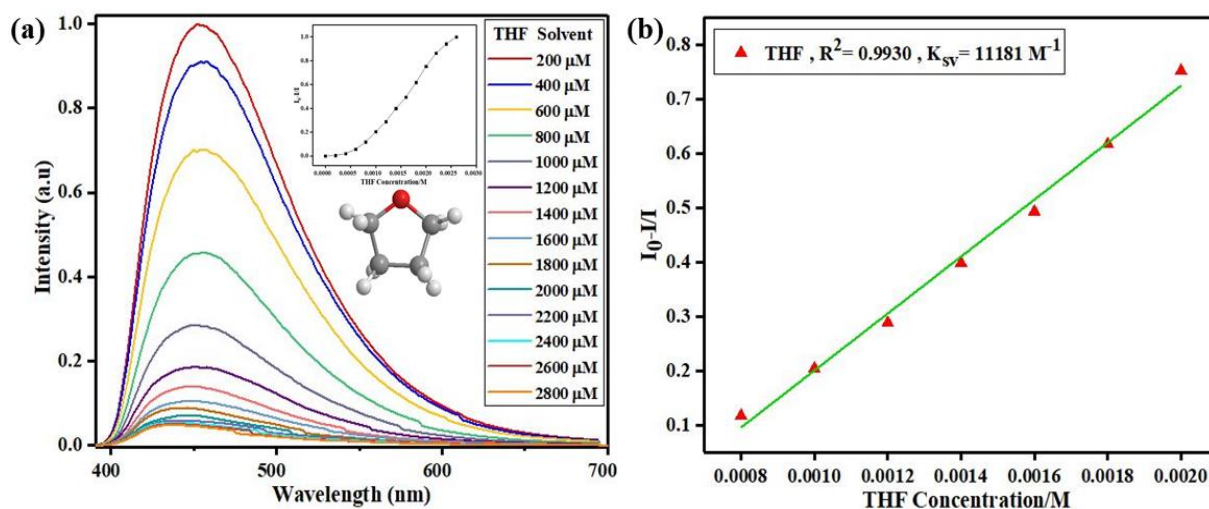


Figure 6. a) Luminescent spectra of 1 emulsion in the presence of a different concentration of THF solvent at ($\lambda_{\text{ex}} = 350 \text{ nm}$) and (b) luminescence spectra of 1 (2800 μM) upon adding THF, (The inset showing picture exhibits the plot of PL intensity at 458 nm against THF concentration).

4.2. Mechanism of Fluorescence Quenching

According to the above studies, we tried to explore the possible detecting mechanism of fluorescence quenching for THF small molecules solvent. Until now, several conclusions for the fluorescence quenching caused by MOFs can be assigned to the following three approaches means by metal ions and solvent: (1) The mechanism of fluorescence for this phenomenon can be regarding the change or collapse of the structure, (2) the competitive photon absorption between the adsorbed ions (or solvent) and MOFs, and (3) the ionic exchange (The UV absorption spectrum of the Cu-based nanostructure material the competitive photon absorption between the adsorbed ions and MOFs its confirm this mechanism) [46,47].

5. Antibacterial Activity

The antibacterial activity is measured from the inhibition zone. In the present work, *Escherichia coli* (a gram-negative bacteria) and *Staphylococcus aureus* (a gram-positive bacteria), were used as the biological agents. This is shown in Fig 7(a) and (b). The results

demonstrated a relationship between the $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]$ (**1**) concentration and antibacterial activity. Kirby–Bauer disk diffusion susceptibility test was used to measure the antibacterial activity of **1**. Colonies of each strain of *E. coli* and *S. aureus* were cultured overnight on trypticase soy agar medium and transferred through a loop in a sterilized test tube containing 5 mL sterilized the normal saline solution. The mixture was completely mixed. Then, uniform suspensions of bacteria with 0.5 McFarland turbidity standards were cultured by swab on Muller Hinton agar. To prepare the disks, 50 mg mL^{-1} synthesized material was added to sterilized blank disks and left for 2 days the prepared, materials were on the paper disks, completely. The disks were then seeded onto the plate at appropriate time intervals and incubation was carried out, at 37 °C for 18 h. Then, the zones of bacterial inhibition were measured. Cu^{2+} is readily released from the **1**. structure in water and interacts with the bacterial membrane. **1**, therefore acts as a Cu ion reservoir. Moreover, the structure undergoes gradual degradation, providing sustained ion release. However, the antibacterial test for both bacteria was shown an excellent effect against *E. coli* and *S. aureus* [48–51].

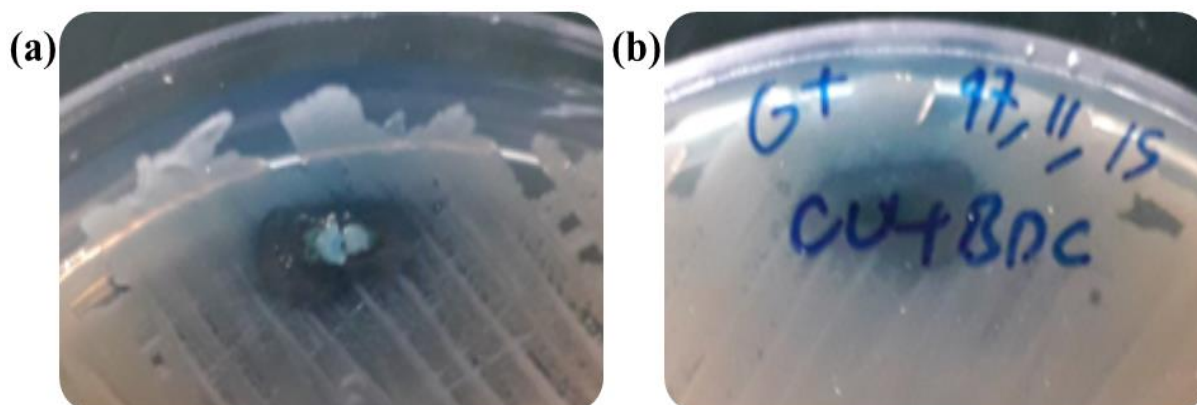


Figure 7. The antibacterial activity zone of inhibition with $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]$ (**1**) powders, for different bacterial strains: (a) *Escherichia coli* (b) *Staphylococcus aureus*.

6. Conclusion

In summary, in this study, we have successfully synthesized the luminescent porous Cu-based nanostructure of $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]$ (**1**) via an ultrasound-assisted method at room temperature. Compound **1** is a good potential candidate for developing novel luminescence sensors for the highly selective sensing of small molecules and antibacterial activity. This luminescent probe displays high selective and sensitive sensor for small organic molecules which display an excellent selection for THF with $K_{sv} = 11181 \text{ M}^{-1}$ plot range and detection limit of $0.0008 \mu\text{M}$. Moreover, the antibacterial activities of **1** were tested against gram-positive and gram-negative species. The as-prepared **1** displayed excellent antibacterial effectiveness against *E. coli* and *S. aureus*. These present work results provide a facile novel route to synthesized $\text{Cu}_2(\text{bdc})_2(\text{bpy})$ -MOF by applications in fluorescent sensors and antibacterial activity.

Acknowledgments: We thank the support of this investigation by Iran University of Science and Technology and Iran's National Elites Foundation is gratefully acknowledged.

Institutional Review Board Statement:

Informed Consent Statement:

Data Availability Statement:

Conflicts of Interest: The authors declare no conflict of interest.

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