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The ability to design new metal-organic structures (MOF) from different functional groups and different metals can lead to multifunctional materials with discrimination capacity between chemically similar structures. Furthermore, MOFs produced at nanoscale (nano-MOF) appear as innovative and highly promising materials for the development of improved bioanalytical applications (e.g. chemical sensing). Here, a water-stable green copper-based nano-MOF, [Cu(DHBDC)(H$_2$O)$_2^{-}$(DMF)$_x$] (1), was prepared at the nanoscale size using polyacrilic acid at 5°C in order to obtain nanocrystals. The resulting nano-MOF display an intense fluorescence behaviour, where the presence of strong basic aliphatic amines with low cone angle lead to “turn-off” of the emission at a rate depending on their nature. The new nano-material proved to be useful as a discriminative sensor of amines either in vapor phase via colorimetric detection or in water solution by luminescence analysis.
ARTICLE

Introduction

Metal–organic frameworks (MOFs), also known as coordination polymers (CPs), are a kind of crystalline porous materials possessing high porosity (up to 90% free volume) and a Langmuir surface beyond of 10 000 m²/g.¹ Their unique chemical (sorptive, chiral, catalytic) and physical (optical, electronic, magnetic) properties² make them valuable for a broad range of applications such as removal of toxics and pollutants, gas adsorption, sensors, catalysis, drug delivery, bioimaging, biomedical and antimicrobial activities. Also, they are components in the fabrication of elements for batteries, supercapacitors or fuel cells.³

In addition, the customizable pore sizes/nature and/or the installation of specific recognition groups in the MOF structure allow for the modulation of the affinity towards distinct classes of chemicals being of high value in development of improved analytical and bioanalytical applications.

MOFs are constructed from metal ions or clusters bridged by polydentate organic groups to form one-, two-, or three-dimensional infinite networks.⁴ The used metals are broadly distributed across the Periodic Table⁵ and most of the linking ligands are neutral N-donor heterocycles or anionic polytopic carboxylates,⁶ although more exotic species like phosphonate⁷ or even “edible”⁸ ligands have been also satisfactorily utilized. In the past decades, the number of papers in the field has been growing incessantly⁹ and, accordingly, the design of the MOFs has improved significantly.¹⁰

Thus, apart from the different methods employed in their preparation¹¹ some other factors have been studied,¹² namely, the nature of the solvent, the concentration and ratio of reactants, the stirring conditions, and the presence of additives. Despite the efforts carried out to prepare novel MOFs with new compositions and structures, only a reduced number of MOFs have been commercialized. That is because the direct synthesized MOFs are usually hindered by physical and chemical limitations, leading to poor performance in practical uses.¹ Fortunately, it has been found that certain MOFs can be modified post-synthetically altering the properties of the pristine material and, consequently, obtaining new MOFs better adapted to realistic applications.¹²

The preparation of nanosized metal-organic frameworks, n-MOFs, have attracted a permanent interest as far as they seem to offer new applications or better performance than their macroscopic counterparts in various research areas do. As an example, nanosized MOFs have higher surface-to-volume ratios in comparison with their larger counterparts, showing faster diffusion rates and therefore faster response to interaction with other species. Although many laboratories have developed particular recipes to synthesize them, only recently¹³ it has been offered a general hypothesis about the conditions that facilitate their formation.

Among MOF materials, the carboxylate linker 2,5-dihydroxy-1,4-benzenedicarboxylic acid, is one of the most utilized.¹⁴ This ligand can act as full deprotonated linker, (2,5-dioxy-1,4-benzenedicarboxylate), DOBDC⁴, giving rise to a whole family of MOFs, named MOF-74 (or CPO-27), [M₂(DOBDC)(Solvent)ₓ]ₙ(Solvent), where M are divalent metal cations.¹⁵ The same ligand can also act as a dihydroxyterephthalate diphenol linker, 2,5-dihydroxy-1,4-benzenedicarboxylate, DHBDC², originating [M(DHBDC)] or [M₂(DHBDC)ₓ] MOFs for di or trivalent metal cations.¹⁶ Surprisingly, although the Cu-MOF-74 has been synthesized long time ago,¹⁷ only recently [Cu(DHBDC)(DMF)₂]·DMF, [Cu(DHBDC)(DMF)·(H₂O)·DMF] and Cu(DHBDC)(H₂O) have been prepared.¹⁸ In any case, it should be stressed that the resulting materials were synthesized in the micro-size scale and it would be desirable, for sensing purposes, to reduce the particle size to the nanoscale. In fact, moving to nanoscopic size implies increasing significantly the surface to volume ratio of the MOF, rising the exposed active sites and improving the diffusion of the analytes towards these active sites.¹³,¹⁹

Herein, we present the synthesis of a light green new nano-MOF, namely [Cu(DHBDC)(H₂O)ₓ]·(DMF)ₙ (1). The procedure here reported led to the formation of particles nearly spherical and having dimensions of only few nanometers in diameter. Resulting nano-MOFs can be used as an efficient dual fluorescent-colorimetric discriminative sensor of amines. Optical sensing of amines is a matter of permanent interest,²⁰ and several MOF materials demonstrated to be appropriate for this purpose.²¹ However the number of MOFs able to use simultaneously luminescence quenching in solution and vapochromism to detect amines is scarce. In this context, a Mg-MOF bearing napthalenediimide ligands was demonstrated to be able to detect organic alkyl amines by photoluminescence quenching and visual color change.²² Furthermore, the quenching luminescent efficiency that undergoes an Eu-MOF containing 1,1’-bis(4-carboxyphenyl)-(4,4’-bipyridinium) ligands in the presence of organic amines in MeOH follow the order of amine sizes. It also changes its color in presence of amine vapors.²³ A Zn-MOF that contains encapsulated naphthalene can serve as a luminescent (in EtOH) and colorimetric probe for the detection of strongly basic organic amines, the quenching by trimethylamine is slower due to its bulky size²⁴ and a Zr MOF UiO-67 containing electron-deficient bipyridinium sites shows fast and reversible vapochromism and luminescence quenching in response to alkylamines.²⁵ Moreover, solid samples of the Zr MOF (UiO-67-DQ–PsO) where DQ is the electron-deficient...
diquat unit and PsO is the electron-rich 1-pyrenesulfonate anion, exhibits vapochromism and luminescent quenching in presence of alkylamines. Ammonia, aniline and small primary aliphatic amines induces vapochromism in a Eu-MOF with a tripyridinium-tricarboxylate linker, while t-butylamine and aniline produce its luminescence quenching. Various post synthetic derivatized of a Zr-bipy MOF exhibit vapochromism and fluorescence quenching in presence of ammonia and different amines. However, it must be highlighted that none of these previously reported examples use nano-MOFs for amines sensing.

Intriguingly, only a few members of the large family of MOFs containing DOBDC have been used as ammonia\(^{16,29}\) or amine sensors. The new n-MOF [Cu(DHBDC)(H\(_2\)O)\(_2\)·(DMF)]\(_x\) (1), here synthesized and characterized, results to be very sensitive to the presence of strong basic amines with low cone angle both, in vapor phase and in solution.

Results and discussion

Synthesis and characterization of [Cu(DHBDC)(H\(_2\)O)\(_2\)·(DMF)]\(_x\). In the first steps of the synthesis of the bright red Cu-MOF-74, we detected the presence of a greenish material. This prompted us to change the reactions conditions in order to isolate it. After several attempts, we found out that lowering the temperature to 5°C, using a ligand to copper 1.5/1 ratio and N,N-dimethylformamide as solvent we were able to prepare a new nano-MOF 1.

Thus, stirring 2,5-dihydroxyterephthalic acid with Cu(CH\(_3\)COO)\(_2\)·H\(_2\)O using DMF as solvent, at 5°C for 72 h, in the presence of of poly(acrylic acid) (PAA),\(^{13}\) we obtained a green solid. This crude was washed successively with water and ethanol to obtain light green nanoparticles of [Cu(DHBDC)(H\(_2\)O)\(_2\)·(DMF)]\(_x\) (1). The average size of the n-MOF 1 particles was found to be of 35 nm diameter, as reveals the TEM micrographs (see Figure 1).

![Figure 1. Transmission electron microscopy (TEM) image and histogram size distribution plot of 1.](Image)

1 nanoparticles are air stable in water solutions as evidenced by IR DRX and TEM (See Supplementary Information Figures S1-S5). This property is remarkable since only a small portion of MOFs are known to be free from problems with water stability.\(^{31}\) In particular, several copper carboxylate MOFs are humid stable only for short periods of time.\(^{32}\) Additional studies on the stability of Cu-MOFs support the need for enhanced stability of these complexes.\(^{33-35}\)

When the reaction was carried out without PAA, the size of the particles was increased (See Supplementary Information Figure S6) but the obtained IR and DRX were identical. When intermediate amounts of PAA are used, particles of different sizes are obtained mixed together. The ζ potential of 1 was determined to be -11 mV (See Supplementary Information Figure S7), which is in accordance with the presence of carboxylic acid groups of the linker on its external surface. It seems to be big enough to ensure the dispersion of the small NP of the nano-MOF 1 in water for several hours without any observable aggregation.

The infrared spectrum of 1 (See Figure S1, Supplementary Information) shows bands in the 3500-3000 cm\(^{-1}\) region are attributable to the ν\(_{O-H}\), and ν\(_{C-H}\) stretching vibrations. The signals between 1631 and 1300 cm\(^{-1}\) correspond to the symmetric and asymmetric stretching ν\(_{COO}\) vibrations of the carboxylate groups and the stretching ν\(_{C-C}\) vibrations of the benzene ring of the linkers and their wavenumber and relative intensities constitute a characteristic pattern of the infrared spectrum of a MOF with a determined set of benzenedicarboxylate ligands. The peak at 1241 cm\(^{-1}\) can be attributed to the stretching ν\(_{C-O}\) vibration of the carboxylate groups.

The band at 1631 cm\(^{-1}\) suggests the ligand is coordinated only through the carboxylate groups, (DHBDC)\(^{36}\) which is also in accordance with a Cu/DHBDC 1/1 ratio as indicates the elemental analysis.

The elemental analysis of 1 (See Experimental Section) and its TGA thermogram (See Supplementary Information, Figure S8) strongly support the proposed molecular stoichiometry.

The powder X-ray diffractogram of [Cu(DHBDC)(H\(_2\)O)\(_2\)·(DMF)]\(_x\) (1) (Figure 4) evidences its low crystallinity probably due to the small size of the obtained nanoparticles. We were able to obtain crystals by slowly adding a solution of 2,5-dihydroxy-1,4-benzenedicarboxylic acid onto a DMF solution of Cu(CH\(_3\)COO)\(_2\)·H\(_2\)O, contained in jacketed Schlenk tube at 5°C, but the DRX diffractogram is quite different of that obtained for nano-MOF 1 and therefore, its structure is not that of the MOF we are using in our experiments. This is not surprising since ref 18 shows that for MOF’s of [Cu(DHBDC)][DMF]\(_x\)(H\(_2\)O)\(_y\) stoichiometry, the structures are very dependent of x and y values and the Cu coordination sphere varies drastically from one MOF to another. Furthermore, our diffractogram is completely different of the related MOFs of [Cu(DHBDC)][DMF]\(_x\)-DMF, [Cu(DHBDC)][DMF][H\(_2\)O]\(_x\)-DMF and Cu(DHBDC)(H\(_2\)O) and it does not contain any mixture of them (See Fig S4 of ref 18).

On the other hand, the n-MOF 1 was found to exhibit an intense fluorescence emission when dispersed in water. In fact, it shows a strong UV absorption band at 350 nm with an luminescence emission centred at 530 nm. (See Supplementary Information Figure S9). Interestingly the resulting n-MOF exhibited a luminescence behaviour showing a high Stokes shift allowing an easy separation between excitation and emission photons, that
results highly valuable in case of designing simple optoelectronic instrumentation. When trying to functionalize the n-MOF 1 we noticed that the product was very reactive, particularly the light green colour of its dispersion in water vanishes in the presence of amines. This observation induced us to study the phenomenon more carefully. Thus, we observed that the fluorescence of the aqueous solutions of n-MOF 1 fade out in the presence of amines and the colour of solid samples of 1 change when exposed to amine vapours. In photoluminescence sensors the MOF serves as a transducer and recognition material. The photoluminescence of MOFs can be attributed to various sources,37 being the most significant: (i) the luminescence characteristics of organic linkers (typically extended π-conjugation systems with rigid structures); (ii) metal-based emissions, like those found in lanthanide-based MOFs; (iii) metal–to–ligand charge transfer, (e.g. that found in Cu(I) or Ag(I) based MOFs); (iv) ligand–to–metal charge transfer, like that occurring in Zn(II)/Cd(II) and carboxylate ligand-based MOFs; (v) ligand–to–ligand charge transfer, also known as the antennae effect, which involves the indirect excitation of the metal, (e.g., in the case of MOFs with absorbing ligands such as π- and α-bonded antenna ligands) and emitting lanthanide ions and (vi) fluorophores loaded as guest molecules in the MOF pores, like guest-centered emission and guest-sensitization. The vast majority of luminescent metal-type MOFs can be classified into two groups: lanthanide-based MOFs (Ln-MOFs) and transition metal-based MOFs.38 Zn- and Cd-MOFs are the most frequently reported luminescent transition metal-based MOFs because d10 metal ions have multiple coordination numbers and geometries and glow when attached to functional ligands. Transition metals typically do not possess intrinsic luminescence; instead, they participate in ligand–to–metal charge transfer (commonly reported in Zn- and Cd-MOFs) or metal–to–ligand charge transfer processes (commonly detected in Cu- and Ag-MOFs) to modulate the MOF emission.39 Fluorescence sensing experiments. Amines are key intermediates in industrial organic synthesis, but they are also environmental pollutants and harmful to human health. They are present in household cleaning products, refrigerant gas, pesticides, plastics, dyes, and other chemicals. In addition, amines are markers for food freshness and medical diagnosis. A major and ongoing hazard to the environment, amines ‘corrosive nature, can also cause lung damage, respiratory issues, and skin irritation, among other health issues.40 Consequently, it is necessary to detect amines at low concentration levels. The presence of amines is commonly determined using complicated, time consuming and expensive centralized analytical techniques. In contrast, simpler and low-cost sensing methods like those based on luminescence measurements are becoming popular due to their simplicity, high sensitivity and capabilities for developing portable devices for in-situ measurements. In this context, MOFs are being used as amine sensors in solid, solution, or vapor phase by the change of color, luminescence quenching or enhancement even by fluorescence shift.30

Thus, fluorescence sensing experiments were conducted in a systematic way where the emission spectra of the n-MOF were recorded in aqueous medium, followed by the measurement every two minutes (until ½ h) of the fluorescence intensity of a water dispersion of 0.005 mg/mL in the presence of the amine under scrutiny at 1mM concentration. The sensing studies were carried out using a selection of different primary, secondary and tertiary amines namely, ethylamine (EA), propylamine (PA), aniline (Ani), diethylamine (DEA), piperidine (Pip), triethylamine (TEA), and pyridine (Py) (See Figure 2).

Figure 2. Evolution with the time of the fluorescence spectra of a water dispersion of 0.005 mg/mL after addition of 0.001 M of: A) propylamine (PA); B) ethylamine (EA); C) piperidine (Pip); D) diethylamine (DEA); E) trimethylamine (TEA); F) Aniline (Ani); G) pyridine (Py). Table 1. The pKa of the conjugated acids (R, NH+) and the cone angle (C.A.) of the used amines

<table>
<thead>
<tr>
<th>Amine</th>
<th>EA</th>
<th>PA</th>
<th>Pip</th>
<th>DEA</th>
<th>TEA</th>
<th>Py</th>
<th>Ani</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKa</td>
<td>10.65</td>
<td>10.54</td>
<td>11.12</td>
<td>10.84</td>
<td>10.75</td>
<td>5.23</td>
<td>4.87</td>
</tr>
<tr>
<td>C.A.</td>
<td>106</td>
<td>106</td>
<td>121</td>
<td>125</td>
<td>150</td>
<td>---</td>
<td>111</td>
</tr>
</tbody>
</table>

Interestingly, the n-MOF materials’ fluorescence intensity was quenched in less than 30 minutes by more than 90% when 1mM of PA (primary amine) was present in the media. Conversely, the fluorescence quenching degree produced by Pip and DEA is lower as compared with PA. The effect of the presence of other amines, such as pyridine (Py) on the fluorescence of the n-MOF 1 was found to be negligible (See Figure 2). Results obtained allowed to order the different amines according to the rate of nano-MOF fluorescence quenching as follows: EA > PA > Pip > DEA ≈ TEA ≈ Py ≈ Ani. This sequence suggests that the basicity of the amines plays an important role in the observed quenching rate (see the pKa of their conjugated
In general, the sensing of amines by MOFs in solution can be fluorescence quenching, EA, with a cone angle of 106°, is the most active, and DEA, with a cone angle of 125°, lies in between. The other amines in the series (Py), triethylamine (TEA), piperidine (Pip), propylamine (PA), ethylamine (EA) and diethylamine (DEA). The MOF sensors that experience fluorescence quenching by the presence of amines in water solutions are scarce. One of them is only sensitive to the aromatic amines. Another one detects amines of different electron donor ability being the less basic amines those with lower luminescent quenching ability, while the other two are very sensitive to the alkyl amines, but there is no an order between them.

Vapochromic behaviour of 1 towards amines. The effect on the luminescence of solid samples of 1, when treated with vapors of all the selected amines previously mentioned, was also investigated. Amines are known to be highly volatile and mostly released to environment as gas or vapor media. Thus, it becomes essential to design a sensing material that can rapidly detect volatile organic amines.

Taking into account the discolouration of the water dispersion of 1 in presence of primary amines we wondered if the presence of amine vapors would also modify the solid samples of 1. It would be of great value in the eventual design vapochromic probes able to detect amines in its vapor phase with a clear color change of the sensor material. Keeping this in mind, as-synthesized n-MOF 1 crystals were deposited in a small petri dish inside a closed container and exposed to different amine vapors during 30 minutes.

In the Figure 3 it is shown the picture of a solid sample of the starting material 1 and of those of the samples of 1 after 30 m in contact with the vapors of aniline (Ani), pyridine (Py), triethylamine (TEA), piperidine (Pip), propylamine (PA), ethylamine (EA) and diethylamine (DEA). Although aniline and pyridine do not appear to affect very much the n-MOF colour, interestingly the other tested amines produced a clear color change in the deposited n-MOF 1, from green to light (TEA and DEA) or dark brown (Pip, PA and EA). This shows that n-MOF 1 has vapochromic properties.

**Monitorization of the process.** The effect of the vapor of these amines upon a sample of n-MOF 1 can be studied comparing the powder X-ray diffractograms of the resulting samples with that of the starting material, all of them included in Figure 4. They exhibit an increasing loss of crystallinity from that of the aniline derivative to the diffractogram of the piperidine derivative; the peaks in the diffractograms are always the same (see Figure 4), indicating that a crystalline core remains along the decomposition processes.

On the contrary, the diffractograms corresponding to final products of the reactions between n-MOF 1 and PA, EA and DEA indicate that new crystalline (unknown) materials have been formed.

![Figure 3. Pictures of a sample solid of 1 before (MOF picture) and after being exposed 30m to vapors of aniline (Ani), pyridine (Py), triethylamine (TEA), piperidine (Pip), propylamine (PA), ethylamine (EA) and diethylamine (DEA).](image1)

![Figure 4. Powder X-ray diffractograms of 1 before (MOF) and after being exposed 30 min to vapors of aniline (Ani), pyridine (Py), triethylamine (TEA), piperidine (Pip), propylamine (PA), ethylamine (EA) and diethylamine (DEA).](image2)
they are exhibited in Figure 5. The IR spectra of the samples treated with aniline and triethylamine vapors are coincident with that of the starting material (see Figure 5), confirming that there is not any reaction of n-MOF 1 with aniline. In the case of TEA, the change of color and the loss of crystallinity (see Figures 3 and 4) clearly indicate that the amine reacts with 1, but the infrared spectrum does not provide any evidence about the nature of this reaction product.

The IR spectrum of the pyridine derivative is almost coincident with that one of 1, but it has some extra weak peaks. The new absorptions could be assigned to a coordinated pyridine Cu-py (1486, 1070, 1046, and 693 cm\(^{-1}\)) \(^{46}\), pyH\(^+\) (1607, 1379 and 757 cm\(^{-1}\)) \(^{17}\) and, tentatively, to DHBDC (\(C_8H_7O_4\)) (1419 cm\(^{-1}\)), which could be the anionic counterion of the pyridinium cation. In fact, a band at 1419 cm\(^{-1}\) is present in the IR spectrum of 2,5-dihydroxy-1,4-benzenedicarboxylic acid (solid) after being exposed to propylamine vapor due to the formation of (\(C_8H_7NH_3\))\(^+\)(\(C_8H_7O_4\)). On the other hand this is the expected product since the reaction of 2,5-dihydroxy-1,4-benzenedicarboxylic acid with ammonia gives (NH\(_2\))(\(C_8H_7O_4\)).

Figure 5. FTIR spectra of 1 before (MOF) and after being exposed 30 min to vapors of aniline (Ani), pyridine (Py), triethylamine (TEA), piperidine (Pip), propylamine (PA), ethylamine (EA) and diethylamine (DEA).

The IR spectra of the other amine derivatives (Pip, PA, EA and DEA) increasingly differ from that of the n-MOF 1, suggesting that the reaction of the amines with 1 destroy more and more the starting material, a process also detected by the corresponding PXRD diffractograms.

On the other hand, the IR spectra of PA, EA and DEA derivatives, show some similarities. Thus, they contain bands characteristic of the alkylammonium salts cations,\(^{37,48}\) including a broad band about 3400 cm\(^{-1}\) due to N-H stretching (see Fig. 5 and Supporting Information). Their counterion should be the anion (\(C_8H_7O_4\)) as indicates the presence of a peak about 1414 cm\(^{-1}\).

Interestingly, their spectra exhibit bands close to characteristic peaks of Cu-MOF-74\(^{49}\) namely, 1552(s), 1419 (s), 1249 (w), 1187 and 828 (m) cm\(^{-1}\), but their PXRD diffractogram differ from that of Cu-MOF-74\(^{40}\). These coincidences suggest the formation of new products containing the moiety DOBDC, (\(C_8H_7O_4\))\(^4\), as ligand, also detected by the lower intensity of the band at 1631 cm\(^{-1}\), due to (\(C_8H_7O_4\))\(^2\) ligand.

Experimental section.

Materials and methods. Polyacrylic acid, copper (II) acetate monohydrate (≥ 99.0%), 2,5-Dihydroxysterephthalic acid (98%), N,N-Dimethylformamide (≥ 99.8%) were obtained from Sigma-Aldrich (Spain) and Ethanol (96% vol) was purchased from VWR chemicals.

The FT-IR measurements were conducted utilizing a Spectrum RXI FT-IR Spectrometer by PerkinElmer (USA), employing KBr pressed disks. The MET JEOL 1011, operating at 100KV, was employed to capture transmission electron microscopy (TEM) images on a copper grid. The ImageJ software was utilized for size estimation by measuring the largest dimension of individual particles. X-ray powder diffraction (XRPD) data for the particles were collected at room temperature (RT) using CuKα1,2 radiation (\(λ = 1.54056\ Å and 1.54439\ Å\) with a Bragg-Brentano reflection setup. This was conducted on a PHILIPS XPERT PRO Panalytical diffractometer within a 2θ range spanning 5–80°, employing a step size of 0.0167. Thermogravimetric analysis (TGA) and elemental analysis were performed using a TG-DSC analyzer, SETSYS Evolution 1750 (Setaram), and a Carlo Erba 1108 elemental analyzer, respectively. These analyses were conducted in collaboration with the C.A.C.T.I. at the University of Vigo. Copper analysis were performed through elemental mass spectrometry (i.e. ICP-MS analysis). For such purpose, nano-MOF samples were dried and digested using aqua regia (30 min under ultrasonic bath). Copper (Cu) quantification was performed in the resulting solution using an ICP-MS/MS equipped with a triple quadrupole (Agilent 8900, Agilent Technologies, Japan). Operation conditions were daily optimized using a tuning solution. Cu isotopes were detected using “on-mass mode” (\(^{65}Cu\), \(^{63}Cu\)). Helium was introduced into the collision/reaction cell at a flow rate of 5 mL min\(^{-1}\). Dwell time for each of the targeted isotopes was 1 s. Cu was quantified using external calibration prepared using certified 1000 mg/L Cu standard solution (Merck, Germany). All fluorescence measurements were carried out using a Varian Cary Eclipse Fluorescence Spectrometer (Agilent, Germany), equipped with...
a xenon discharge lamp and a photomultiplier tube detector (Model R-298). Fluorescence spectra were registered with a fixed excitation wavelength of 350 nm and with excitation and emission slit widths of 5 nm. The measurements were performed at room temperature and atmospheric pressure, employing quartz fluorescence cells.

Synthesis of [Cu(DHBDC)(H$_2$O)$_2$·DMF]$_2$ (1). For MOF synthesis, dissolve 0.5300 g of polyacrylic acid (PAA) (7.35 mmol) in 10 mL DMF. After dissolving the PAA, 0.3000 g of 2,5-dihydroxyterephthalic acid (DHBDC) (1.47 mmol) is added to the vial containing the PAA and shaken until dissolved. At the same time, 0.2000 g of copper (II) acetate monohydrate (CuAc$_2$·H$_2$O) (0.99 mmol) is dissolved in 10 mL DMF in a Jacketed glass Schlenk. The DHBDC+PAA mixture is slowly added to the Jacketed glass Schlenk, stirring vigorously for about 5 minutes. During addition, a chocolate brown color is observed in the area where the drop falls, which disperses on stirring. When all the ligand has been added, the entire content of the Jacketed Schlenk is observed to become brown, but after a few minutes it turns a bright light green color in a perfectly transparent solution. The mixture is left to stir for 72 h at 5°C. The resulting product has a very intense light pastel green color, and is centrifuged in two 10 mL portions at 9158 g for 10 min. Each portion is washed with 5 mL DMF and re-centrifuged twice. The centrifugate is washed with 10 mL milli-Q water and re-centrifuged in two 10 mL portions at 9158 g for 10 min. Each portion is washed with 5 mL DMF and re-centrifuged twice. The centrifugate is washed with 10 mL milli-Q water and re-centrifuged, repeating this process one more time. On washing with water, the pastel colour of the compound is slightly lost in favor of a slightly darker color. Finally, the contents of both tubes are suspended in one in 10 mL of ethanol, centrifuged and dried under vacuum. Anal. Calcd for Cu(DHBDC)(H$_2$O)$_2$·2DMF·13·C, 33.27; H, 2.88; N, 0.61; Cu, 20,9. Found: C, 32.21; H, 2.95; N, 0.53; Cu, 17,20.

Conclusions

In summary, a novel copper-based nano MOFs was synthesized and investigated in detail for discriminative sensing of amines. The synthetic method proposed here produces nano MOFs with a fairly homogeneous size and morphology. Furthermore, the produced nano MOF maintains its chemical stability in aqueous media, which is of utmost importance if it is intended to be used for bio-applications. The resulting frameworks are efficient luminescent probes for discriminative detection of different amines via “turn-off” fluorescence emission. The solid n-MOF 1 do not react with aniline, the less basic of the used amines and reacts moderately with py, also a very weak base. The attack of the other amines destroy the starting material, although in the case of PA, EA and DEA new crystalline unknown products are formed. The mechanism of reactions could have some similarities. Initially the amines would replace the coordinated water entering the copper coordination sphere, then the amines extract the carboxylic ligand giving the salts (ammonium)$^+$ (C$_2$H$_4$O$_3$)$^-$, liberating OH$^-$ anions which eventually could favor the generation the (2,5-dioxy-1,4-benzenedicarboxylate) tetra-anion ligand.

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Data availability statements

The data supporting this article have been included as part of the Supplementary Information. See DOI: 10.1039/x0xx00000x