

## PAPER

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[View Journal](#) | [View Issue](#)Cite this: *Mater. Adv.*, 2023,  
4, 5730Enhancing the sensitivity of a water stable MOF  
as a H<sub>2</sub>S gas sensor by the fabrication of a  
mixed-matrix membrane†Mouli Das Dawn,<sup>a</sup> Karabi Nath,<sup>a</sup> Subhajit Saha,<sup>a</sup> Pritam Kumar Roy,<sup>b</sup>  
Mahitosh Mandal<sup>b</sup> and Kumar Biradha<sup>a</sup>✉

Hydrogen sulfide (H<sub>2</sub>S) is a smelly, colorless, and hazardous gas even at sub-ppm level, produced predominantly from natural and anthropogenic sources. It is also called a 'knock-down gas' as its inhalation at higher concentrations can cause death. Therefore, several researchers are working on designing sensors with high stability and robustness for the real-time detection of H<sub>2</sub>S gas. Apart from many other materials, metal–organic framework (MOF)-based fluorescent probes are of high interest for the detection of H<sub>2</sub>S. Herein, we present a cost-effective acryl-amide functionalized 2D **Zn-bdc** MOF, which was shown to function as an excellent probe for the real-time detection of H<sub>2</sub>S in liquid as well as in the gaseous form through a nucleophilic addition mechanism to olefinic bonds of the MOFs. Interestingly, in the aqueous phase, **Zn-bdc** was found to exhibit turn-off and subsequent turn-on fluorescence spectra with the gradual addition of H<sub>2</sub>S. Furthermore, the realistic sensing of H<sub>2</sub>S by the MOF was investigated by preparing a mixed-matrix membrane of MOF with PVDF as a binder. Notably, the membrane with 60% loading of **Zn-bdc** increased the probe's sensitivity by two-fold. Furthermore, we note that this is the first example of an essential metal based mixed-matrix membrane for H<sub>2</sub>S detection with the LOD value as low as 5.3 μM. *In vitro* cell imaging of **Zn-bdc** in the presence of H<sub>2</sub>S displays a vibrant bright red fluorescence signal of LN-18 glioblastoma cells.

Received 8th September 2023,  
Accepted 10th October 2023

DOI: 10.1039/d3ma00681f

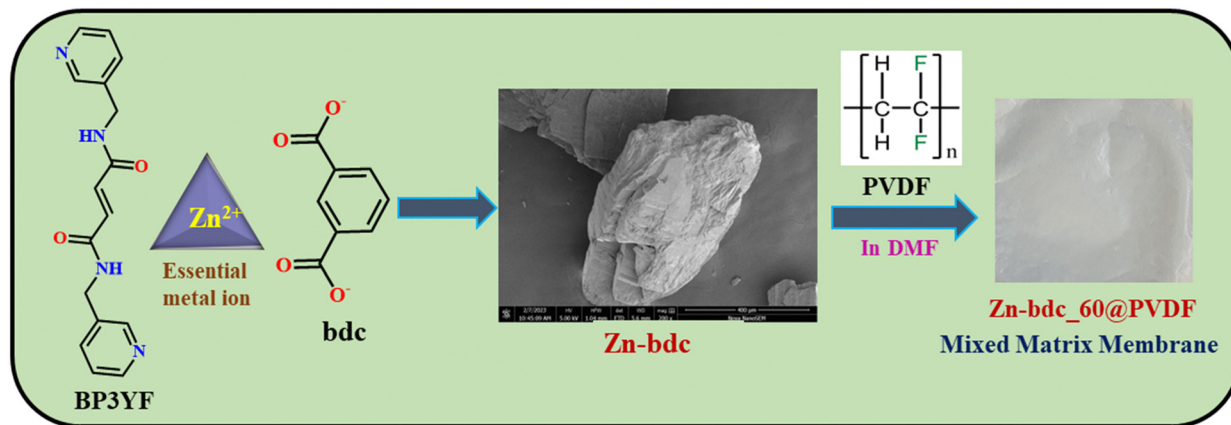
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## Introduction

A recent upsurge in the development of thin-film based sensors for detecting toxic gases such as H<sub>2</sub>S, CO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub>, and NO<sub>2</sub> has drawn rigorous attention given their industrial applications.<sup>1,2</sup> Among these gases, hydrogen sulfide (H<sub>2</sub>S) is a flammable, colorless, and deadly poisonous gas with the odour of rotten eggs and plays an effective role as a hazardous chemical in the environment.<sup>3</sup> H<sub>2</sub>S is released into the environment as a by-product through various industrial processes in the chemical and pharmaceutical industries of natural gas production, petroleum refining and drilling, and also by the decomposition of sulfur-containing bio-molecules.<sup>4</sup> In mammals, the endogenous concentration of H<sub>2</sub>S normally is at

10–100 micromolar level.<sup>5</sup> The deregulation of endogenous concentration of H<sub>2</sub>S in the human body causes various types of diseases like Alzheimer's, Parkinson's, diabetes, and cancer.<sup>6,7</sup> In addition to this, prolonged exposure to H<sub>2</sub>S vapor in a healthy body may also cause irritation of the eyes, nausea, headaches, respiratory failure, conjunctivitis, loss of sleep, and even death. Thus, the detection of H<sub>2</sub>S in its gaseous phase is just as important as in the solution phase. Therefore, it is essential to develop a quantitative technique for the fast, selective, and sensitive detection of exogenous as well as endogenous H<sub>2</sub>S in solution and in the gaseous phase. In this context, fluorescent H<sub>2</sub>S probes are advantageous over other conventional techniques,<sup>8–12</sup> given their rapid response, simplicity in implementation, cell permeability, economic friendliness, and suitability for real-time detection.<sup>13–17</sup> To date, three fundamental strategies are in use for the development of fluorescent H<sub>2</sub>S probes based on their reaction with H<sub>2</sub>S: (a) reductive reaction with H<sub>2</sub>S: reduction of nitro or azide to amine, and reduction of selenoxide to selenide; (b) nucleophilic addition reaction by H<sub>2</sub>S: Michael addition reactions, addition to double bonds, dual nucleophilic reactions and thiolysis reactions; (c) precipitation reactions by H<sub>2</sub>S as Hg<sup>2+</sup>/Cu<sup>2+</sup>/Au<sup>2+</sup>/Ag<sup>+</sup> sulfides.<sup>18–24</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, India. E-mail: [kbiradha@chem.iitkgp.ac.in](mailto:kbiradha@chem.iitkgp.ac.in)<sup>b</sup> School of Medical Science and Technology, Indian Institute of Technology, Kharagpur 721302, India† Electronic supplementary information (ESI) available: Synthesis of BP3YF, Synthesis of MOF, Membrane preparation, XRPD patterns, TGA analysis, XPS plot, FTIR, <sup>1</sup>H-NMR data, cytotoxicity assay analysis, and a comparison table of H<sub>2</sub>S sensing by MOFs. CCDC 2282228–2282230. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3ma00681f>



**Scheme 1** Chemical structures of the ligand, metal, and ancillary ligand of **Zn-bdc** with FESEM image and preparation of the mixed-matrix membrane of **Zn-bdc\_60@PVDF**.

Coordination polymers (CPs)/metal-organic frameworks (MOFs) have been at the center of attraction over the last two decades owing to their multi-dimensional applications in gas separation and storage,<sup>25–29</sup> guest inclusion,<sup>30</sup> proton conductivity,<sup>31</sup> sensing,<sup>32–37</sup> magnetism,<sup>38</sup> and catalysis.<sup>39,40</sup> MOFs are considered for these applications given their high thermal, and chemical, stability, large porosity, tunable surface area, and amenability for post-synthetic modifications. One of the most developing applications of MOFs is associated with selective sensing of various analytes such as anions, cations, nitro-aromatics, and biological signaling molecules like H<sub>2</sub>S with very low detection limits.<sup>41–44</sup> In very recent years, post-synthetic modification of the functional groups on the well-known MOFs for the detection of H<sub>2</sub>S has been shown as an efficient methodology (Table S5, ESI†). In this regard, vinyl functionalized MOFs of UiO-66 and CAU-10 were demonstrated for their ability in quantitative detection of H<sub>2</sub>S in physiological conditions, which occurs through nucleophilic addition reaction of H<sub>2</sub>S to the vinyl groups of MOFs.<sup>45,46</sup> Further, Huang and co-workers reported malononitrile functionalized UiO-66-NH-BQB MOF for the detection of H<sub>2</sub>S and cysteine simultaneously.<sup>47,48</sup> Recently, we have shown the importance of nitro and azide groups containing Zn-CPs for the detection of H<sub>2</sub>S by following the reductive reaction strategy.<sup>49</sup> Among all the three mentioned methodologies, the synthesis of a fluorescent H<sub>2</sub>S probe based on nucleophilic addition reaction to the olefinic double bond of MOFs is very scarce. For the realistic sensing application of MOFs as a device, it is essential to fabricate their powder forms into thin-film membranes, which is not well explored to date. One such type of reported example is flexible Al-MIL-53-NO<sub>2</sub> MOF-based mixed-matrix membranes used as an H<sub>2</sub>S sensor following the reductive reaction mechanism from the nitro to azide group.<sup>50</sup>

In this endeavor, we wish to present three Zn(II) MOFs (**Zn-bdc**, **Zn-cpb**, **Zn-btc**) containing acryl-amide functionalized organic struts, which have the propensity to detect H<sub>2</sub>S in the solution state as well as in the gaseous state by undergoing the nucleophilic addition reaction. Until now, most of the

MOF-based probes have been explored for H<sub>2</sub>S detection either in the solution or gaseous phases.<sup>51–55</sup> Interestingly, in the aqueous phase, **Zn-bdc** was found to show turn-off and subsequent turn-on fluorescence responses with the gradual addition of H<sub>2</sub>S and proved to be a better probe than **Zn-cpb** and **Zn-btc** in terms of stability, sensitivity, selectivity, and low response time with the detection limit of 10.7 μM. However, for real-time sensing applications using a thin-film based mixed-matrix membrane as a fluorescent H<sub>2</sub>S probe has not yet been fully established. Taking this into account, we synthesized mixed-matrix membranes with highly stable 2D MOF **Zn-bdc** as a filler and poly(vinylidene fluoride) (PVDF) as a binder (Scheme 1). This mixed-matrix membrane was shown to exhibit turn-on fluorescence emission upon exposure to H<sub>2</sub>S vapor following the nucleophilic addition reaction. The limit of detection (LOD) value of the **Zn-bdc** composite membranes was found to be reduced by 2 times compared to the dispersed aqueous phase of **Zn-bdc** MOF. In addition, **Zn-bdc\_60@PVDF** is the first reported essential metal-based mixed-matrix membrane for H<sub>2</sub>S detection with the lowest LOD value of 5.3 μM.

## Results and discussion

BP3YF was synthesized by a simple condensation reaction of 3-(aminomethyl)pyridine and fumaric acid (Scheme S1, ESI†).<sup>56</sup> It was reported by our group earlier that the CPs composed of BP3YF function as adsorbents of oxoanion pollutants and toxic dyes.<sup>57</sup> The complexation reactions were conducted in solvothermal conditions by reacting **BP3YF** with three polycarboxylates such as flexible 4-(4'-carboxyphenoxy)benzoic acid (H<sub>2</sub>cpb), angular benzene-1,3-dicarboxylic acid (H<sub>2</sub>bdc), and rigid benzene-1,2,4,5-tetracarboxylic acid (H<sub>4</sub>btc) with an essential metal Zn(NO<sub>3</sub>)<sub>2</sub>. These reactions produced single crystals of  $\{[\text{Zn}(\text{BP3YF})(\text{cpb})]\}_n$ , (**Zn-cpb**),  $\{[\text{Zn}(\text{BP3YF})(\text{bdc})]\}_n$ , (**Zn-bdc**), and  $\{[\text{Zn}_2(\text{BP3YF})(\text{btc})(\text{H}_2\text{O})_2]\}_n$ , (**Zn-btc**) (Scheme S2, ESI†). **Zn-cpb** and **Zn-bdc** contain dicarboxylate as an ancillary



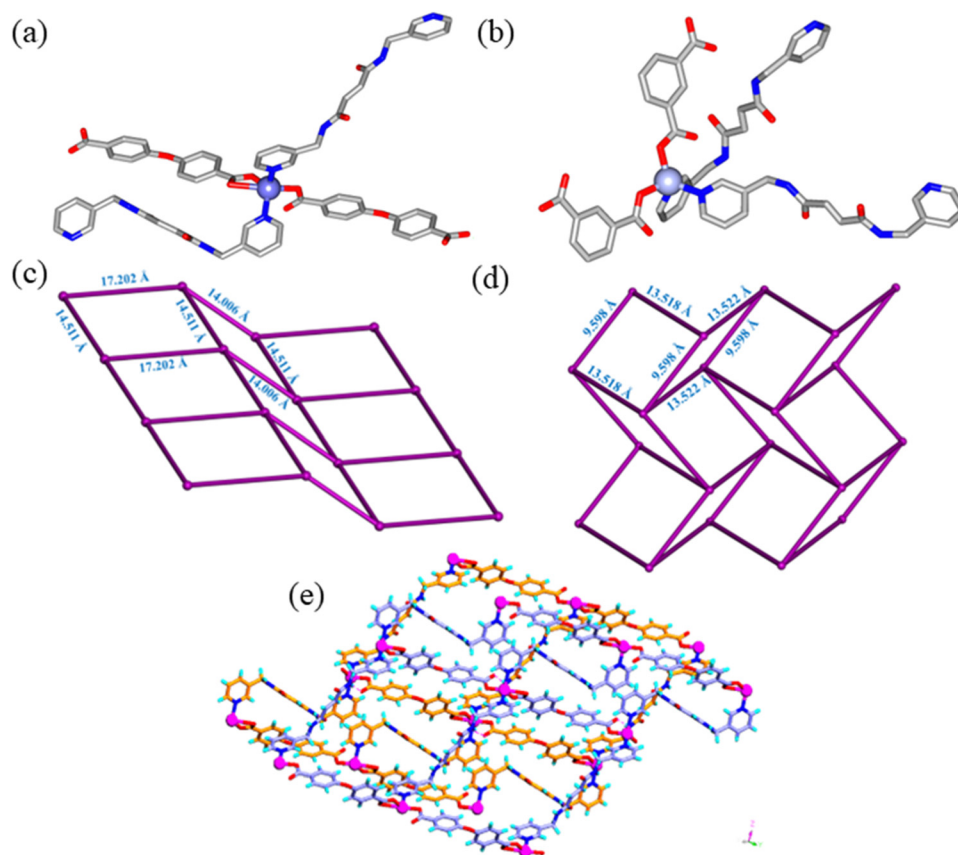


Fig. 1 (a) Coordination environment around the Zn metal centers of **Zn-cpb**; (b) coordination environment around the Zn metal centers of **Zn-bdc**; (c) node connected view of the corrugated 2D-layer in **Zn-cpb**; (d) formation of the node connected corrugated 2D-layered architecture of **Zn-bdc**; (e) packing of the layers of a **Zn-cpb** due to N–H...O interactions.

ligand and resulted in 2D corrugated networks, whereas **Zn-btc** with tetra carboxylate forms a 3D-network. The relevant crystallographic details, selected bond lengths, bond angles, and geometrical parameters of hydrogen bonding of **Zn-cpb**, **Zn-bdc**, and **Zn-btc** are shown in Tables S1, S2 and S4 (ESI†).

Single crystal X-ray diffraction analysis revealed that **Zn-cpb** and **Zn-bdc** crystallized in the  $P\bar{1}$  and  $P2_1/c$  space groups, respectively. The asymmetric unit in **Zn-cpb** is composed of two half units of BP3YF, one unit each of cpb and a Zn(II) ion and that of **Zn-bdc** is composed of one unit of BP3YF, bdc, and Zn(II) metal centers. The Zn(II) central ion adopts distorted square pyramidal coordination geometry in **Zn-cpb** as it coordinates two pyridine units of BP3YF and two cpb units, one of which forms chelation (Fig. 1a). In **Zn-bdc**, the Zn(II) metal centers exhibit distorted tetrahedral geometry as they coordinated to two pyridyl units of BP3YF and two carboxylates of the bdc unit (Fig. 1b). In both structures, Zn(II) ions with the carboxylate of cpb/bdc form a wavy one-dimensional chain (Fig. S1a, ESI†). These one-dimensional chains are further connected through the ligand BP3YF that results in the formation of the corrugated 2D network in both **Zn-cpb** and **Zn-bdc**. In **Zn-cpb**, the 2D-network contains rectangular (14.511 × 17.202 Å) as well as square cavities (14.511 × 14.006 Å) (Fig. 1c and S1b). Whereas the 2D-layers of **Zn-bdc** contain only

rectangular cavities (9.592 × 13.522 Å) (Fig. 1d and Fig. S1c, ESI†). These 2D corrugated layers are packed on each other *via* N–H...O (N...O: 2.8162.826 Å, 159°, 170° in **Zn-cpb** and N...O: 2.30 Å, 177° in **Zn-bdc**) hydrogen bonds (Fig. 1e).

The **Zn-btc** MOF crystallized in the  $P\bar{1}$  space group and the asymmetric unit is composed of one unit of Zn(II) ion, half units each of coordinated BP3YF and btc, and one coordinated water molecule. The Zn(II) metal center in **Zn-btc** adopts a distorted trigonal bipyramidal geometry where the two apical positions are occupied by carboxylate ions and coordinated water molecules whereas the three equatorial positions are occupied by two carboxylate O-atoms and one pyridyl unit (Fig. S1d, ESI†). The Zn(II) metal center and btc units by connecting with each other, resulted in a neutral 2D layer (Fig. 2a). The layers are formed by a bimetallic secondary building unit in which Zn(II) centers are separated by 3.336 Å, and capped by two carboxylates in a  $\mu_2$ -bridging fashion. The 2D-layers are further pillared by BP3YF to generate a 3D-network (Fig. 2b) containing interlayer separation of 12.095 Å. The amide N–H groups form N–H...O hydrogen bonding with the carboxylate O atoms of btc (N–H...O, 1.92 Å; N...O, 2.827 Å, 154.79°).

In order to examine the H<sub>2</sub>S sensing abilities of MOFs in water, the stability of the MOFs was investigated by immersing them in an aqueous medium for seven days. Comparison of the





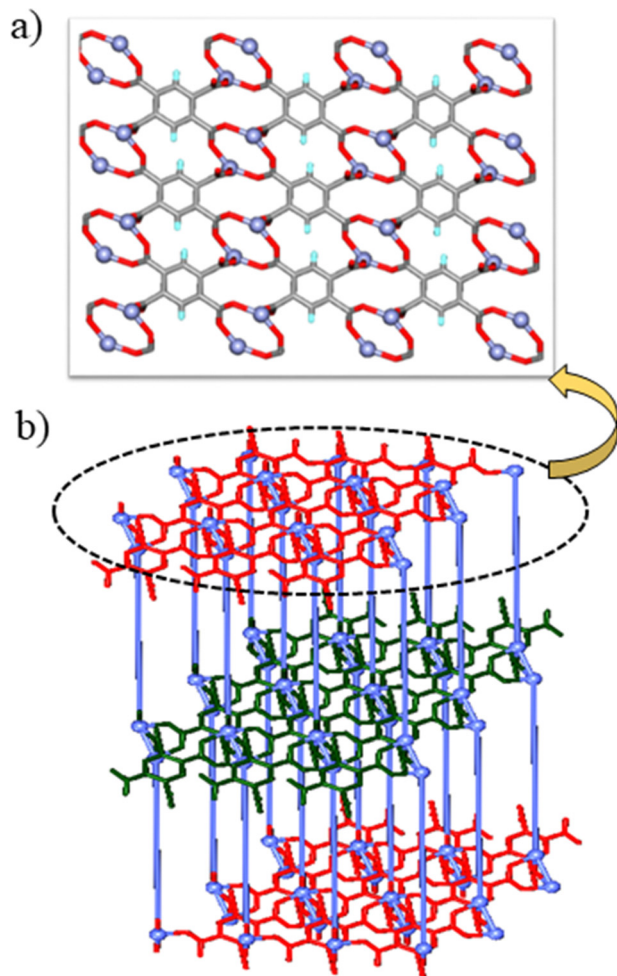


Fig. 2 (a) Formation of a 2D-layer by metal centers and btc moieties; (b) connection of the 2D-layers via the BP3YF ligand as pillars to generate the overall 3D-network.

XRPD patterns of the immersed samples with those of crystallized samples confirmed that two of the three MOFs, namely **Zn-bdc** and **Zn-btc**, are stable in water (Fig. S5, ESI†). The thermal stability of the MOFs was also checked by thermogravimetric analysis (TGA) (Fig. S6, ESI†). **Zn-cpb** and **Zn-bdc** are thermally stable up to 460 °C and 420 °C, respectively. In the case of **Zn-btc**, the initial 8% weight loss was observed at about 203 °C due to the loss of two coordinated water molecules and the network was found to be stable up to 481 °C. Prior to sensing studies, the solid-state luminescence properties of three MOFs and ligand BP3YF were examined at room temperature (Fig. S8, ESI†). BP3YF and all three MOFs have exhibited a luminescence emission maximum at  $\sim 460$  nm ( $\lambda_{\text{ex}} = 290$  nm), which can be attributed to  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  transitions due to Ligand-to-Ligand Charge Transfer (LLCT).<sup>58</sup> The solution state absorbance spectra of BP3YF, **Zn-cpb**, **Zn-bdc**, and **Zn-btc** display a peak around 290 nm wavelength (Fig. S7b, ESI†).

### H<sub>2</sub>S sensing in the dispersed aqueous phase

Interestingly, preliminary investigations on H<sub>2</sub>S sensing in aqueous solutions of MOFs have indicated that they exhibit

initial turn-off and subsequent turn-on fluorescence with the gradual addition of aq. Na<sub>2</sub>S solution. The stock solutions of the MOFs (100  $\mu$ M) were prepared by dispersing the finely ground samples in water such that a uniform suspension was formed. The aqueous solution of **Zn-bdc** was found to exhibit fluorescence at 405 nm with an excitation wavelength of 290 nm, which can be regarded as the ligand-based emission.<sup>59</sup> A blue shift by 55 nm was observed in the fluorescence spectra of **Zn-bdc** in the aqueous phase compared to that of the solid phase (Fig. S8, ESI†). This shift could be due to the differences in the intermolecular interactions in the solid and aqueous phase.<sup>60</sup> In order to explore the H<sub>2</sub>S sensing abilities of the MOFs, an aqueous solution of Na<sub>2</sub>S was prepared as a source of H<sub>2</sub>S (10  $\mu$ M). The quantitative detection of the H<sub>2</sub>S by **Zn-bdc** was studied by systematically adding 2  $\mu$ L portions of the aqueous Na<sub>2</sub>S solution to the 200  $\mu$ L solution of MOFs and monitoring its fluorescence. A gradual fluorescence quenching by 65 percent was observed with the addition of 10  $\mu$ L of Na<sub>2</sub>S solution (0.5 equivalents) in five portions (Fig. 3a).

The subsequent increase of Na<sub>2</sub>S from 10  $\mu$ L to 50  $\mu$ L (2.5 equivalent) resulted in the enhancement of the fluorescence intensity by 4.5-fold (Fig. 4a) with respect to that MOF solution without analyte. To further increase the fluorescence intensity, the addition of Na<sub>2</sub>S also resulted in a clear 6 nm blue shift (hypsochromic shift) that can be attributed to the nucleophilic addition of H<sub>2</sub>S to the olefinic double bond (Fig. 4b). Furthermore, the Stern-Volmer equation ( $I_0/I = 1 + K_{\text{SV}}[X]$ ) was used to

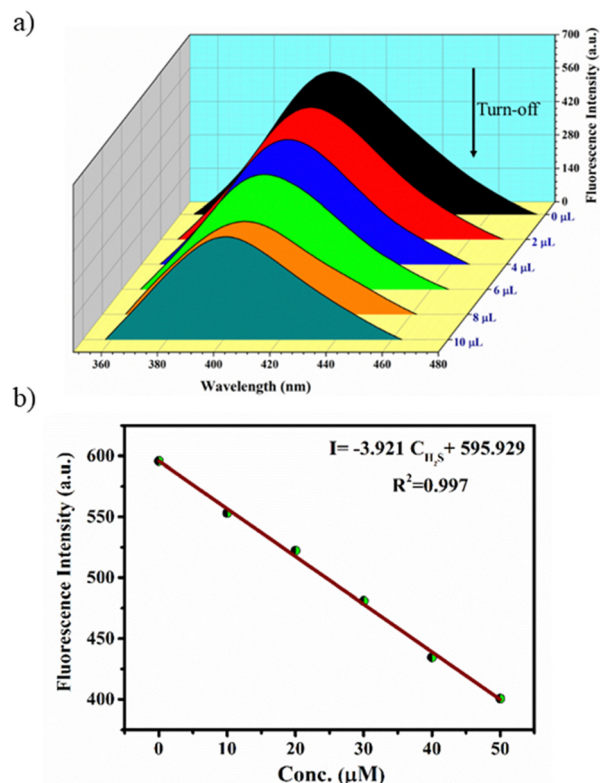


Fig. 3 (a) Fluorescence turn-off response of **Zn-bdc** upon addition of 10  $\mu$ L H<sub>2</sub>S and (b) concentration-dependent fitting curve for turn-off.

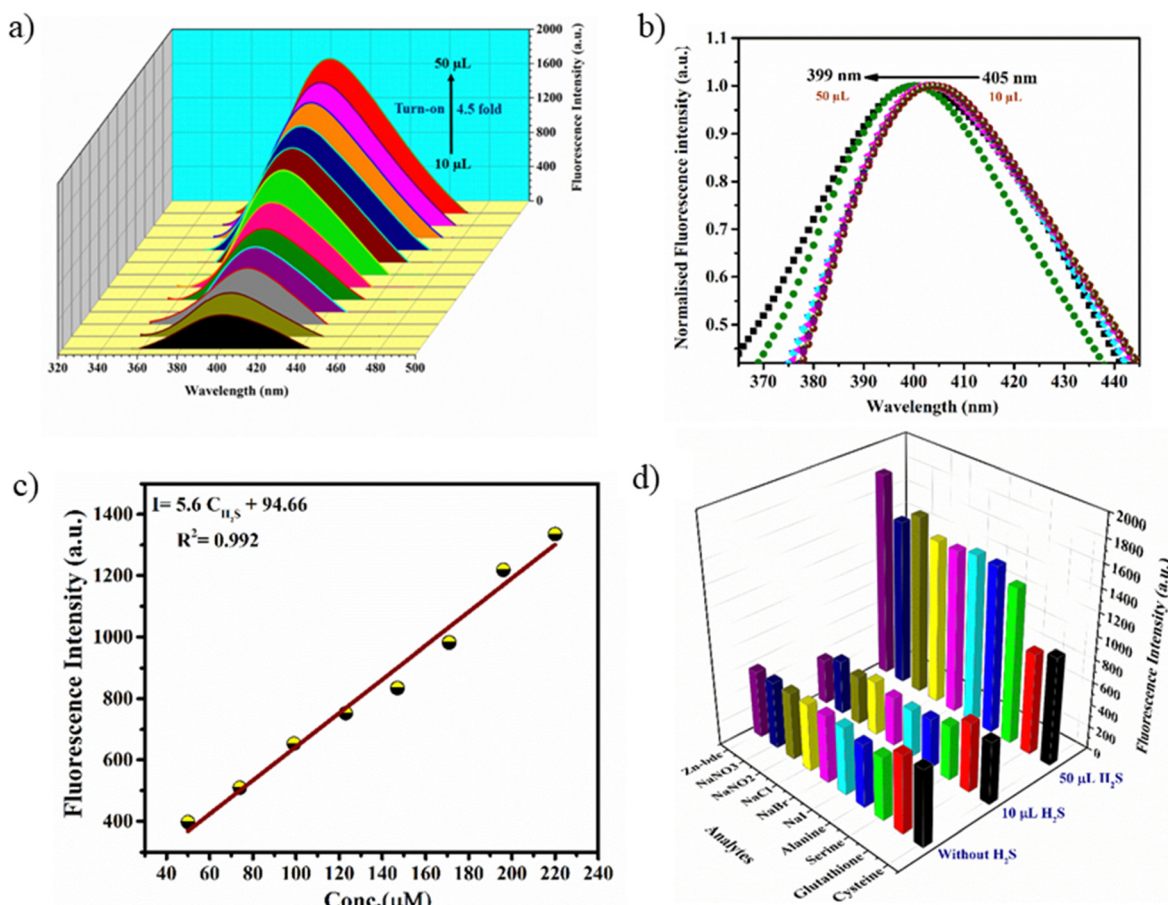


Fig. 4 (a) Turn-on fluorescence response of **Zn-bdc** upon addition of H<sub>2</sub>S up to 50 μL, (b) blue shift of the fluorescence spectrum with turn-on, (c) concentration-dependent fitting curve for turn-on and (d) competitive fluorescence response of **Zn-bdc** towards various interfering analytes.

calculate the LOD value and quenching constant. In the equation,  $I_0$  and  $I$  represent the fluorescence intensities of the probe before and after the addition of the analyte, respectively,  $[X]$  is the molar concentration of the H<sub>2</sub>S solution, and  $K_{SV}$  is the quenching constant ( $M^{-1}$ ) (Fig. S9, ESI†). These calculations reveal that **Zn-bdc** exhibits a quenching constant ( $K_{SV}$ ) of  $9.747 \times 10^3 M^{-1}$  and the LOD for turn-off is 15.3 μM (Fig. 3b). For the turn-on measurements, the calibration curve showed a perfect linear relationship with the correlation coefficient  $R^2$  of 0.99. The slope was calculated to be 5.6 with an intercept of 94.66 from the calibration curve. Therefore, using this slope ( $S$ ) and the standard deviation ( $\delta$ ), which was calculated by measuring the fluorescence five times with a blank solution, the LOD ( $3\delta/S$ ) for **Zn-bdc** towards sulfide was estimated to be 10.7 μM (Fig. 4c). A time-dependent fluorescence experiment with **Zn-bdc** reveals the increase of the fluorescence by 5.6-fold within 18 min for 50 μL of H<sub>2</sub>S (Fig. S10, ESI†). Along similar lines, the H<sub>2</sub>S sensing experiments were carried out with **Zn-btc**. It also exhibited turn-off fluorescence with the gradual addition of 10 μL of H<sub>2</sub>S solution. However, **Zn-btc** was not found to show any turn-on fluorescence spectra even after the addition of 50 μL of H<sub>2</sub>S (Fig. S11, ESI†). Due to the lower selectivity and sensitivity of **Zn-btc**

towards H<sub>2</sub>S, further detailed investigation was performed with the **Zn-bdc** MOF.

The sensing medium contains multiple analytes in real-life sensing experiments. Therefore, the selectivity towards the target analyte over other intrusive biomolecules is a very important aspect to consider the probe as a smart sensor. Thus, the selective detection of H<sub>2</sub>S by **Zn-bdc** in the presence of other interfering biomolecules, such as cysteine, serine, glutathione, and alanine, and also in the presence of usual biological reducing anions, such as NaCl, NaBr, NaI, NaNO<sub>2</sub>, and NaNO<sub>3</sub>, was examined. All fluorescence analyses were performed in the same conditions as above with the presence of other competitive analytes. The fluorescence spectra showed significant fluorescence turn-off and turn-on also with the presence of other interfering biomolecules (Fig. S12, ESI†). In conclusion, **Zn-bdc** as a fluorescence chemosensor is selective towards H<sub>2</sub>S in an aqueous medium with the presence of other congeners (Fig. 4d).

To ascertain the H<sub>2</sub>S sensing mechanism and framework stability, the X-ray powder diffraction (XRPD), fluorescence resonance energy transfer (FRET), Fourier transform infrared spectroscopy (FTIR), time-correlated single photon counting (TCSPC), nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR),





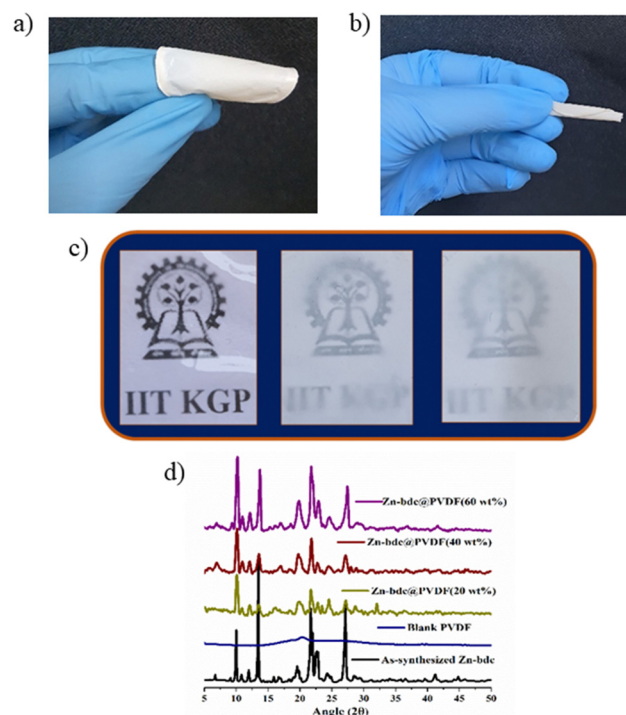
and X-ray photoelectron spectroscopy (XPS) analyses were performed. The XRPD pattern of **Zn-bdc** after the addition of  $\text{H}_2\text{S}$  remains to be same as that of as-synthesized **Zn-bdc** (Fig. S13, ESI†) indicating the phase stability of the material. Notably, the emission spectrum of the **Zn-bdc** probe was found to be overlapped with the absorption spectra of the aqueous  $\text{Na}_2\text{S}$  solution, which indicates possible energy transfer between the analytes and the host (Fig. S14, ESI†).<sup>60,61</sup> Therefore, the initial fluorescence turn-off can be attributed to the interaction of  $\text{Na}_2\text{S}$  with **Zn-bdc** in the solution phase. The fluorescence lifetime measurement was performed by monitoring the fluorescence decay profile in the presence and absence of analyte  $\text{H}_2\text{S}$  (Fig. S15, ESI†). The excited state lifetime of **Zn-bdc** is found to be 0.24 ns in the absence of an analyte. No effective overlap was observed in the fluorescence lifetime measurement curves before and after the addition of 10  $\mu\text{L}$  of  $\text{H}_2\text{S}$  to the probe solution, which may imply a dynamic quenching effect. Further addition of  $\text{H}_2\text{S}$  up to 50  $\mu\text{L}$  increased the fluorescence lifetime by 8.7 times due to the fluorescence turn-on. FTIR spectra were analysed for understanding the sensing mechanism of  $\text{H}_2\text{S}$  by **Zn-bdc**. In FTIR, the disappearance of the characteristic peak of  $\text{C}=\text{C}$  of **BP3YF** at  $1665\text{ cm}^{-1}$  was observed upon the addition of 50  $\mu\text{L}$  of  $\text{H}_2\text{S}$  (Fig. S16a and b, ESI†). This indicates the nucleophilic addition of  $\text{SH}^-$  to the olefinic double bond of **BP3YF** of **Zn-bdc**. Furthermore, the appearance of a peak at  $630\text{ cm}^{-1}$  indicates the presence of a  $\text{C}-\text{S}$  bond.<sup>62</sup> Furthermore, a peak around  $2895\text{ cm}^{-1}$  appeared indicating the presence of a  $-\text{SH}$  group that is added to the olefinic carbon atom. In  $^1\text{H-NMR}$  (Fig. S17 and S18, ESI†), a peak at 6.9 ppm disappeared after the treatment of  $\text{H}_2\text{S}$  indicating the nucleophilic addition to the olefinic double bond. Furthermore, the peaks of the aromatic moiety were found to shift around 7–9 ppm due to the addition of  $-\text{SH}$  to the olefin. These analyses suggest that the  $\text{H}_2\text{S}$  sensing mechanism by the MOF occurs through  $\text{H}_2\text{S}$  addition to the double bond of **BP3YF** in **Zn-bdc**. Furthermore, the XPS analysis on MOF-bdc was carried out before and after the  $\text{H}_2\text{S}$  sensing experiments to analyses the changes in the elemental composition. The as-synthesized MOF-bdc displays the signals corresponding to Zn, C, N, and O in the full-survey spectrum, whereas the presence of S was observed after the treatment with  $\text{H}_2\text{S}$  (Fig. S19a, ESI†). The Zn 2p peaks were observed at 1021.36 eV and 1044.65 eV for  $2\text{p}_{3/2}$  and for  $2\text{p}_{1/2}$ , respectively, both in as-synthesized and  $\text{H}_2\text{S}$ -treated MOFs indicating no interaction of  $\text{H}_2\text{S}$  with Zn(II) (Fig. S19b, ESI†). The C 1s spectra for the as-synthesized MOF can be deconvoluted into three peaks at the binding energies of 284.30 eV, 285.30 eV, and 287.30 eV corresponding to the  $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ , and  $\text{C}-\text{O}$ , respectively. For the  $\text{H}_2\text{S}$ -treated MOF, these three peaks were found to be slightly shifted to 284.10 eV, 285.10 eV, and 287.49 eV as well as a new peak appeared at 286.48 eV corresponding to the  $\text{C}-\text{S}$  bond (Fig. S19c, ESI†).<sup>63,64</sup> The high-resolution spectra of S 2p were deconvoluted into two peaks at 160.67 eV and 162.05 eV, which can be marked for S  $2\text{P}_{3/2}$  and S  $2\text{P}_{1/2}$  splitting (Fig. S19f, ESI†). Therefore, these studies indicate the nucleophilic addition to the olefinic double bond of **Zn-bdc** by  $\text{SH}^-$ . In summary,

**Table 1** Determination of  $\text{H}_2\text{S}$  in real water samples by the standard addition method

Samples		Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery (%)	RSD (%)
Tap water	1	100	99.92	99.92	4.98
	2	150	152.78	99.87	5.12
	3	200	193.74	96.87	3.42
Lake water	1	100	99.67	99.67	4.63
	2	150	147.13	98.08	2.33
	3	200	200.15	100.07	2.80
River water	1	100	96.10	96.10	5.18
	2	150	146.37	97.58	4.30
	3	200	188.65	94.32	3.22

formation of the new  $\text{C}-\text{S}$  bond in the MOF could be the probable reason for fluorescence turn-on.

A substantial quantity of  $\text{H}_2\text{S}$  is being released every day into water in the form of waste by the pulp and paper industry, natural gas and petroleum refinery, manufacturing industries of chemicals, volcanoes, human wastes, *etc.* The excellent selectivity and sensitivity of **Zn-bdc** towards  $\text{H}_2\text{S}$  prompted us to test its sensing ability quantitatively. The real water samples are procured from the tap (lab tap water), a lake (collected from the serpentine lake of IIT Kharagpur, India), and a river (Ganga River). The samples are prepared with varied concentrations (100  $\mu\text{M}$ , 150  $\mu\text{M}$ , and 200  $\mu\text{M}$ ) of  $\text{H}_2\text{S}$ . The  $\text{H}_2\text{S}$  concentrations of these solutions were estimated using **Zn-bdc** and it was found that the estimated values are close to the original added concentrations of  $\text{H}_2\text{S}$  in those solutions (Table 1). For all the



**Fig. 5** (a) Optical image of the mixed-matrix membrane **Zn-bdc**<sub>60</sub>@PVDF, (b) flexibility checking of the membrane **Zn-bdc**<sub>60</sub>@PVDF, (c) gradual decrease of transparency of the membrane from **Zn-bdc**<sub>0</sub>@PVDF to **Zn-bdc**<sub>40</sub>@PVDF to **Zn-bdc**<sub>60</sub>@PVDF and (d) XRPD patterns of the as-synthesized **Zn-bdc** and the MOF-loaded mixed-matrix membranes.



samples, the found  $\text{H}_2\text{S}$  concentrations indicate a good recovery percentage and low Relative Standard Deviation (RSD) value.<sup>65</sup> This result concludes that the **Zn-bdc** sensor was able to detect  $\text{H}_2\text{S}$  quantitatively from real water samples.

### Detection of $\text{H}_2\text{S}$ Gas

According to a survey by the U.S. Bureau of Labor Statistics, about 60 workers expired from 2001 to 2010 due to exposure of  $\text{H}_2\text{S}$  gas. Therefore,  $\text{H}_2\text{S}$  sensing in its gaseous phase is also as important as its detection in the solution phase.

However, most of the MOF-based probes are inadequate for the detection of  $\text{H}_2\text{S}$  in the gaseous phase. Therefore, we have explored the  $\text{H}_2\text{S}$  gas detection ability of the finely ground powdered form of the MOF and also of the MOF loaded mixed-matrix membrane.

### $\text{H}_2\text{S}$ gas detection by powdered MOF

Finely ground powder material of **Zn-bdc** was taken in two vials and placed in two wider vials containing 10  $\mu\text{L}$  and 50  $\mu\text{L}$  aqueous solution of  $\text{Na}_2\text{S}$  as a source of  $\text{H}_2\text{S}$  vapor. The fluorescence of the exposed material was monitored at different

time intervals. No change in fluorescence intensity was observed for the material that is exposed to 10  $\mu\text{L}$  of  $\text{H}_2\text{S}$ . Notably, a fluorescence turn-on phenomenon was observed with the material that is exposed to 50  $\mu\text{L}$  of  $\text{H}_2\text{S}$  vapor at an excitation wavelength of 290 nm. The fluorescence intensity of the spectrum increases about 1.2-fold after the vapor deposition of  $\text{H}_2\text{S}$  for nucleophilic addition in the olefinic double bond (Fig. S22, ESI†). In summary, we can conclude that the powder form of the **Zn-bdc** probe can detect  $\text{H}_2\text{S}$  in the gaseous phase by following the nucleophilic addition mechanism.

### Preparation of the mixed-matrix membrane of MOF

Rapid and selective detection of  $\text{H}_2\text{S}$  by the **Zn-bdc** probe prompted us to explore the  $\text{H}_2\text{S}$  sensing application by the mixed-matrix membrane of the MOF. The membrane was synthesized by blending the microparticles of the MOFs with PVDF in DMF solution through the slurry casting method. A total of four membranes were prepared with different loading percentages of MOFs in the membranes: **Zn-bdc\_0@PVDF**, **Zn-bdc\_20@PVDF**, **Zn-bdc\_40@PVDF** and **Zn-bdc\_60@PVDF** with 0%, 20%, 40% and 60% **Zn-bdc**, respectively (Fig. 5a).

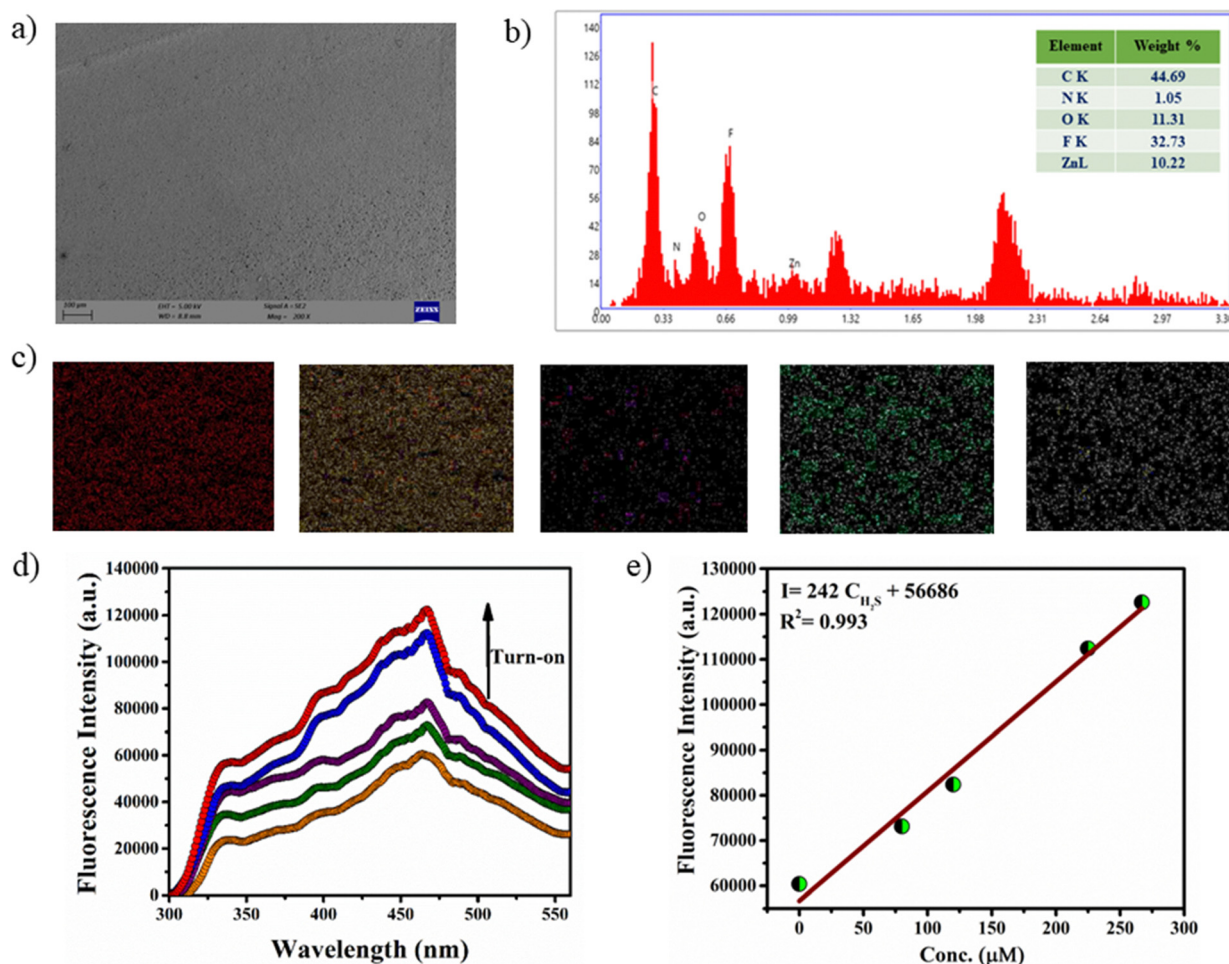


Fig. 6 (a) FESEM image, (b) EDX analysis and (c) elemental mapping (C, O, F, N, Zn) of the **Zn-bdc\_60@PVDF** mixed-matrix membrane. (d) Fluorescence turn-on response of the **Zn-bdc\_60@PVDF** membrane upon addition of  $\text{H}_2\text{S}$  vapor and (e) concentration dependent fitting curve for turn-on of **Zn-bdc\_60@PVDF**.



Furthermore, it was found that loading of beyond 60% of **Zn-bdc** resulted in unstable membranes, which leach out the **Zn-bdc** into the DMF solution due to the lack of proper integration of the MOFs in the polymeric blend. The XRPD pattern of all four membranes was found to exhibit characteristic peaks of **Zn-bdc** (Fig. 5d) confirming the phase stability and crystallinity of the MOF in the membranes. The membranes were further characterized by field emission scanning electron microscopy (FESEM) (Fig. 6a) and energy-dispersive X-ray spectroscopy (EDX) (Fig. 6b). The elemental mapping shows a uniform distribution of carbon, nitrogen, oxygen, fluorine, and zinc, indicating the uniform dispersion of **Zn-bdc** in the composite membrane (Fig. 6c). The pure PVDF film was found to be transparent; however, the transparency of the membrane was found to decrease as the loading percentage of **Zn-bdc** increased (Fig. 5c). We would like to note here that the composite membranes are found to be mechanically robust, free of cracks, and flexible (Fig. 5b). These are some of the very important features for further application in real-time chemical sensing.

#### H<sub>2</sub>S gas detection by the mixed-matrix membrane of the MOF

The H<sub>2</sub>S sensing ability of the MOF-loaded membranes is investigated by monitoring the fluorescence of H<sub>2</sub>S exposed

membranes. The bare PVDF membrane exhibited no fluorescence and exhibited a negligible spectral change after H<sub>2</sub>S vapor deposition, suggesting that the pure PVDF does not influence the fluorescence intensity of the H<sub>2</sub>S detection process. Interestingly, a remarkable increase in fluorescence intensity was observed with increasing the loading percentage of **Zn-bdc** in the membranes (Fig. S23, ESI†). More interestingly, **Zn-bdc**\_60@PVDF showed more pronounced fluorescence enhancement upon H<sub>2</sub>S vapor treatment, and hence 60% film loading was selected for further investigation in detail. Similar to the solution detection, fluorescence turn-on was observed with the incremental addition of H<sub>2</sub>S vapor (Fig. 6d). As described earlier, the nucleophilic addition reaction to the olefinic bond of the ligand is responsible for the turn-on fluorescence. Furthermore, the calibration curve for turn-on shows a perfect linear relationship with the correlation co-efficient  $R^2$  0.99. From the linear fitted curve, the calculated slope value was 242 with an intercept of 56 686 (Fig. 6e). By using the slope value ( $S$ ) and the standard deviation, which is calculated with five times blank fluorescence measurements ( $\delta$ ) using the PVDF film, the value of detection limit ( $\text{LOD} = 3\delta/S$ ) of **Zn-bdc**\_60@PVDF toward sulfide ( $\text{S}^{2-}$ ) was calculated to be 5.3  $\mu\text{M}$ . Interestingly, the LOD value of the **Zn-bdc**\_60@PVDF membrane is considerably lower than that of the **Zn-bdc** in

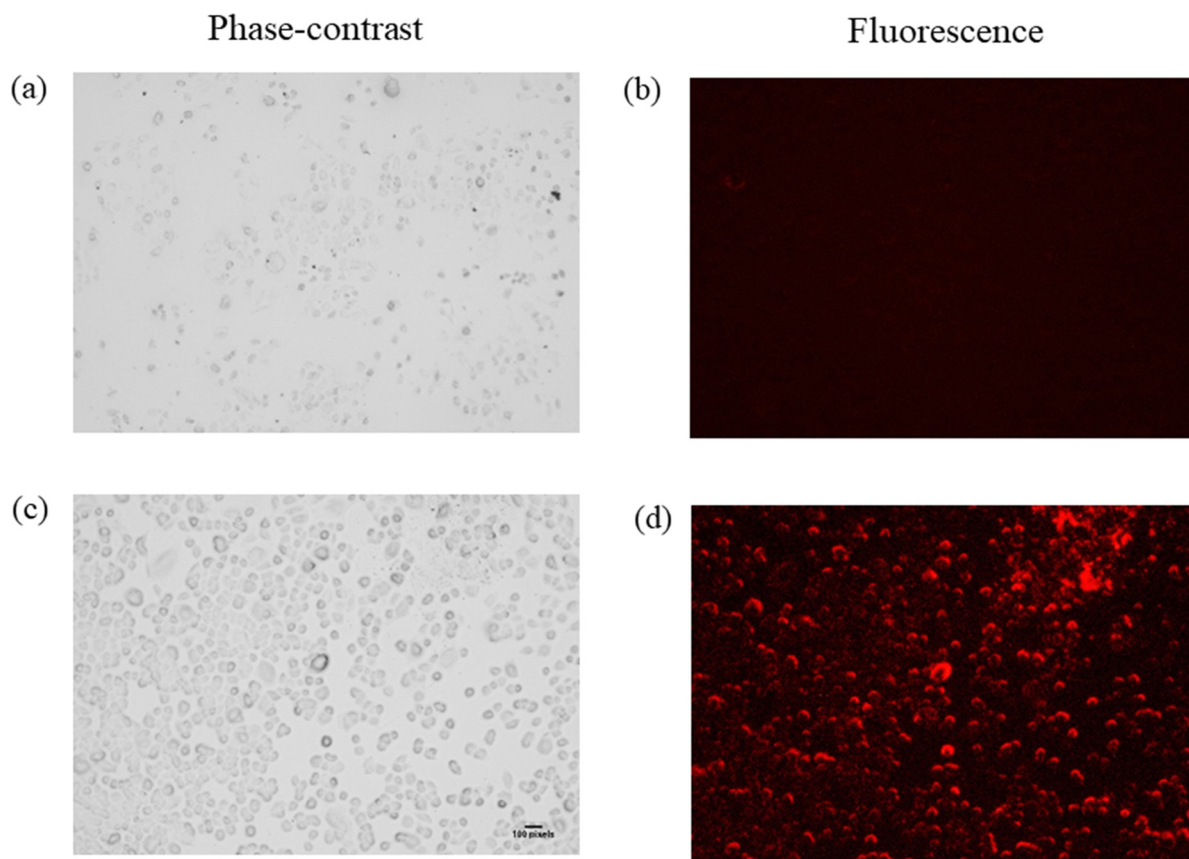


Fig. 7 Intracellular behavior of the **Zn-bdc** probe in LN-18 glioblastoma living cells: (a) phase contrast image of probe-loaded cells before H<sub>2</sub>S treatment, (c) phase contrast image of probe-loaded cells after H<sub>2</sub>S treatment, (b) fluorescence image of the probe-loaded respective cells before H<sub>2</sub>S treatment and (d) fluorescence image of the probe-loaded cells after H<sub>2</sub>S treatment.





aqueous solution. We note here that this LOD value is the lowest among all the reported Zn-based probes to date.

### *In vitro* cell imaging of LN-18 glioblastoma cells

The fast response, excellent selectivity, and sensitivity of **Zn-bdc** towards extracellular H<sub>2</sub>S in an aqueous medium motivated us to investigate the detection ability of **Zn-bdc** for intracellular H<sub>2</sub>S. In this regard, cellular imaging was investigated by LN-18 glioblastoma cells in a biological medium. For a live cell imaging study of a probe, it is important to test the biocompatibility of the cell. Therefore, cytotoxicity assay analysis was performed, and the percentage of cell viability was plotted against the dose concentration of **Zn-bdc**, from which fifty percent cell growth inhibition (IC<sub>50</sub>) was calculated at 98.38  $\mu$ M (Fig. S26, ESI†). The cellular morphology of the LN-18 glioblastoma cell remained intact with the different probe concentrations even after 48 hours of incubation. These results suggest that **Zn-bdc** can be considered a convenient probe for conducting cellular imaging analysis. Thus, no fluorescence was detected when cells were treated with the probe at the concentration of 98.38  $\mu$ M. However, when 10  $\mu$ M Na<sub>2</sub>S solution was added as a source of endogenous H<sub>2</sub>S and the cells were incubated for 48 hours in that solution a signal of bright red fluorescence was observed in LN-18 glioblastoma cells while maintaining their entire morphology (Fig. 7). In brief, **Zn-bdc** proved itself to be an excellent potential aspirant for *in vitro* cell imaging.

## Conclusion

In conclusion, herein, three Zn(II) MOFs containing acryl-amide functionalized bis pyridyl ligands and different polycarboxylates are synthesized and structurally characterized. Two of the three MOFs (**Zn-bdc** & **Zn-btc**) were found to exhibit water stability and their utility towards H<sub>2</sub>S sensing was explored in detail. These studies reveal that **Zn-bdc** has better H<sub>2</sub>S sensing ability in terms of sensitivity, selectivity and stability, and exhibits turn-off and subsequent turn-on fluorescence upon exposure with the gradual addition of H<sub>2</sub>S in the solution phase. The detection limits for **Zn-bdc** are found to be 10.7  $\mu$ M in the solution phase for the nucleophilic addition. The real-time application of the MOF in a device has been demonstrated by synthesizing a mixed-matrix membrane of the **Zn-bdc** MOF using PVDF binder. Interestingly, the MOF as a film offers a brand-new sensing platform with improved permeation fluxes and contact area with the analyte. The 60% **Zn-bdc** MOF-loaded membrane exhibited highly sensitive (5.3  $\mu$ M) and selective sensing capacity for gaseous phase H<sub>2</sub>S detection. The mechanism of sensing has been established by characterizing the resultant chemical changes in the MOF upon exposure to H<sub>2</sub>S. These studies reveal that the sensing mechanism operates through the nucleophilic addition of H<sub>2</sub>S to the olefinic double bonds of the **BP3YF** of the MOF. Furthermore, it was also shown that the MOFs are useful for biomedical imaging as they produce red fluorescence in LN-18

glioblastoma cells upon exposure to H<sub>2</sub>S. These results reveal that the incorporation of the MOF into mixed-matrix membranes results in an increase in the sensitivity of H<sub>2</sub>S detection by the MOF.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We acknowledge the financial support from DST-SERB (CRG/2022/000606), New Delhi, India, and DST-FIST for providing the single-crystal X-ray diffractometer. MDD thanks CSIR for the research fellowship. MM acknowledges the Indian Council of India, New Delhi, UGC, Govt of India, and SERB India for providing the JC Bose Fellowship.

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