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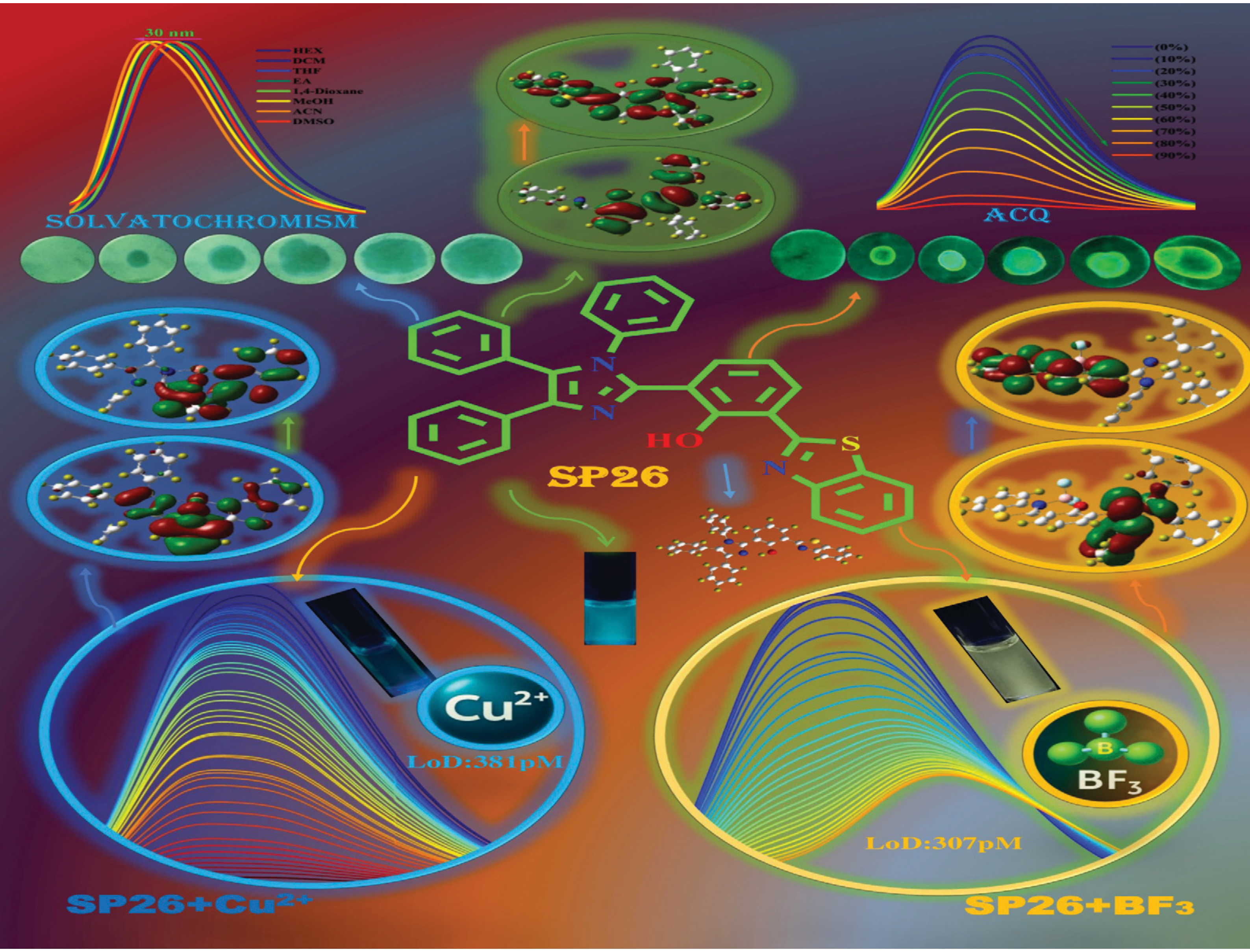


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**PAPER**
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PAPER

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# An imidazole-based fluorescent sensor for selective detection of $Cu^{2+}$ and $BF_3$ with environmental applications

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The specific detection of $Cu^{2+}$ and $BF_3$ provided the basis for the design of the distinctive dual-sensing chemosensor, 2-(benzo[*d*]thiazol-2-yl)-6-(1,4,5-triphenyl-1*H*-imidazol-2-yl) phenol (**SP26**). **SP26** was synthesized successfully using a multi-step process, with its identity confirmed by NMR spectroscopy and HR-MS analysis. The studies were conducted in an 8 : 2 THF/water mixture. The ligand was solubilized in THF/water, whereas the cation salts were dissolved in water. The absorption measurements indicated no detection of cations other than $Cu^{2+}$. The emission experiments revealed that the optical selectivity for the $Cu^{2+}$ ion leads to a reduction in emission intensity. Likewise, with $BF_3$, the emission intensity diminishes with the bathochromic shift. The limit of detection (LoD) for $Cu^{2+}$ is 381 pM, and for $BF_3$ it is 307 pM. After adding $BF_3$ and $Cu^{2+}$ to **SP26**, the complex formation was so quick that it happened within a fraction of a second. Triethylamine (TEA) was used for $BF_3$, and ethylenediamine tetraacetic acid (EDTA) for $Cu^{2+}$ to determine the reversibility. FT-IR, HR-MS, Job's plot, DFT, and $^1$H NMR titration analyses confirmed that chemosensor **SP26** was bound to $Cu^{2+}$ and $BF_3$. Paper test strips showed the potential of the chemosensor **SP26** for the environmental detection of $Cu^{2+}$ and $BF_3$. The quantitative analysis of $Cu^{2+}$ was examined with environmental water samples.

## 1. Introduction

Copper is one of the most prevalent transition metal ions in the human body due to its important applications in biology, chemistry, and the environment, and it has garnered much attention. It is essential for haemopoiesis and other processes catalyzed by proteins and enzymes. While $Cu^{2+}$ is necessary for human health, an excess of it can tilt the delicate balance within cellular functions and leads to severe neurodegenerative illnesses, including Parkinson's, Wilson's, and Alzheimer's diseases, and similar conditions.[1,2] Furthermore, $Cu^{2+}$ is widely used in industry and daily life, even though it is considered a significant metal pollutant. Thus, creating straightforward, effective, sensitive, and precise techniques for $Cu^{2+}$ detection is imperative.

Numerous methods have been developed in the last few decades for the detection of $Cu^{2+}$, including electrochemical methods,[3,4] atomic absorption spectrometry (AAS),[5,6] inductively coupled plasma-atomic emission spectrometry (ICP-AES),[7,8] inductively coupled plasma mass spectroscopy (ICPMS),[9] and emission methods.[10–15] Fluorescent probes have emerged as one of the most effective tools for detecting metal ions and other pollutants because of their many exceptional benefits, including simplicity, ease of manipulation, great sensitivity and selectivity, and real-time detection. Notwithstanding, most documented emission probes for $Cu^{2+}$ detection utilize emission quenching or augmentation,[16–19] in which the instrument, auto-emission, manipulation errors, and surroundings can be readily impacted.

They are unable to offer measures that are quantitatively accurate enough. The current probe is capable of detecting a very low level of $Cu^{2+}$ (381 pM). However, ratiometric chemosensor probes for $Cu^{2+}$ detection are still uncommon as of right now. $Cu^{2+}$ ions are also harmful to marine plants such as algae.[20] These things make the detection of $Cu^{2+}$ ions indispensable and immediately warranted. The synthesis and application of a good fluorescent sensor should be straightforward, as on-site chemical information can be easily obtained. The design of a fluorescent sensor is the art of clubbing the points of attachment with the fluorophore. In the case of $Cu^{2+}$ ion detection sensors containing quinoline,[21–23] naphthalimide,[24,25] rhodamine,[26,27] and pyrene,[28] development has been achieved. However, the stability and ease of synthesis are the major stumbling blocks for these sensors.

The important inorganic compound boron trifluoride ($BF_3$) is frequently employed as a catalyst in various organic synthesis processes,[29] including condensation, ionic polymerization, and isomerization.[30] However, $BF_3$ is extremely poisonous and

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corrosive, and even small leaks can result in biological dangers and other environmental problems. Moreover, $BF_3$ has a very high reactivity and can react violently with metals, organic materials, *etc.* $BF_3$ will produce a powerful explosion and break down into HF, which can irritate the nose, eyes, skin, respiratory tract, or even cause death, especially when it comes into contact with water or even humid air.[31] In summary, $BF_3$ is a hazardous gas that must be handled carefully during application, transportation, production, and disposal activities. Dependable gas leak detection systems for $BF_3$ are now vitally needed to provide a safe working environment and reduce production loss.[32]

The chemisorption of $BF_3$ and its monohydrate with a gas-reactive thin film placed on a slice of quartz served as the basis for the construction of the quartz microbalance (QMB) sensor technology. They have the following shortcomings, which should be noted: complicated instruments, lengthy response times, high detection limits, and operating procedures. Thus, the benefits of the fluorescence sensing approach, which include easy operation, high sensitivity, fast response, and field test availability, have led to its widespread application in recent years.[33] T.-H. Tran-Thi and colleagues[33] in 2008 demonstrated a hybrid mesoporous organo-silica functionalized with grafted dibenzoylmethane (DBM) exhibiting fluorescence that can be enhanced in the presence of $BF_3$ over a few hours at a low sensitivity concentration (<1 ppm) to break the $Et_2O–BF_3$ complex and permit $BF_3$ to diffuse and react with DBM. A novel molecular design for sensing $BF_3$ was used by Eric T. Kool *et al.* in 2011. DNA-polyfluorophores may produce distinct selective responses at concentrations as low as 20 ppm when seen under an epifluorescence microscope.[34] This system offers straightforward operation, fast response time, and *in situ* detection, and it does not require large-scale sensors as previous approaches did. However, the sensitivity of this approach exceeds the permissible exposure limit (PEL) and threshold limit value (TLV) of 1 ppm set by the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH).

Imidazole-based fluorescent sensors were studied. However, they have some disadvantages, like some imidazole sensors' limited solubility. Imidazole possesses a nitrogen donor capable of coordinating with several metal ions (*e.g.*, $Cu^{2+}$, $Zn^{2+}$, $Fe^{3+}$), making the differentiation between analogous ions challenging.

An imidazole sensor ensures precision and dependability in selective detection. Certain imidazole-based sensors demonstrate sluggish reaction times or irreversible interactions with the target, rendering them inadequate for real-time or dynamic monitoring.

For example, a highly fluorescent imidazole-based diboron complex has been synthesized, and only photophysical studies were carried out.[35] Similarly, imidazoyl-phenol-based boron complexes have been studied extensively.[36] $Cu^{2+}$ sensing and electrochemical removal were done using triphenyl-imidazole-based sensors.[37] A novel imidazole-derived chemosensor was developed for the detection of $Cu^{2+}$ and sulphide ions.[38] Similarly, a bifunctional chemosensor for the detection of $Cu^{2+}$ and $Fe^{2+}$ was developed using push–pull imidazole–triazole.[39] However, an imidazole-derived Schiff base was used for the identification of $Cu^{2+}$ and applied in fingerprint images from our laboratory.[40] Similarly, from our laboratory, an imidazole-tethered benzothiazole sensor was developed for the detection of picric acid and latent fingerprint images.[41]

To effectively synthesize fluorescent chemosensors for the recognition of both $Cu^{2+}$ and $BF_3$, we have established a new chemical technique for the synthesis through the cyclocondensation reaction yielding **2-(benzo[*d*]thiazol-2-yl)-6-(1,4,5-triphenyl-1*H*-imidazol-2-yl) phenol (SP26)**. To address this, we have created the small-molecule chemosensor **SP26**, which interacts with $Cu^{2+}$ and $BF_3$ by deprotonation. **SP26** has outstanding selectivity, sensitivity, and optical responsiveness due to multiple points of attachment (N, O, N) to the sensor.

Furthermore, the chemosensor **SP26** has robust electron-donating characteristics that facilitate energy induction and electron transfer and facilitate fluorescence quenching through fluorophore–analyte interactions. For $Cu^{2+}$ and $BF_3$ in test strips, **SP26** was used to demonstrate practical applicability. Therefore, the information from this work will be useful in designing more sophisticated fluorescent chemosensors for precise and targeted detection at very low concentrations.

### 1.1 General

All the chemicals used in this investigation, including solvents like ethanol and tetrahydrofuran (THF), were of analytical reagent (AR) grade. $B(OMe)_3$, borax, $BPh_3$, $H_3BO_3$, $BCl_3$, $NaBF_4$, $H_2S$, $HClO_4$, NaF, HCl, NaCN, $N_2H_4$, $NH_3$, and $NH_4Cl$, and the metal salts containing $Ag^+$, $Al^{3+}$, $Ba^{2+}$, $Ca^{2+}$, $Cr^{3+}$, $Cd^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Hg^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Zr^{2+}$, and $Th^{4+}$, were obtained from Sigma Aldrich and Spectrochem and were used without any additional purification. The supplier of boron trifluoride diethyl etherate ($C_4H_{10}BF_3O$) was Avra Chemicals. Nuclear Magnetic Resonance (NMR) spectra, comprising $^1H$ and $^{13}C$, were acquired using Bruker Avance III 400 MHz and 100 MHz. A JASCO FP-8655 fluorophotometer was used for fluorescence spectroscopy. The instrument utilized for UV-visible spectroscopy was a JV-750. Column chromatography, which combines stationary (silica gel) and mobile (ethyl acetate-hexane) phases, was used to purify reaction mixtures.

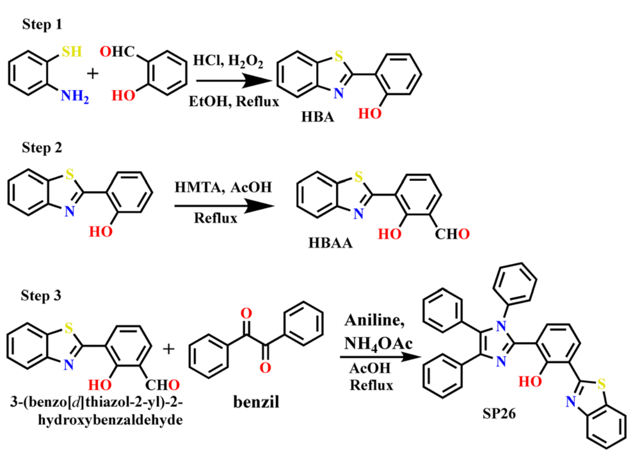
### 1.2 Synthesis and characterisation

A solution of salicylaldehyde (1.5 g, 12.3 mmol) and 2-aminothiophenol (1.25 mL, 11.9 mmol) in EtOH (25 mL) was mixed dropwise with aq. HCl (37%, 30 mmol) and aq. $H_2O_2$ (30%, 48.0 mmol). We refluxed the mixture for one hour. After the reaction mixture attained room temperature, we filtered it and was given an ethanol wash followed by air drying. We obtained 1.4 g of pure white solid **2-(2-hydroxyphenyl) benzothiazole (HBA)** with a yield of 82%. Hexamethylenetetramine (HMTA) (0.926 g, 6.6 mmol) was mixed into a solution of **HBA** (1 g, 5 mmol) in $CH_3COOH$ (20 mL) and refluxed for 3 hours. The reaction mixture was cooled to room temperature. Then, the reaction mixture was quenched in cold water, pH-neutralized, filtered, and dried. Then, the precipitate was purified by column chromatography using silica gel 100–200 mesh and using ethyl acetate : *n*-hexane (1 : 9) as a solvent system, yielding 420 mg (45%). The solid of **3-(benzothiazole-2-yl)-2-hydroxybenzaldehyde (HBAA)** is light-yellow colored.[42]

**Synthesis of 2-(benzo[*d*]thiazol-2-yl)-6-(1,4,5-triphenyl-1*H*-imidazol-2-yl) phenol (SP26) through cyclocondensation.** 3-(Benzo[*d*]thiazol-2-yl)-2-hydroxybenzaldehyde 0.300 g (1 equivalent), benzil 0.240 g (1 equivalent), and 0.1 mL (1 equivalent) of aniline were all dissolved in glacial acetic acid[43] and refluxed for 3 hours. The reaction's progress was seen using TLC with ethyl acetate : *n*-hexane (3 : 7). After the reaction's completion, the reaction mixture was cooled to room temperature, and cold water was added. After that, sodium hydroxide solution was added to neutralize the reaction mixture. The solid was separated and allowed to air dry. For purification, the reaction mixture was separated and purified using column chromatography with a silica gel mesh size of 100–200 and ethyl acetate : *n*-hexane as the eluent. In the end, a solid light-yellow compound with a yield of 76% was achieved. The compound purity was 99.20% (Fig. S3). High-resolution mass spectrometry and NMR spectroscopy were used to analyze the molecule (M. P.: 237 °C). The estimated mass of the compound was 521.1628, while its observed mass with the proton adduct was 522.1636 (Fig. S4). $^1$H NMR (400 MHz, DMSO) $\delta$: 11.835 (s) (1H), 8.305–8.299 (d) 2.4 Hz (1H), 8.143–8.123 (d) 8 Hz (1H), 8.060–8.041 (d) 7.6 Hz (1H), 7.196–7.551 (m) (18H), 6.988–6.966 (d) 8.8 Hz (1H) SI (Fig. S1). $^{13}$C NMR (100 MHz, DMSO) $\delta$: 164.81, 156.73, 156.65, 151.86, 156.81, 145.87, 134.90, 134.77, 132.42, 131.78, 131.60, 131.50, 130.90, 130.13, 129.79, 129.34, 129.24, 129.15, 129.09, 129.05, 128.94, 128.85, 128.66, 126.87, 126.57, 125.68, 122.78, 122.69, 121.51, 122.42, 118.62, 117.22 SI (Fig. S2) (Scheme 1).

### 1.3 Stock solution preparation

Metal nitrate salts were dissolved in double-distilled water to yield solutions with a concentration of $1 \times 10^{-3}$ M. Meanwhile, a $2 \times 10^{-5}$ M stock solution of the chemosensor (**SP26**) was prepared using tetrahydrofuran–water (8 : 2-THF : $H_2O$) as the solvent before conducting every photophysical study, and the excitation wavelength is 360 nm for all photophysical studies.




**Scheme 1** The synthesis of 2-(benzo[*d*]thiazol-2-yl)-6-(1,4,5-triphenyl-1*H*-imidazol-2-yl) phenol (**SP26**).

## 2. Results and discussion

### 2.1 Absorption studies at different $H_2O$–THF combinations

**SP26** produces a green color in solution when dissolved in THF. After that, several combinations of THF/water fraction of 0–90% were created; the absorption spectrum was recorded with each solution; there are two peaks at 300 and 360 nm, and there is a slight decrease at 300 nm in the absorption up to 70% of water. At 80% and 90% of water, there is a sudden increase in absorption (Fig. 1a).

### 2.2 Aggregation caused quenching (ACQ) of emission

Similar to the absorption spectrum, the emission spectrum was recorded, and there is a considerable reduction in the emission intensity as we increase the water content of the solvent system. The FL spectrum shows that emission intensity is gradually decreasing up to 50% of water. After 60% of water, the emission disappeared as the water was added, due to the aggregation-caused quenching (ACQ) effect (Fig. 1b). It is shown in the form of a bar chart with different water fractions, under 365 nm UV light, as seen in Fig. 1c. In this particular study, the ACQ may help the detection of $Cu^{2+}$, since the addition of $Cu^{2+}$ leads to quenching.

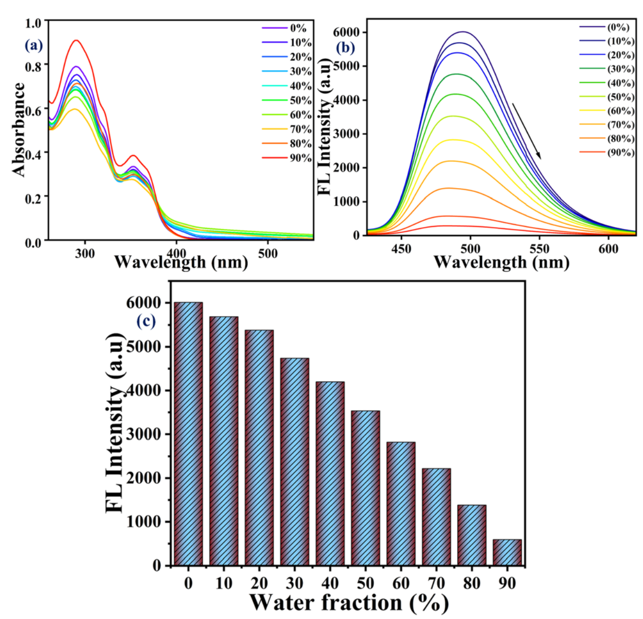



**Fig. 1** (a) Absorption spectra of **SP26** in various combinations of THF/water. (b) Emission spectra of **SP26** in various combinations of THF/water; the excitation wavelength is at 360 nm and the emission wavelength is at 500 nm, and the scanned wavelength is 400 to 650 nm at room temperature. (c) The bar graph of **SP26** at various combinations of THF/water under 365 nm UV light.

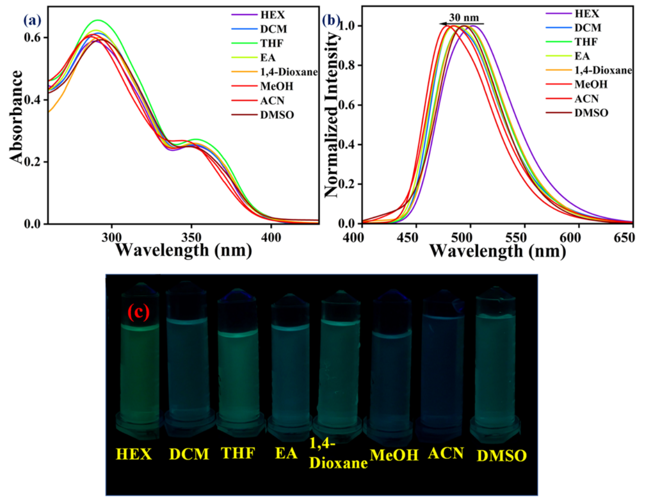



**Fig. 2** (a) Absorption spectra of **SP26** in various solvents (solvatochromism). (b) Emission spectra of **SP26** in various solvents (solvatochromism); the excitation wavelength is at 360 nm and the emission wavelength is at 500 nm, and the scanned wavelength is 400 to 650 nm at room temperature. (c) Colours of **SP26** in various solvents under 365 nm UV light.

### 2.3 Solvatochromism properties

The absorption and emission spectra of compound **SP26** in different solvents, such as *n*-hexane (HEX), dichloromethane (DCM), tetrahydrofuran (THF), ethyl acetate (EA), 1,4-dioxane, methanol (MeOH), acetonitrile (ACN) and dimethyl sulfoxide (DMSO), show a broad signal as shown in Fig. 2(a) and (b). The photophysical properties of the compound are summarized in Table 1 in various solvents. The sensitivity of the absorption spectrum is weak because the local environment of the molecules in the ground and excited states remains unchanged during the fast absorption process, and there is not much difference. On the other hand, a blue shift to 30 nm was observed in the emission spectra in different solvents when the solvent system's polarity was increased from hexane to DMSO. As a result, it displays negative solvatochromism, which shifts from the longer wavelength to the shorter wavelength as polarity increases. This shows that the ground state is more stabilised than the excited state due to a large energy gap.[44,45] The interaction between the dipoles of the solvent and ligand makes the ligand unstable in the excited state, leading to a very high energy state. This was evident from the difference between the HOMO and LUMO of the ligand from theoretical calculations.

### 2.4 Selectivity studies

In the presence of several boron species and metal ions ($BF_3$, $B(OMe)_3$, borax, $BPh_3$, $H_3BO_3$, $BCl_3$, $NaBF_4$, $H_2S$, $HClO_4$, NaF, HCl, NaCN, $N_2H_4$, $NH_3$, and $NH_4Cl$, $Ag^+$, $Al^{3+}$, $Ba^{2+}$, $Ca^{2+}$, $Cr^{3+}$, $Cd^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Hg^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Zr^{2+}$, and $Th^{4+}$), the UV-vis absorption and emission studies were conducted on **SP26** in $2 \times 10^{-5}$ M concentration in a solvent ratio of 8 : 2 tetrahydrofuran : water (THF : $H_2O$). Two absorption bands at 300 nm and 360 nm in the absorption spectrum of **SP26** are due to the π–π* and n–π* transitions, respectively. New absorption bands appeared after complexation with the addition of $BF_3$ and $Cu^{2+}$. When $BF_3$ was added gradually, the absorption band that had first emerged at 360 nm moved hypsochromically to 340 nm. The band at 360 nm disappears when we add $Cu^{2+}$, and a second, smaller absorption band at 400 nm appears, as seen in Fig. 3a. Thus, for fluorescence spectroscopic examination of the sensor **SP26**, the excitation wavelength was set at 360 nm. Similarly, the sensor gave an emission band at 500 nm. The sensor **SP26's** emission band was measured in the presence of $Cu^{2+}$, the emission band was quenched at 500 nm, and for $BF_3$, the emission band was quenched and gradually redshifted to 550 nm.

### 2.5 Absorption and emission titration studies

The π–π* transition of sensor **SP26** appears at 300 nm for the absorption; the n–π* transition is exhibited at 360 nm. Fig. 4a shows that the intensity of the absorption peak at 300 nm increases and a new peak at 400 nm increases progressively, and the peak at 360 nm decreases, when 0 to 3 equivalents of $Cu^{2+}$ are added (Fig. 4a). Hence, we obtained an isosbestic point at 372 nm and there is a marked red shift in the absorption spectra. However, upon adding 0 to 2 equivalents of $BF_3$ to **SP26**, a new peak at 260 nm emerges at the expense of the peak at 300 nm. Unlike copper, in the case of $BF_3$, the absorption increases as the $BF_3$ concentration is increased, and also there is a clear blue shift. Another new absorption peak at 310 nm decreases till 320 nm, again it increases up to 362 nm, then it decreases. A regular

**Table 1** Photophysical properties of **SP26** in different solvents at room temperature

| Probe | Solvent[a] | $\lambda_{max}$[b] (nm) | log $\varepsilon$[c] ($10^4$ $M^{-1}$ $L^{-1}$ $cm^{-1}$) | FWHM[d] (nm) | $\lambda_{em}$[e] (nm) | $\lambda_s$[f] ($cm^{-1}$) | $\phi$[g] |
|---|---|---|---|---|---|---|---|
| **SP26** | HEX | 355 | 1.2 | 134.6 | 503 | 8289 | 0.0221 |
| **SP26** | DCM | 354 | 1.25 | 125 | 485 | 7630 | 0.0198 |
| **SP26** | THF | 351 | 1.35 | 126.4 | 495 | 8288 | 0.0181 |
| **SP26** | EA | 351 | 1.3 | 130.5 | 487 | 7957 | 0.0202 |
| **SP26** | 1,4-Dioxane | 353 | 1.25 | 137.7 | 496 | 8167 | 0.0200 |
| **SP26** | MeOH | 348 | 1.3 | 132.4 | 486 | 8159 | 0.0252 |
| **SP26** | ACN | 351 | 1.2 | 132.4 | 479 | 7614 | 0.0220 |
| **SP26** | DMSO | 354 | 1.2 | 130.9 | 494 | 8006 | 0.0174 |

[a] Polar to non-polar solvents. [b] Maximum absorbance in UV-vis spectra. [c] Extinction coefficient. [d] Full-width at half maximum. [e] Wavelength of the maximum emission intensity. [f] Stokes shifts. [g] Quantum yield.

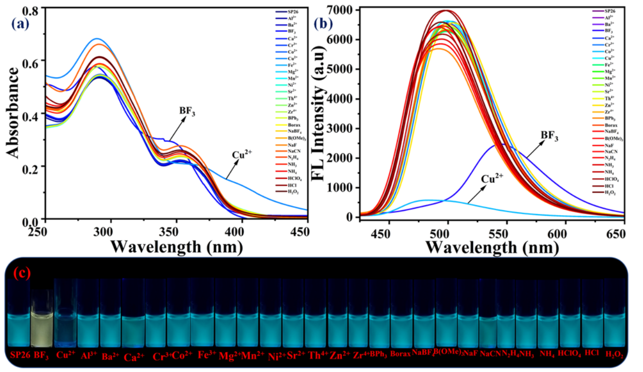



Fig. 3 (a) Absorption spectra of chemosensor **SP26** with different metal ions and different boron species in 8 : 2 THF : $H_2O$ solution. (b) Emission spectra of chemosensor **SP26** with different metal ions and different boron species in 8 : 2 THF : $H_2O$ solution; the excitation wavelength is at 360 nm and the emission wavelength is at 500 nm, and the scanned wavelength is 400 to 650 nm at room temperature. (c) Colours of **SP26** with different metal ions and boron species upon adding $1 \times 10^{-3}$ M metal ions into $2 \times 10^{-5}$ M concentrations of **SP26** in 8 : 2 THF : $H_2O$ solution under 365 nm UV light.

blue shift was seen, unlike copper. As a result, we obtained three isosbestic points at 300, 320, and 362 nm upon adding $BF_3$. However, in the case of copper, we obtained only one isosbestic point. As a result, the shapes of the absorption spectra of $Cu^{2+}$ and $BF_3$ are different. The complex formation between **SP26** and $BF_3$ was verified (Fig. 4b). Similarly, the fluorescence titration of **SP26** was performed by gradually adding $Cu^{2+}$ (0 to 3 equivalents) (Fig. 4c). When the concentration of $Cu^{2+}$ increases, the **SP26** fluorescence band at 500 nm was quenched. Similarly, adding 0 to 2 equivalents of $BF_3$ resulted in a redshift towards 550 nm and diminished with an increase in $BF_3$ concentration. However, we also detected a second emission peak at 680 nm, which slightly increases as the $BF_3$ concentration rises. Hence, we obtained the isoemissive point at 600 nm (Fig. 4d). It is observed that fluorescence is quenched in the case of $Cu^{2+}$ without any shift in the emission, and the fluorescence is red-shifted (cyan to yellow) in the case of $BF_3$.

Absorption coefficients were found to be 11 000 $cm^{-1}$ $M^{-1}$ for **SP26**, and for **SP26** with $Cu^{2+}$ and $BF_3$, they were found to be 6500 and 14 500 $cm^{-1}$ $M^{-1}$, respectively. The limit of quantification was determined to be as low as 1.27 nM for $Cu^{2+}$ and 1.025 nM for $BF_3$. The receptor's quantum yield ($\phi_{fl}$) was determined to be 0.94, using quinine sulfate as a standard reference ($\phi_{fl}$ = 0.54). Upon addition of $Cu^{2+}$ and $BF_3$ to the chemosensor **SP26**, the fluorescence intensity decreases and increases, respectively, with a quantum yield of 0.98 for **SP26** with the $BF_3$ complex and 0.53 for **SP26** with the $Cu^{2+}$ complex.

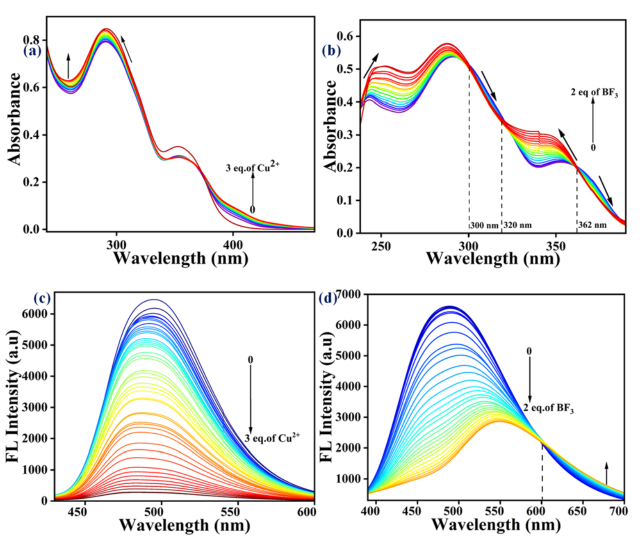



Fig. 4 (a) Absorption spectra of chemosensor **SP26** ($2 \times 10^{-5}$ M) in 8 : 2 THF : $H_2O$ solution with 0–3 equivalents of $Cu^{2+}$. (b) Absorption spectra of chemosensor **SP26** ($2 \times 10^{-5}$ M) in 8 : 2 THF : $H_2O$ solution with 0–2 equivalents of $BF_3$ analytes. (c) Emission spectra of chemosensor **SP26** ($2 \times 10^{-5}$ M) in 8 : 2 THF : $H_2O$ solution with 0–3 equivalents of $Cu^{2+}$. (d) Emission spectra of chemosensor **SP26** ($2 \times 10^{-5}$ M) in 8 : 2 THF : $H_2O$ solution with 0–2 equivalents of $BF_3$ analytes, and for both, the excitation wavelength is at 360 nm and the emission wavelength is at 500 nm, and the scanned wavelength is 400 to 650 nm at room temperature.

### 2.6 Binding constant and limit of detection

After FL titration, the limit of detection (LoD) of **SP26** towards $Cu^{2+}$ ions and $BF_3$ was computed utilizing the formula $3\sigma$/slope from the analyte concentration of $Cu^{2+}$ and $BF_3$ against emission intensity, where $\sigma$ represents the standard deviation and the slope value is obtained from the linear graph. The results were 381 pM for $Cu^{2+}$ and 307 pM for $BF_3$ respectively [Fig. 5(a) and (b)]. The Benesi–Hildebrand graph was obtained, illustrating the connection between the

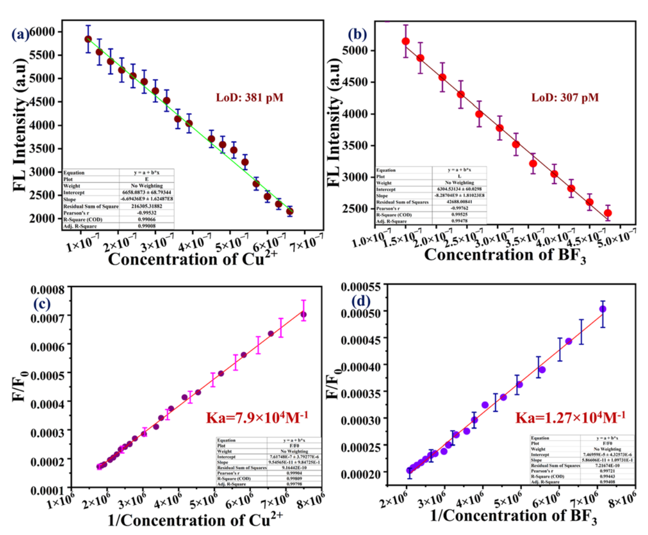



Fig. 5 (a) Calibration plot between the concentration of $Cu^{2+}$ and measured emission intensity. (b) Calibration plot between the concentration of $BF_3$ and measured emission intensity. (c) Benesi–Hildebrand plot for chemosensor **SP26** with 1/concentration of $Cu^{2+}$ with emission intensity. (d) Benesi–Hildebrand plot for chemosensor **SP26** with 1/concentration of $BF_3$ with emission intensity.

reciprocal of concentrations of $Cu^{2+}$ and $BF_3$ against $1/[F - F_0]$ (Fig. 4b). The binding association constants ($K_a$) for the **SP26 + $Cu^{2+}$** and **SP26 + $BF_3$** complexes were calculated to be $7.9 \times 10^4\ M^{-1}$ and $1.27 \times 10^4\ M^{-1}$ [Fig. 5(c) and (d)].

### 2.7 Job's plot, response time studies, and pH studies

In Job's plot analysis (Fig. 6a and b), it is possible to determine the binding ratio of the analyte to chemosensor **SP26.** The 0.5-mole fraction suggests that the binding ratio is 1 : 1 for both **SP26 : $Cu^{2+}$** and **SP26 : $BF_3$**. Additionally, as shown in Fig. 6c and d, the fluorescence intensity is drastically reduced within a fraction of a second when $Cu^{2+}$ and $BF_3$ are added to **SP26.** This indicates that the emission intensity decreased immediately, since a complex was generated by **SP26 + $Cu^{2+}$** and **SP26 + $BF_3$** as soon as analytes are added. The emission spectrum of the chemosensor **SP26** revealed an observable shift in the pH range of 5.0 to 12.0; below 5.0 pH, the emission intensity was high as a result of an increase in the supply of $H^+$, as seen in Fig. 6e and f. The protonation of nitrogen causes a small increase in emission intensity. Then, the emission intensity varies randomly with pH, influencing the chemosensor **SP26** with $Cu^{2+}$. The stability at pH 8 up to 12 is observed to some extent. The stability in emission intensity is observed in **SP26** with $BF_3$ in the pH range of 8.0 up to 12.0. As in the previous case, nitrogen is protonated at lower pH values between 2.0 and 7.0, resulting in the poor complexation of **SP26** with $BF_3$ lacking a single pair of electrons. Hence, emission intensity changes with different pH on treating **SP26** with $BF_3$ (Fig. 6f).

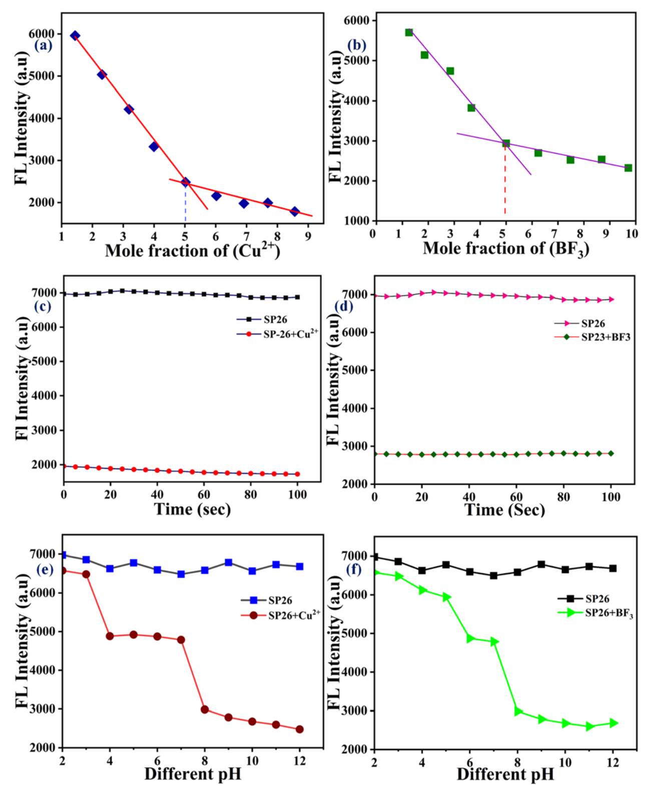



Fig. 6 (a) Job's plot of **SP26** with various mole fractions of $Cu^{2+}$ and emission intensities. (b) Job's plot of **SP26** with various mole fractions of $BF_3$ and emission intensities. (c) Response time for change in emission intensity after adding $Cu^{2+}$ to **SP26** in 8 : 2 THF : $H_2O$ ($2 \times 10^{-5}$ M). (d) Response time for change in emission intensity after adding $BF_3$ to **SP26** in 8 : 2 THF : $H_2O$ ($2 \times 10^{-5}$ M); for both, the excitation wavelength is at 360 nm and the emission wavelength is at 500 nm, and the scanned wavelength is 400 to 650 nm at room temperature. (e) The pH effect on the emission intensity of chemosensor **SP26**, and the emission intensity of chemosensor **SP26** with $Cu^{2+}$ pH (2.0–12.0). (f) The pH effect on the emission intensity of chemosensor **SP26**, and the emission intensity of chemosensor **SP26** with $BF_3$ pH (2.0–12.0).

### 2.8 Interference studies and reversibility studies

The interference experiments were carried out for chemosensor **SP26.** Along with $Cu^{2+}$ and $BF_3$, different metal ions and boron species were added separately to chemosensor **SP26**, and there were no changes except for $Cu^{2+}$ and $BF_3$.

In the case of $Cu^{2+}$ and $BF_3$, the emission intensity decreases even in the presence of other analytes. This shows the selectivity of chemosensor **SP26** towards $Cu^{2+}$ and $BF_3$ (Fig. 7(a) and (b)). Additionally, the reversibility of sensor **SP26** was evaluated using EDTA for $Cu^{2+}$ ions. When $Cu^{2+}$ was added to **SP26**, the colour changed from cyan to light blue, and the emission intensity falls (Fig. 7c). The emission intensity increased, and the colour of the **SP26** fluorescence changed from light blue to cyan upon the addition of EDTA. This phenomenon was repeatedly evaluated three times. Similarly, when $BF_3$ was added to **SP26**, the colour was shifted from cyan to light yellow, and the emission intensity diminished. However, the emission intensity

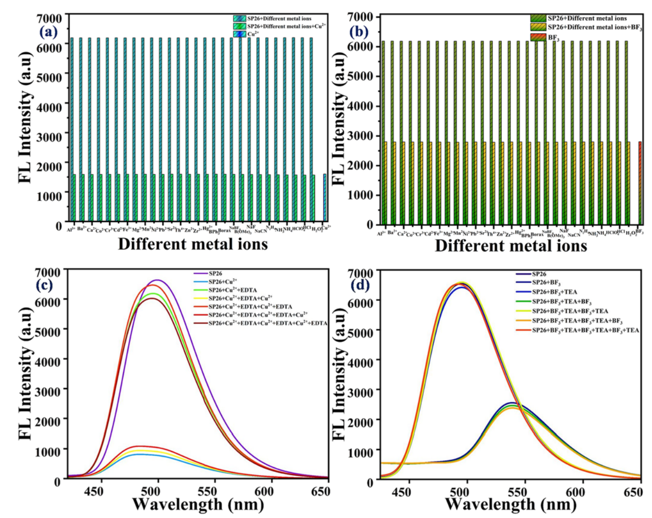
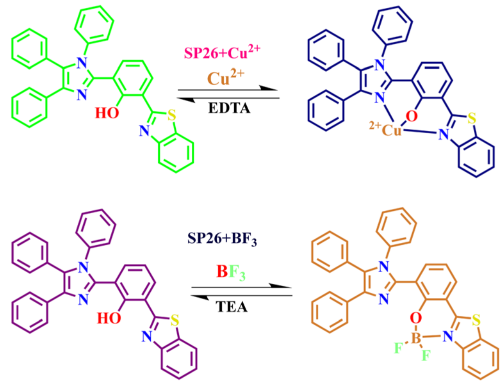



Fig. 7 (a) Interference of other metal ions and boron species ($1 \times 10^{-3}$ M) along with $Cu^{2+}$ on **SP26** in an 8 : 2 THF : $H_2O$ solution ($2 \times 10^{-5}$ M); the excitation wavelength is at 360 nm and the emission wavelength is at 500 nm, and the scanned wavelength is 400 to 650 nm at room temperature. (b) Interference of other metal ions and boron species ($1 \times 10^{-3}$ M) along with $BF_3$ on **SP26** in an 8 : 2 THF : $H_2O$ ($2 \times 10^{-5}$ M) solution. (c) The reversibility studies of **SP26** in 8 : 2 THF : $H_2O$ ($2 \times 10^{-5}$ M) solution with $Cu^{2+}$ by adding EDTA. (d) The reversibility studies of **SP26** in 8 : 2 THF : $H_2O$ ($2 \times 10^{-5}$ M) solution with $BF_3$ by adding TEA.




**Scheme 2** The mechanism of the reversibility of the chemosensor **SP26** with the addition of $Cu^{2+}$ + EDTA and **SP26** with the addition of $BF_3$ + TEA.

increases and the color changes back to cyan upon adding triethylamine (TEA) (Fig. 7d). This is due to the formation of a stronger complex between EDTA and $Cu^{2+}$ than between **SP26** and $Cu^{2+}$. Hence, EDTA replaces **SP26**, and similarly a stronger complex is formed between $BF_3$ and TEA than between **SP26** and $BF_3$. Hence, TEA replaces **SP26** (Scheme 2). After this, the chemosensor **SP26** was recovered, and this phenomenon was regularly examined for reproducibility over three cycles.

### 2.9 Study of the binding mechanism

We have performed $^1$H NMR for the sensor before and after adding $BF_3$. Between $BF_3$ and $Cu^{2+}$, $Cu^{2+}$ is paramagnetic and hence NMR cannot be recorded. Hence, we have recorded the FT-IR spectrum for the complex, and it has been compared with that of the ligand. By comparing these two, in the spectrum of the complex, the –OH stretching peak at 3400 cm$^{-1}$ completely disappears, and there is a change in the shape of the –C═N stretching peaks at 1300 and 1600 cm$^{-1}$, indicating that copper forms a complex through oxygen and nitrogen (Fig. 8a).

Binding interactions between **SP26** and $BF_3$ were studied using $^1$H NMR titration experiment in DMSO-d$_6$ and FT-IR. $BF_3$ binds with the phenolic oxygen when **SP26** is added. In $^1$H NMR, the –OH proton disappears completely since boron is getting attached to oxygen after removing $H^+$. Similarly, electrons from the carbon in the benzene ring, next to the nitrogen of benzothiazole, flow to the nitrogen due to the attachment of $BF_3$. As a result, the peak of the particular proton (H-1) becomes more pronounced and shifted downfield (8.692 ppm). However, all other protons also shifted downfield due to the attachment of $BF_3$ (8.053, 8.131, 8.169, 8.237 ppm) (Fig. 8c). Also in FT-IR, the –OH peak disappears completely, and there is a change in the shape of the –C═N stretching peaks at 1321 and 1614 cm$^{-1}$, indicating that boron forms a complex through oxygen and nitrogen (Fig. 8b).

The HR-MS spectrum of **SP26 + Cu$^{2+}$** shows a peak at 583.1092 *m*/*z* (Fig. S5), and **SP26 + BF$_3$** shows a peak at 570.1635 *m*/*z* (Fig. S6). Utilizing the Gaussian 16W package and

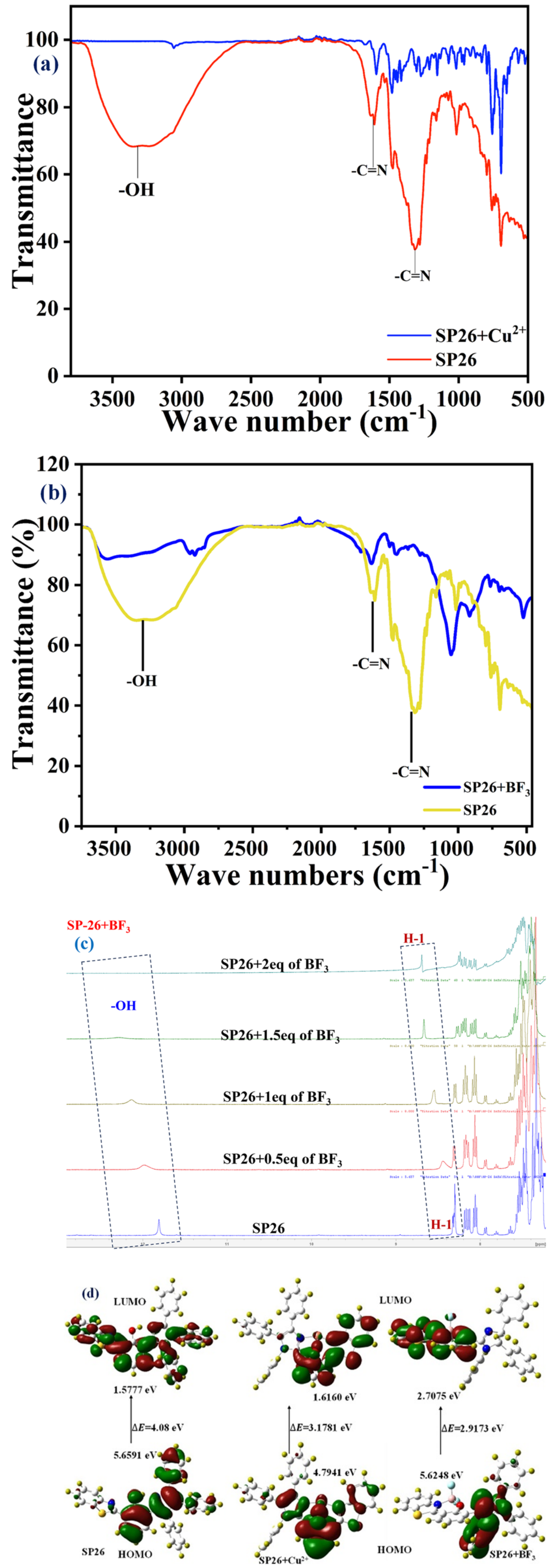



**Fig. 8** (a) IR spectra of **SP26** and **SP26** with $Cu^{2+}$. (b) IR spectra of **SP26** and **SP26** with $BF_3$. (c) $^1$H NMR spectra of **SP26** and **SP26** with $BF_3$ in DMSO-d$_6$. (d) The optimized structures of the HOMO and LUMO of **SP26** and **SP26** with $Cu^{2+}$ and $BF_3$ complexes at the DFT/B3LYP analysis.

Table 2 Determination of $Cu^{2+}$ ions in environmental samples

| Various water samples | SD (%) | Con. of spiked $Cu^{2+}$ ions (μM) | Con. of the found $Cu^{2+}$ ions (μM) | Recovery of $Cu^{2+}$ added (%) |
|---|---|---|---|---|
| Tap water | 0.458 | 25 | 24.85 | 99.4 |
| Lake water | 0.503 | 25 | 24.7 | 98.8 |
| Drinking water | 0.529 | 25 | 24.85 | 99.4 |

theoretical calculations at the B3LYP level with the 6-31'G(d,p) level of theoretical analysis,[46] density functional theory (DFT) was employed to determine the energy of the optimized structures of **SP26** and **SP26** with $Cu^{2+}$ and $BF_3$ complexes. In **SP26**, the electron density is concentrated in two phenyl groups, one of which is connected to nitrogen in the HOMO. Upon transitioning to a linear molecular orbital LUMO, the electron density disperses across the molecule, sparing all but one phenyl group; as a result, $\Delta E$ is 4.08 eV. The HOMO and LUMO of the **SP26 + $Cu^{2+}$** combination do not differ significantly due to electron spreading. However, the band gap decreases from 4.08 to 3.1781 eV. In the case of the **SP26 + $BF_3$** complex, the difference in electron spreading further decreases ($\Delta E$). As a result, the band gap is further closed to 2.9171 eV. The energy gap suggests that the **SP26 + $Cu^{2+}$** and $BF_3$ complexes stabilize the system (Fig. 8c). The chemosensor demonstrates that the interaction of **SP26** with $Cu^{2+}$ and $BF_3$ affects both twisted intramolecular charge transfer (TICT) and intramolecular charge transfer (ICT).

## 3. Application in real water samples

Human health suffers significant harm when copper sources contaminate water. The identification of $Cu^{2+}$ ions in environmental samples is therefore essential. $Cu^{2+}$ ion detection was carried out utilizing water samples from several locations across Vellore Institute of Technology, including tap, drinking, and lake water, to track the practical application of sensing probe **SP26**. Chemosensor **SP26** shows high sensitivity and selectivity towards $Cu^{2+}$. To test how well it can detect $Cu^{2+}$ in real water, we performed a spike and recovery test by checking the brightness of chemosensor **SP26** in tap water, lake water, and drinking water with the addition of $Cu^{2+}$. All the water samples were centrifuged and filtered before use. The water samples were spiked with a set amount of $Cu^{2+}$ (25 μM). As shown in Table 2, $Cu^{2+}$ was tested in each sample with satisfactory accuracy, which means chemosensor **SP26** could be used for $Cu^{2+}$ detection in water samples. It was discovered that the $Cu^{2+}$ ion concentrations in $Cu^{2+}$ spiked samples agreed fairly well. Further, over 98% of $Cu^{2+}$ was recovered, demonstrating the developed probe's ability to detect $Cu^{2+}$ ions in practice (Table 2).

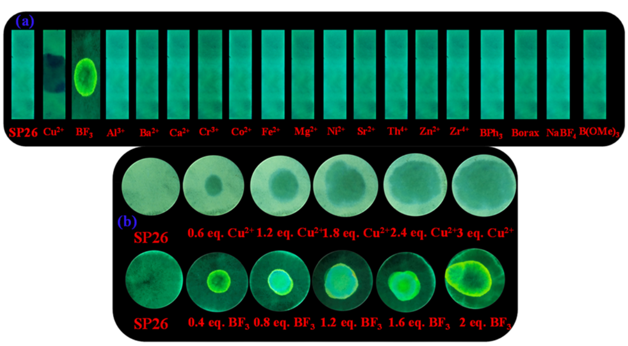



Fig. 9 (a) The photographs exhibiting the emission color change of **SP26** on paper strips, on the addition of different analytes under UV light at 365 nm, and (b) the gradual addition of different equivalents of $Cu^{2+}$ and $BF_3$ of **SP26**.

### 3.1 Application of chemosensor SP26 in the paper strip test

We created paper strips to detect $Cu^{2+}$ and $BF_3$ levels, which were simple to use and convenient. The paper strips were created by dipping Whatman filter paper into a solution of $2 \times 10^{-5}$ M concentration of **SP26**, followed by air drying. Three drops of analyte at a concentration of $1 \times 10^{-3}$ M were applied to paper strips. We illuminated the strips under a 365 nm UV lamp after allowing them to air dry. Except for $Cu^{2+}$ and $BF_3$, there was no change in colour. $Cu^{2+}$ produces a colour shift from cyan to light blue. In contrast, $BF_3$ causes a color change from cyan to yellow (Fig. 9a). The emission color was then gradually altered for both $Cu^{2+}$ and $BF_3$ (Fig. 9b), as the gradual addition of $Cu^{2+}$ and $BF_3$ to the paper strips increased from 0 to 3 equivalents and 0 to 2 equivalents, respectively. The results revealed the qualitative detection of $Cu^{2+}$ and $BF_3$ by the chemosensor **SP26**.

## Conclusion

We have synthesized and presented **SP26**, a new imidazole chemosensor characterized by NMR and HRMS analytical techniques. $Cu^{2+}$ quenches emission intensity at 500 nm, and $BF_3$ reduces emission intensity at 550 nm with a corresponding red shift. The chemosensor **SP26** can be made reversible using EDTA; emission intensity was first quenched by $Cu^{2+}$, and then it was restored by adding EDTA to **SP26**. Similarly, adding $BF_3$ to **SP26** caused the emission to move to 550 nm with a reduction in intensity; however, adding TEA to the same solution caused the emission intensity to reversibly change back to **SP26** emission. After that, we studied the binding mechanism using Job's plot, mass spectroscopy, DFT investigations, NMR titration, and FT-IR spectroscopy. For **SP26** with $Cu^{2+}$ and $BF_3$, a 1 : 1 complex was produced with coordinated imidazole nitrogen and phenolic oxygen atoms. The limit of detection was 381 pM for $Cu^{2+}$ and 307 pM for

$BF_3$, and the response time was within a second. The rapid qualitative application of paper strip studies and quantitative application in environmental water samples were carried out with our synthesized chemosensor **SP26**.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

Supplementary information: Copies of $^{1}H/^{13}C$ {$^{1}H$} NMR and HRMS spectra for the sensing receptor **SP26** and the **SP26** + **Cu** and $\mathbf{BF_3}$ complexes, along with HRMS spectra and a comparison of results with previous work reported in the literature. See DOI: https://doi.org/10.1039/D5SD00021A.

The data supporting this article have been included as part of the SI.

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