



3-Pyrrolyl BODIPY Based Selective Cu²⁺ Ion “Off-On” Fluorescent Sensor

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Abstract. 3-Pyrrolyl BODIPY-Schiff base conjugate was synthesized by treating α -formyl 3-pyrrolyl BODIPY with *o*-hydroxy aniline in ethanol at reflux followed by recrystallization. The conjugate was thoroughly characterized by HR-MS, 1D & 2D NMR and X-ray crystallography. The X-ray analysis revealed that the BODIPY core was in planar arrangement, with the central boron atom coordinated with two pyrrole nitrogens of dipyrin moieties and two axial fluoride ions in a tetrahedral geometry. The 3-pyrrolyl BODIPY-Schiff base conjugate exhibited a strong absorption band at 616 nm and broad weak fluorescence band at 660 nm. The absorption and fluorescence titration studies with various metal ions revealed that 3-pyrrolyl BODIPY can act as colorimetric optical sensor and specific “off-on” fluorescent sensor for Cu²⁺ ion.

Keywords. BF₂ Complexes; Off-on sensor; Cu²⁺ sensor; 3-Pyrrolyl BODIPY.

1. Introduction

The development of new fluorescent chemosensors for transition metals and other heavy metals have drawn continuous interest for several years because of their importance in the fields of biological, environmental and chemical systems.^{1–3} Copper(II) ion is the third most abundant element in the human body and plays an important role in various biological processes. Living cells must maintain an optimal concentration of copper ions to keep the normal functioning of enzymes and intracellular metabolic balance. Deficient or excessive levels of Cu²⁺ ions may cause a series of severe diseases such as Menkes syndrome, Wilson’s disease, Alzheimer’s disease, etc., and long term exposure to Cu²⁺ ions can cause liver and kidney damage.^{4–6} The average concentration of Cu²⁺ ion in human blood is in the range of 15.7–23.6 μ M and the maximum allowed level of Cu²⁺ ions in drinking water is about 30 μ M and intake of Cu²⁺ ions should not exceed 10–12 mg per day for adults. Thus, the development of more sensitive and selective fluorescent chemosensors that can be used efficiently to

detect and evaluate the Cu²⁺ ion levels in environmental and biological systems is of great importance.^{7–10}

There are several fluorescent chemosensors with various molecular structures and different recognition mechanisms have been developed for detection of copper ions. The fluorescent Cu²⁺ ion sensors can be classified into the following categories based on their recognition mechanism as well as their fluorescence response to Cu²⁺ ions: (i) “on-off”, (ii) “off-on”, (iii) ratiometric and (iv) Cu²⁺ ion promoted reaction-based chemosensors. Among all the above-mentioned categories, the “on-off” fluorescence of chemosensors for Cu²⁺ ion are the most common and extensively investigated. Due to the intrinsic paramagnetic nature of Cu²⁺ ion, quite a large number of fluorescent chemosensors for Cu²⁺ often show a fluorescence quenching to some extent. In other words, the free chemosensors which are fluorescent show strong fluorescence quenching upon interaction with Cu²⁺ ions. However, fluorescence “on-off” sensors have certain disadvantages.^{11–20} Hence research was focussed on developing fluorescent sensors which work on “off-

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on” mechanism. These chemosensors are very weakly fluorescent or completely non-fluorescent but in the presence of Cu^{2+} ions, these chemosensors become highly fluorescent.

Among several fluorescent chemosensors, the BF_2 complexes of dipyrrens popularly known as BODIPYs (Figure 1) have received tremendous attention because of their excellent spectroscopic properties like narrow absorption and fluorescence in the visible to NIR region depending on substituents, high molar extinction coefficients, high fluorescent quantum yields, moderate redox potentials, negligible triplet formation, excellent chemical, thermal and photostability, high solubility and relative insensitivity to environmental perturbations such as solvent and pH. BODIPYs showed extensive applications in various fields including sensors for cations and anions.^{21–29} Our research is involved in the design and synthesis of different new derivatives of BODIPYs & azaBODIPYs and studied their photophysical properties.^{30–36} During the course of our investigations, a few years back we reported³⁷ the synthesis of BODIPY having pyrrolyl group at α -position of dipyrren moiety which are known as 3-pyrrolyl BODIPYs **2**. The electronic properties of 3-pyrrolyl BODIPYs are quite different from BODIPYs and we have been used the free pyrrolyl group as a handle to prepare various interesting fluorescence compounds.^{38–42} In continuation of our research on 3-pyrrolyl BODIPYs, herein we report the synthesis of a new 3-pyrrolyl BODIPY based chemosensor and showed its use as an exclusive “off-on” fluorescent sensor for Cu^{2+} ions as judged by absorption and fluorescence studies.

2. Experimental

2.1 Materials and methods

Chemicals such as $\text{BF}_3 \cdot \text{OEt}_2$ and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 4-aminophenol and all-metal chloride salts were obtained from Aldrich. Silica (60–120 mesh) used for column chromatography was obtained from Acme Chemicals, India. Dichloromethane (HPLC grade), acetonitrile (A. R. grade) from Merck India, was used for all the absorption and fluorescence measurements, analysis without further purification. Deuterated DMSO-D_6 was purchased from Sigma-Aldrich, USA and used for NMR studies. The ^1H and ^{13}C NMR spectra were recorded in DMSO-D_6 on Bruker 400 and 500 MHz instruments. Tetramethylsilane $[\text{Si}(\text{CH}_3)_4]$ was used as

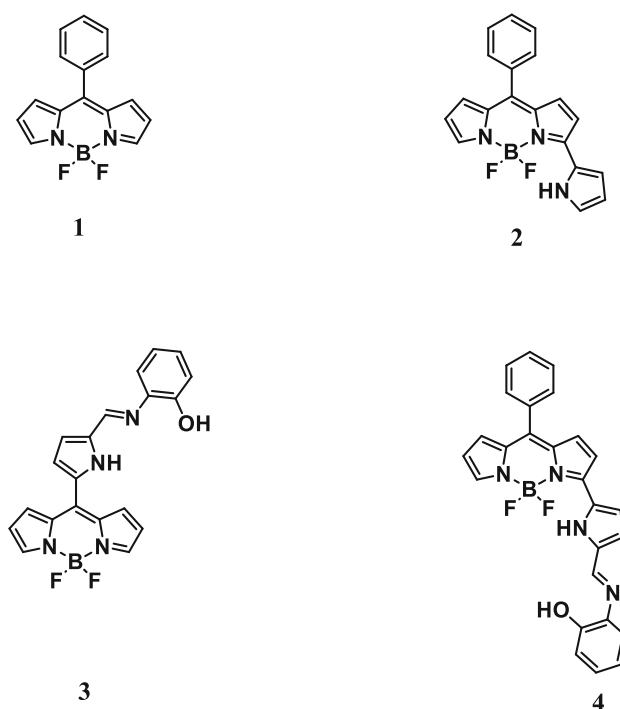


Figure 1. Structures of boron-dipyrromethenes **1–3** and 3-pyrrolyl BODIPY conjugate **4**.

an internal standard for ^1H and ^{13}C NMR. Absorption spectra were obtained with a Shimadzu UV–vis-NIR spectrophotometer. The HR mass spectra were recorded with a Q-TOF micro mass spectrometer. The Single-crystal X-ray structure analyses were carried out on a Rigaku Saturn 724 diffractometer conjugated with a low-temperature attachment. Data were collected at 100 K by means of graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by the ω -scan method. The structures were solved by direct methods and refined by least-squares against F^2 employing the software packages SHELXL-97,18 SIR-92,19 and WINGX.20. All non-hydrogen atoms were refined anisotropically. CCDC no. 2073337, for compound **4** contain the supplementary crystallographic data of these compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For UV–vis titration experiments, the stock solution of BODIPY **4** ($2.5 \times 10^{-5} \text{ M}$) was prepared by using spectroscopic grade CH_3CN , and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution was prepared ($7.5 \times 10^{-4} \text{ M}$) in CH_3CN .

2.2 Synthesis of Compound 4

The sample of α -formyl 3-pyrrolyl BODIPY **5** (100 mg, 0.35 mmol, 1 eq.) was added to a 100 mL round bottomed flask containing ethanol (40 mL) and

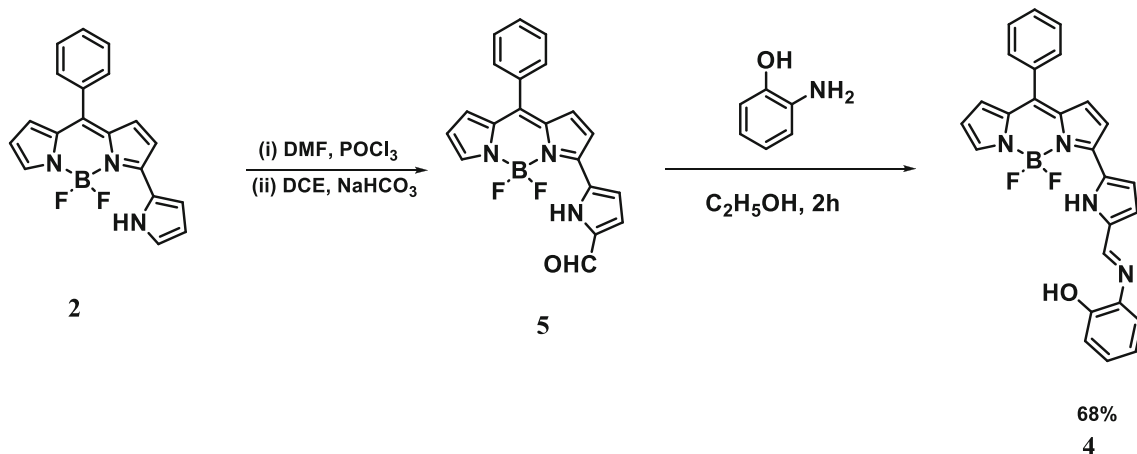
stirred at room temperature under inert atmosphere for 5 min. One equivalent of 2-amino phenol (38 mg, 0.351 mmol, 1 eq) was added to the reaction flask and the resulting solution was then refluxed for 2 h. The progress of the reaction was monitored by TLC analysis at frequent intervals. After the completion of reaction, the solvent was completely removed on a rotary evaporator under vacuum and the crude compound thus obtained was recrystallized twice from petroleum ether/CH₂Cl₂ to afford pure desired compound **4** as red powder in 68% yield. Red Powder; Yield: 72%; ¹H NMR (500 MHz, DMSO) δ 11.90 (s, 1H, pyrrole NH), 9.09 (s, 1H, Ph-OH), 8.71 (s, 1H, CH), 7.94 (s, 1H, Pyrrole-H), 7.70–7.59 (m, 6H, Ph-H), 7.56 (d, *J* = 3.7 Hz, 1H, pyrrole-H), 7.46 (d, *J* = 4.7 Hz, 1H, pyrrole-H), 7.38 (d, *J* = 7.6 Hz, 1H, Ph-H), 7.17–7.09 (m, 2H, pyrrole-H, Ph-H), 7.00 (d, *J* = 4.0 Hz, 1H, pyrrole-H), 6.94 (d, *J* = 8.0 Hz, 1H, Ph-H), 6.87 (t, *J* = 7.6 Hz, 1H, Ph-H), 6.80 (d, *J* = 3.7 Hz, 1H, pyrrole-H), 6.65–6.60 (m, 1H, pyrrole-H). ¹³C NMR (126 MHz, DMSO-d₆) δ 152.64, 150.08, 147.17, 141.91, 140.47, 137.63, 136.58, 134.03, 133.70, 133.61, 130.94, 129.08, 128.84, 127.63, 127.29, 121.65, 120.02, 118.99, 118.41, 118.30, 118.17, 116.15, 40.31, 40.15, 39.98, 39.81, 39.65. ¹¹B NMR (160 MHz, DMSO-d₆) δ 1.22 (t, *J* = 31.2 Hz). ¹⁹F NMR (471 MHz, DMSO-d₆) δ -141.45 (dd, *J* = 63.1, 29.2 Hz). HRMS Calcd for (C₂₀H₁₆BF₂N₄O): 453.1693 (M+H)⁺, found 453.1690 (M+H)⁺.

3. Results and Discussion

The required 3-pyrrolyl BODIPY based sensor **4** was synthesized as shown in Scheme 1. The precursor, 3-pyrrolyl BODIPY **2** was prepared by following our reported procedure.³⁷ It was shown earlier that the

appended pyrrole of 3-pyrrolyl BODIPY **2** can be easily functionalized with halogens, aldehyde, nitro group, etc., at its α-position as this position is very reactive and the functionalized 3-pyrrolyl BODIPYs can be used as building blocks to prepare several interesting 3-pyrrolyl BODIPY based fluorescent systems. The α-formyl 3-pyrrolyl BODIPY **5** was prepared by subjecting 3-pyrrolyl BODIPY **2** to Vilsmeier-Haack reaction conditions as reported earlier.³⁸ The target 3-pyrrolyl based Schiff base fluorescent sensor **4** was synthesized by reacting **5** with *o*-hydroxy aniline in ethanol at reflux for 2 h followed by recrystallization and afforded the fluorescent sensor **4** in 68% yield. We also synthesized our reported⁴³ *meso*-pyrrolyl BODIPY based fluorescent sensor **3** which has a similar functionalized handle for sensing cations at *meso*-position like sensor **4** for comparison purpose.

Compound **4** was freely soluble in common organic solvents and the identity of compound **4** was confirmed by molecular ion peak at 453.1690 in HR-MS spectrum. Compound **4** was thoroughly characterized by ¹H, ¹H-¹H COSY, ¹⁹F & ¹¹B NMR spectroscopy as presented in Figure 2. All resonances observed in ¹H NMR spectrum were identified based on their location, integration, coupling constant and cross peak correlations observed in COSY spectrum. The seven pyrrole protons of compound **4** appeared as seven separate resonances in the region of 6.5–8.0 ppm and the pyrrole protons were identified based on their cross-peak correlation observed in ¹H-¹H COSY as shown in Figure 2b. In ¹H NMR, the appended pyrrole NH appeared as broad resonance at 11.9 ppm; the CH proton appeared as sharp singlet at 8.71 ppm and the –OH proton also appeared as a sharp singlet at 9.09 ppm. Compound **4** showed a triplet resonance at



Scheme 1. Synthesis of 3-pyrrolyl BODIPY-Schiff base conjugate **4**.

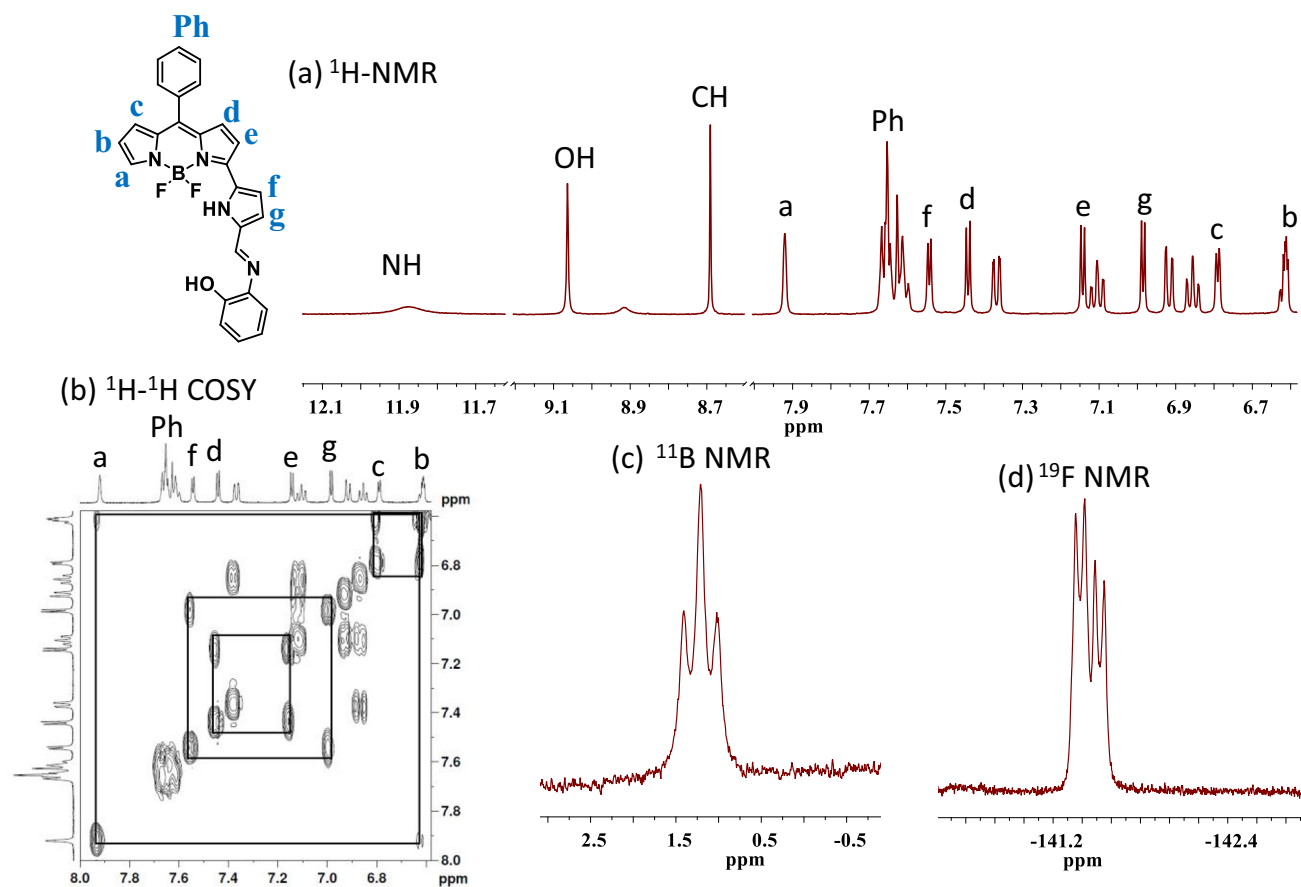


Figure 2. Partial a) ^1H NMR, b) ^1H - ^1H COSY c) ^{11}B NMR and d) ^{19}F NMR spectra of compound **4** recorded in DMSO-d_6 at 25°C .

1.22 ppm in ^{11}B NMR and a quartet resonance at -140.45 ppm in ^{19}F NMR. Compound **4** exhibited a weak absorption band at 360 nm with a shoulder and a relatively strong absorption band at 616 nm. Compound **4** was very weakly fluorescent with a broad fluorescence band at 660 nm.

The single-crystal X-ray diffraction study of the green coloured crystals supported the formation of 3-Pyrrolyl Bodipy-Schiff base conjugate **4** and the crystals were obtained *via* slow diffusion of compound **4** in dichloromethane and *n*-hexane in two days. The compound **4** crystallized in the orthorhombic space group $\text{P2}_1\text{2}_1\text{2}_1$. The crystal structure of **4** (CCDC no. 2073337) is shown in Figure 3 and relevant crystallographic data, selected bond lengths and bond angles are presented in Tables S1-S3 (Supplementary Information). In the crystal structure of compound **4**, the BODIPY core was in planar arrangement, with the central boron atom coordinated with two pyrrole nitrogens of dipyrroin atoms and two axial fluoride ions in a tetrahedral geometry with bond angles of $107.3^\circ(7)$ (N2-B1-N1), $107.8^\circ(7)$ (F2-B1-F1), $111.6^\circ(7)$ (F2-B1-N1) and $109.6^\circ(6)$ (F2-B1-N2). In compound **4**, the

meso-aryl group was oriented at 66.30° relative to the BODIPY core and the phenyl substituent also showed out of plane arrangement by an angle of 35.30° with respect to the dipyrroin core. The appended pyrrole was almost in plane with a small deviation of 10.86° from the 12-atom mean plane of dipyrromethene and boron atom. The deviation of appended pyrrole ring clearly reflected in their NH-F distances which were 2.45 and 2.15\AA , supporting the existence of intramolecular hydrogen bond. The C14-N4 bond length was ~ 1.28 (10) \AA which supports the imine bond present in 3-pyrrolyl BODIPY-Schiff base conjugate **4**.

3.1 Metal Sensing Studies

Compound **4** was tested for its potential ability for sensing different metal cations by treating it with different metal salts in CH_3CN . First, by using visual inspection, we checked the colour changes of compound **4** both ambient and UV light with the addition of the various metal salts (Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Ca^{2+} , Mg^{2+} , Cd^{2+} , Hg^{2+} , Ba^{2+} , Li^+ , Na^+ , and K^+).

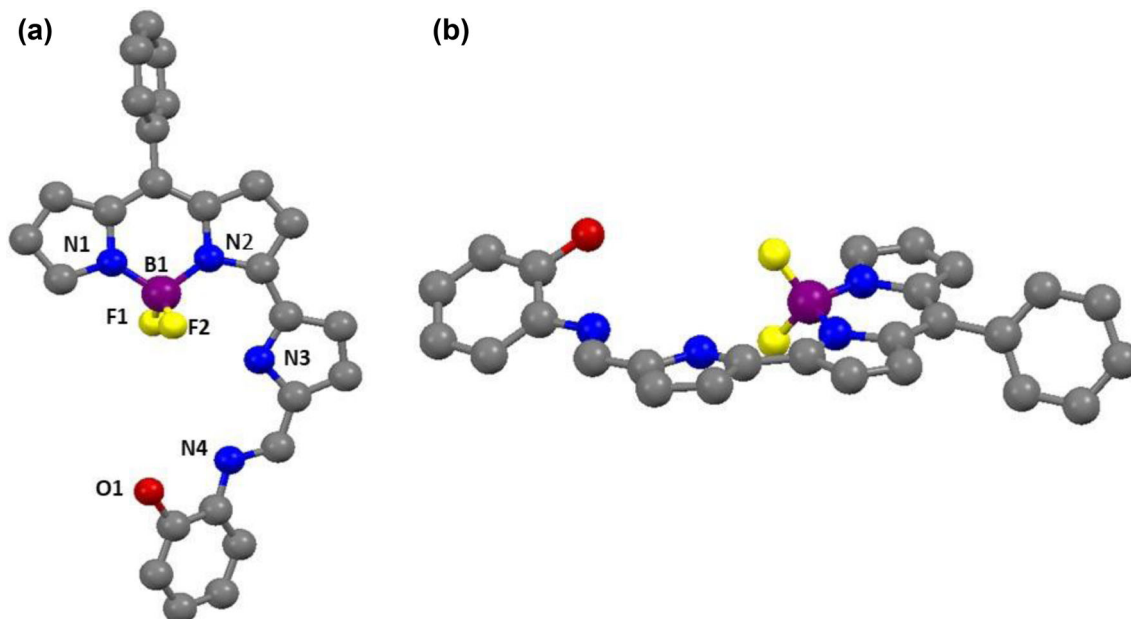


Figure 3. X-ray single crystal structure of the compound **4**: (a) top view (thermal ellipsoids are drawn at 50% probability) and (b) side view.

Only addition of Cu^{2+} ion resulted in a clear colour change from blue to grey-green which was distinctly visible to the naked eye and significantly enhanced orange-red fluorescence under UV light indicating that

compound **4** has the potential to act as a sensor for Cu^{2+} ions. This observation was also confirmed by qualitative absorption and fluorescence spectral studies. Upon addition of different metal salts to the

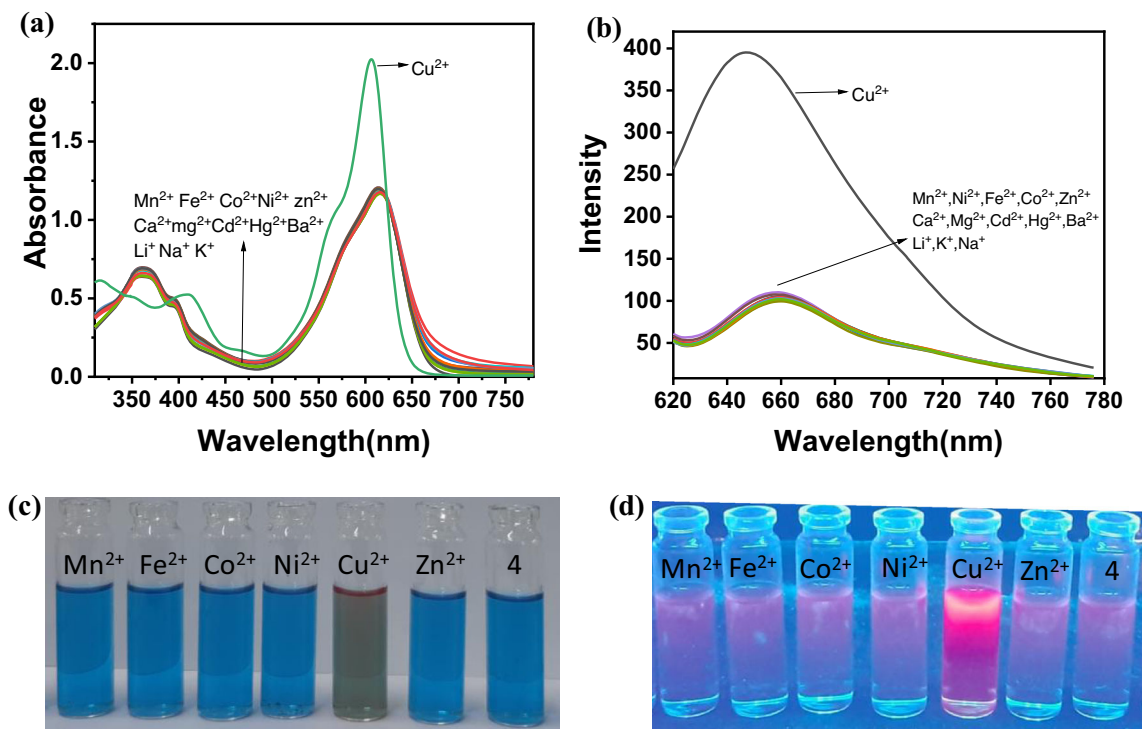


Figure 4. (a) Absorption spectra of compound **4** (conc.) upon addition of different metal ions in CH_3CN ; (b) Emission spectra of compound **4** (conc.) upon addition of different metal ions in CH_3CN (c) Colour change induced upon addition of excess equivalents of various metal salts to BODIPY-conjugate **4** (2.5×10^{-5} M) in CH_3CN solution under daylight; (d) Colour change induced upon addition of excess equivalents of various metal salts to BODIPY-conjugate **4** (2.5×10^{-5} M) in CH_3CN solution under UV light.

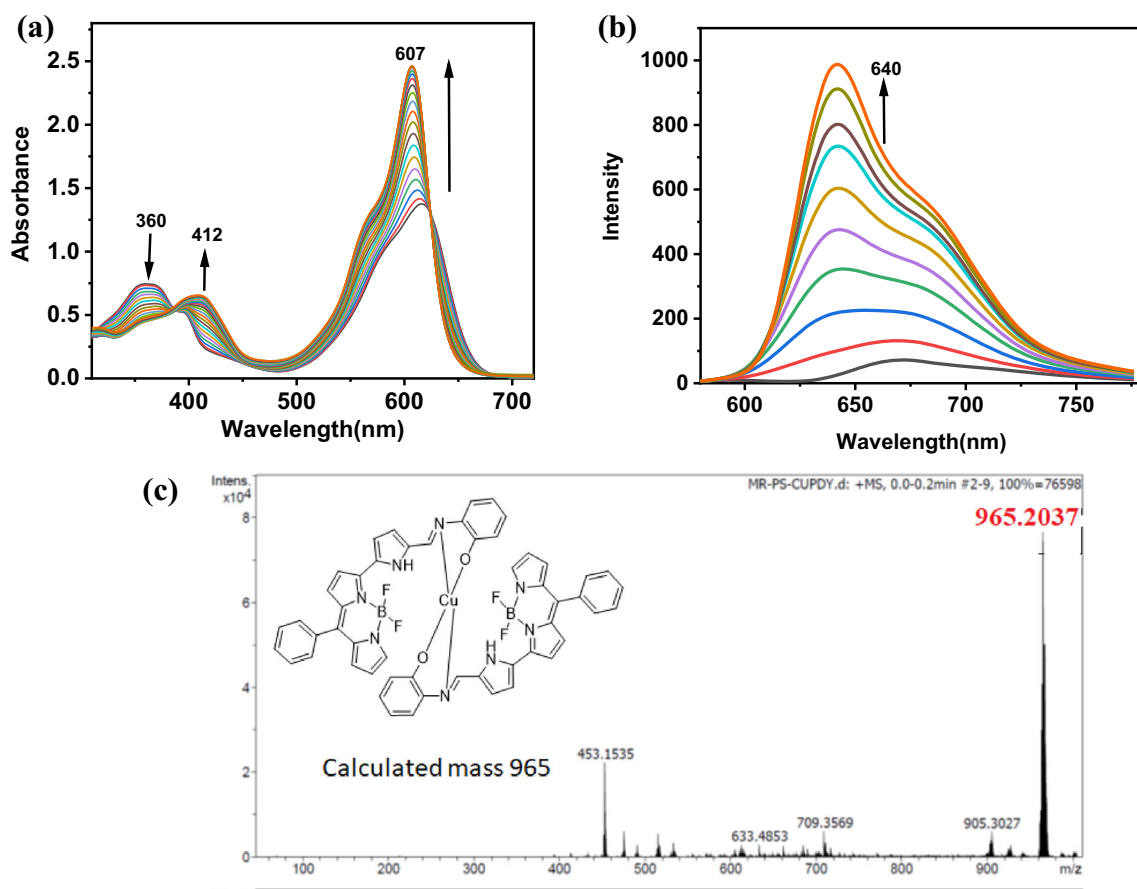


Figure 5. (a) Absorption spectra of **4** (conc.) upon addition of increasing equivalents of CuCl_2 in CH_3CN solvent. (b) Emission spectra of **4** (conc.) upon addition of increasing equivalents of CuCl_2 in CH_3CN solvent. The excitation wavelength (λ_{ex}) used was 570 nm. (c) Mass spectra of compound $(\mathbf{4})_2\text{Cu}^{2+}$.

compound **4** in CH_3CN , the absorption spectrum of compound **4** showed a slightly blue-shifted strong absorption band at 607 nm only in the presence of Cu^{2+} ion whereas there was no change in the absorption spectral pattern in the presence of other metal ions. In addition, a significant enhancement in the fluorescence band was observed with a slight blue shift in emission maxima only in the presence of Cu^{2+} ions whereas the fluorescence band remained unaltered in the presence of other metal ions which portrays that compound **4** acts as a highly selective sensor for the detection of Cu^{2+} ions in solution (Figure 4). Interestingly, our previously reported compound **3** which has a similar pyrrolyl based handle at *meso* position did not show any sensing behaviour towards Cu^{2+} ions.

Figure 5 shows the changes in absorption and fluorescence spectra of sensor **4** in CH_3CN upon the addition of increasing amounts of Cu^{2+} ions. Figure 5a shows that with increasing Cu(II) ions concentration, the absorption band centered at 607 nm undergoes slight blue-shift and increases in intensity whereas the

weak band at 360 nm experiences redshift to 412 nm with clear two isosbestic points at 623 and 385 nm suggesting the presence of two species, the free compound **4** and Cu^{2+} ion bound compound **4**.

4. Conclusions

The fluorescence spectral studies also showed that with increasing concentration of Cu^{2+} ion, the fluorescence spectrum of compound **4** which was a very low intense broadband showed a continuous blue-shift in conjunction with a significant increase in the emission intensity (Figure 5b). All these results indicated that compound **4** acts as a selective “off-on” sensor for Cu^{2+} ion. Based on our preliminary mass spectral analysis which showed a molecular ion peak at 965.2, we tentatively propose that the Cu^{2+} ion was bound to two units of ligand **4** in a tetrahedral fashion (Figure 5c). Our attempts to obtain good crystals of Cu^{2+} ion bound **4** complex were unsuccessful at this stage and we continue our efforts in this direction in near future.

Notes The authors declare no competing financial interest.

Supplementary Information (SI)

Tables S1-S3 are available at www.ias.ac.in/chemsci.

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