

Dipyridine-Thiophene-Based Fluorescent Probe: Synthesis, Crystal Structure, and Selective Recognition of Cu²⁺ Ions

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An efficient fluorescent sensory platform was designed and synthesized for recognition of copper ion (Cu²⁺) in presence over other competing ions. The probe DTBPA 1 was displayed fluorescence color change upon addition of Cu²⁺ ion which was also characterized by spectroscopic techniques especially the fluorescence and colorimetric methods. The probe showed turn-off fluorescence response to the Cu²⁺ ion. The limit of detection for the probe was found to be 0.789 μM while binding stoichiometry for the probe to metal ion was found to be 2:1 tested by Jobs analysis. The binding constant for the

probe was found to be 1.13×10⁶ M⁻¹. Further the probe was utilized for detection of trace amount of Cu²⁺ ion in real water sample with recoveries 98.24%~104%. The molecule was further utilized in test strip application. The calculated fluorescence quantum yield was found to be 3.2. The theoretically Density Functional Theory (DFT) calculations were performed for the probe using Gaussian 16 *ab initio*/DFT quantum chemical simulation and the DFT calculations were supporting the experimental findings.

Introduction

The recent development in the field of fluorescence chemo sensing is playing tremendous and excellent role in specific detection of transition metal ion because of their wide scope in various fields such as biological, chemical, medical and environmental remediation. Amongst all the metal ions copper is an essential and most abundant transition metal ion which is considered to be important in human metabolism and plant photosynthesis.^[1-3] Many biological and physiological processes such as antioxidant defence, neurotransmitter, and metabolism are dependent on the Cu²⁺ ion as it acts as an important cofactor/catalyst for electron transport and various oxidoreductase reactions.^[4-6] Deficiency of copper ion in human may lead to gastrointestinal diseases and abnormal growth of bones however in plants the low level of plants may inhibit the proper

growth and other processes.^[7] Nearly around 40 μg L⁻¹ is essential for the normal metabolic processes in the biological system. In addition, excessive amount of copper intake in the body may result in to various neurodegenerative diseases such as Alzheimer's Parkinson's, Menkes and Wilson diseases and other genetic disorders, it may result in to cancer, in turn the high level of copper in body may denature the proteins.^[8] The limit of copper in drinking water as per the US Environmental protection agency (EPA) is 1.3 ppm (20 μM).^[9-12]

Therefore, there is need of developing convenient and fast method for detection of copper metal ion. There are several instrumental methods such as Inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry and cyclic voltammetry for detection and quantifying the explored its application in the detection Cu (II) ion but due to their drawbacks such as high instrumentation cost, time consuming and tedious handling with complex the instrumentation which limits its application.^[13,14] Hence other alternative analytical methods have attracted great attention of many researchers in the field of fluorescence sensing for detection of various metal ion that are considered environmentally important and toxic pollutant. This method is regarded as most powerful due to its high selectivity, sensitivity, easy operation, simple to use and ease of synthesis. By using the different strategies till today number of fluorescent chemo sensing devices have been designed and synthesized for detection of metal ion, anions and neutral biomolecules.^[15-17] Thus, introducing to few fluorescent probes that are used for detection of copper such as various functionalized organic dyes, magnetic nanoparticles, quantum dots, fluorescent metal organic framework, and so on. All this material has high photostability, biocompatibility, low photobleaching, large stokes shift and low toxicity.^[18-20]

On the part of current ongoing research herein we have synthesized N,N-diphenyl-4-(6-thiophene-2-yl)-[2,2'-bipyridin]-4-

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yl)aniline [DTBPA 1] fluorescent probe which exhibits turn off fluorescence response towards copper metal ion. The probe was synthesized by reacting 4-(diphenylamino)benzaldehyde with Michael salt of pyridine in presence of ammonium hydroxide and catalytic amount of acetic acid via Krohnke pyridine synthesis.^[21–23] The probe consists of dipyridine and thiophene moiety. There are several derivatives which are used for detection of Mercury and Zinc with three pyridine moieties.^[24,25] From the earlier reported work, we synthesized another derivative using diphenylamine as donor. The probe comprising of the two pyridine and thiophene unit showed good selectivity towards the Cu (II) ion in presence over other ions. Usually, Cu²⁺ ion in *d*⁹ configuration is considered as quencher in fluorescent analysis.^[26] While in our analytical study we also observed the same phenomenon of Quenching upon addition of Cu²⁺ ion. The recognition moiety binds with Cu²⁺ ion by sharing of lone pair of the electrons present on the two nitrogen of pyridine present in the core. The probe was well characterized by using ¹HNMR, ¹³CNMR, ESI-Mass, elemental analysis. In addition, its optical and photophysical properties were studied by UV-Vis and fluorescence spectroscopy.

Results and Discussion

Solvent Study

The probe DTBPA was successfully synthesized and characterized by ¹HNMR, ¹³CNMR, ESI-Mass, Single crystal XRD. Further its optical and photophysical properties were performed in various solvents. Therefore, the solubility is the important parameter that is considered before analysis and it was found that the probe was completely soluble in organic polar aprotic solvent. The study of solvatochromic effect in different solvent such as dimethyl sulphoxide (DMSO), Acetonitrile (ACN), tetrahydrofuran (THF), chloroform (CHCl₃) and water (H₂O) was performed. The absorption and fluorescence analysis showed good solvatochromism effect. The probe DTBPA 1 showed good absorption peak at 285 nm and 358 nm with strong emission at 495 nm in ACN. While in DMSO and THF the absorption was observed at 285 and 358 nm and emission for DMSO was 498 nm but for THF emission was shifted to 448 nm. Similar shift in emission was observed for CHCl₃ at 448 nm with decrease in fluorescence intensity. But when the probe was added in water absorption intensity was weak compared to the other polar aprotic solvent and emission intensity was also weak as shown in plot Figure 1. This reveals that the probes DTBPA 1 shows solvatochromism effect in different solvent. From the solvent analysis study, we choose ACN as good solvent for further sensing studies.

Sensing Performance

After the solvent analysis our next approach was to use the probe DTBPA 1 for studying the response of the recognition moiety for detection of various cations such as Cu²⁺, Fe³⁺, Fe²⁺,

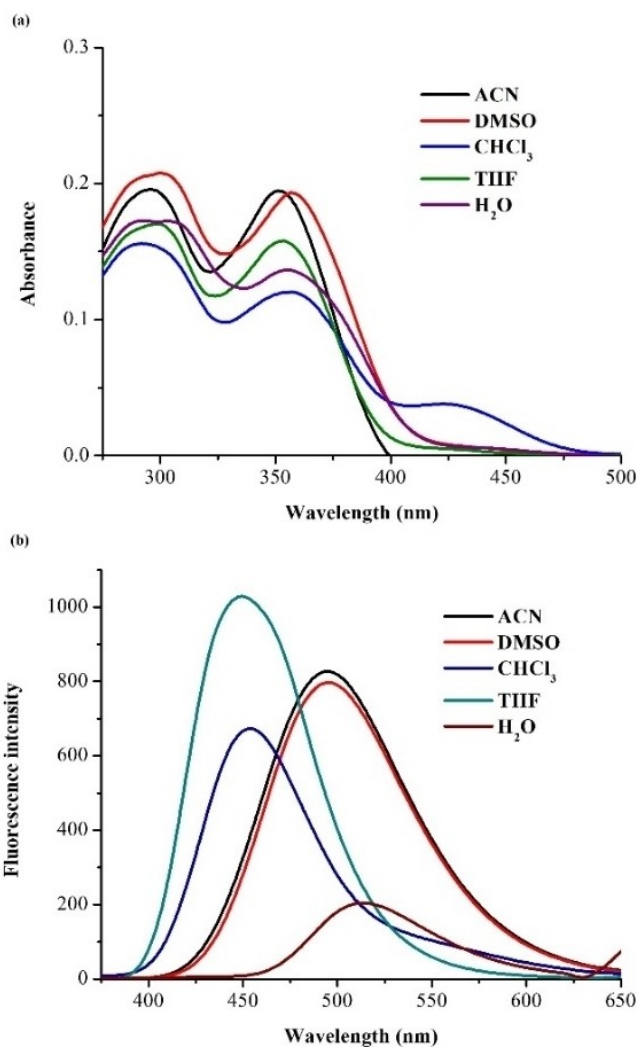


Figure 1. (a) The absorption spectra recorded for DTBPA probe in different solvent to study the solvatochromic effect (b) the emission plot for DTBPA probe in different solvents.

Hg²⁺, Pb²⁺, Ni²⁺, Zn²⁺, Mn²⁺, Co²⁺, Al³⁺, Ca²⁺, Ba²⁺, Cd²⁺, K⁺. The sensing performance for the probe was carried out in acetonitrile solvent by placing 1 mM stock solution in 2 ml of ACN. To the series of probe solution different cations were added (~1 mM). Upon addition of different cation vials were placed under UV light illumination at 365 nm. It was observed that the green fluorescence of the probe quenches with addition of Cu²⁺ ion while there was no change in fluorescence observed for other cation. Therefore, we could conclude that the probe DTBPA 1 has high selectivity towards Cu²⁺ ion in presence over other metal ions. While no change is observed in naked eye. The fluorescence color change is observed as shown in Figure 2.

UV-Vis Absorption Study

As confirmed from the sensing performance the probe DTBPA 1 showed selectivity towards Cu²⁺ ion in presence over other



Figure 2. The sensing performance for DTBPA 1 over different cations representing the quenching of fluorescence upon addition of Cu^{2+} ion.

ions (Figure 3a). As from the earlier reported work the core containing bipyridine and thiophene unit shows high selectivity and sensitivity towards Cu^{2+} ion.^[30] Thus, we studied its absorption changes in order to confirm its selectivity towards various ions. To study its detecting ability towards metal ions 5 μM of the probe DTBPA 1 solution was taken in series of vial and to that metal ions such as Cu^{2+} , Fe^{3+} , Fe^{2+} , Hg^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Al^{3+} , Ca^{2+} , Ba^{2+} , Cd^{2+} , K^{+} were added. As shown in Figure 3a upon addition of different ions there was prominent change in absorption that exhibits good selectivity

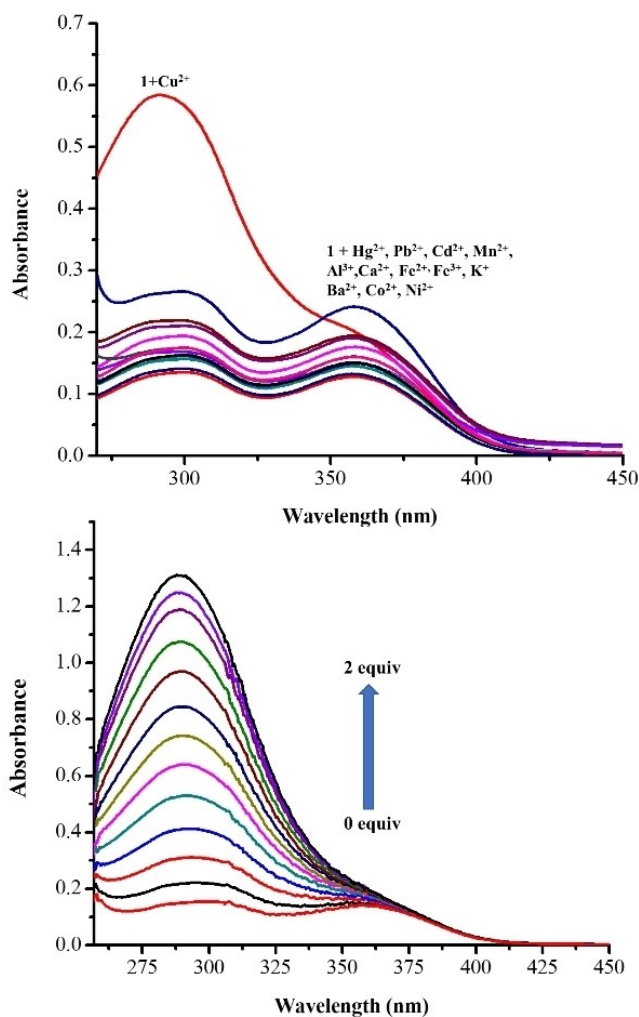


Figure 3. (a) Plot representing the absorption change upon addition of different metal ions Cu^{2+} , Fe^{3+} , Fe^{2+} , Hg^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Al^{3+} , Ca^{2+} , Ba^{2+} , Cd^{2+} , K^{+} . (b) UV-Vis absorption titration for the DTBPA 1 with incremental addition (0–2 equiv.)

towards Cu^{2+} ion. Initially the probe showed two clear absorption peaks at 298 nm and 358 nm but upon addition of Cu^{2+} there was disappearance of absorption peak that appeared at 358 nm with strong increase in absorption peak at 298 nm. In addition, the UV-Vis titrations studies revealed that upon incremental addition of copper from 0–2 equiv., absorption increasing with disappearance of the peak at 358 nm and increase in absorption intensity at 298 nm Figure 3b. Therefore, upon addition of Cu^{2+} ion to the solution containing DTBPA 1 probe there was change in absorption intensity which depicts that the bipyridine and thiophene recognition unit shows the binding to copper ion. The absorption change is observed mainly due to charge transfer process occurring between metal and ligand.

Fluorescence Study

The fluorescence studies were performed for the probe DTBPA 1 in acetonitrile solvent upon excitation at 340 nm where the emission intensity was observed at 498 nm (Figure 4a). As observed under UV light at 365 nm that when the different metal ions were added the prominent fluorescence quenching was observed which was confirmed by fluorescence study. It is observed that when the different ions were added to the solution containing probe there was initially no change observed in the fluorescence intensity while upon addition of 2 equiv. of Cu^{2+} ion there was abrupt decrease in the fluorescence while there was no prominent change observed for the other metal ions except Cu^{2+} . This fluorescence quenching in the molecule occurs mainly due to electron transfer the lone pairs present on the pyridine are easily available for the metal ion for coordination (Figure 4b). The quenching percentage was observed to be 73% with the addition of Cu^{2+} ion. The quenching may be due to coordination of metal ion inhibits the ICT in the probe and results in to PET process which is frequently observed in many fluorophores.

Competitive Study

From the above absorption and fluorescence studies it clear that the probe is highly selective and sensitive towards Cu^{2+} ion. But sometimes interference from other competing metal ions study is required in order to study the competition between the Cu^{2+} in presence over other metal ion. Herein fluorescence study was performed for determining the interference from other ionic species towards the probe DTBPA 1. The binding event was studied by adding different ions in the solution containing probe DTBPA 1. To the probe containing different cations Cu^{2+} ion was added as shown in the bar graph probe DTBPA 1 blue bar represents the probe DTBPA 1 and red bar represents the probe with various ion along with Cu^{2+} ion. The probe did not show any change upon addition of various cations but with the addition of Cu^{2+} ion there was decrease in fluorescence intensity observed for the probe. Thus, when the Cu^{2+} ion was added to the solution probe containing different

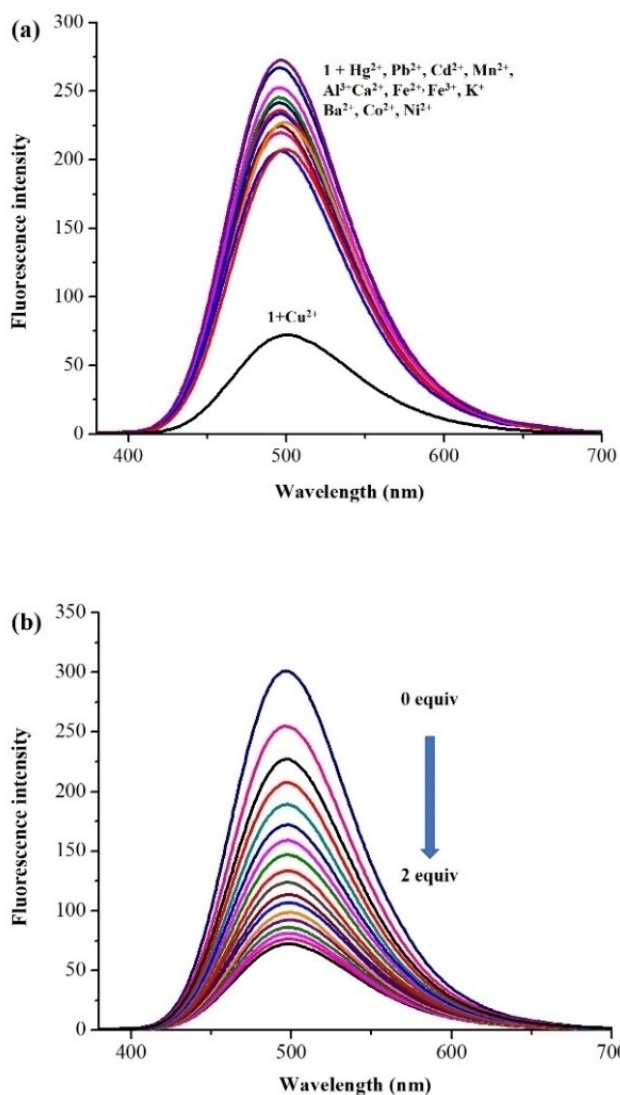


Figure 4. (a) Plot representing the emission intensity upon addition of different metal ions Cu^{2+} , Fe^{3+} , Fe^{2+} , Hg^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Al^{3+} , Ca^{2+} , Ba^{2+} , Cd^{2+} , K^{+} . and (b) fluorescence titration for the DTBPA 1 with incremental addition (0–2 equiv.)

cation there was quenching of fluorescence with decrease in fluorescence intensity. The decrease in the fluorescence intensity upon addition of Cu^{2+} ion in presence over another ion clearly depicts that the probe is highly selective towards Cu^{2+} (Figure S2). Thus we could conclude the selectivity of the probe towards Cu^{2+} ion in presence over another interfering cation.

Stoichiometry analysis and binding constant

The stoichiometry and binding constant for the compound DTBPA 1 was investigated by Jobs Plot and Benesi-Hildebrand Plot respectively. The Jobs plot was plotted against fluorescence emission intensity and mole fraction of $[\text{DTBPA 1}]/[\text{DTBPA 1} + \text{Cu}^{2+}]$. From the Jobs plot the stoichiometry of the complex with Cu^{2+} was found to be 2:1 ($1:\text{Cu}^{2+}$). Figure in supporting information Binding constant was calculated by Benesi-Hilde-

brand plot which was found to be $1.13 \times 10^6 \text{ M}^{-1}$. Figure S1. Subsequently the quantum yield of the DTBPA 1 was calculated and found to be 3.2 in ACN solvent at room temperature while the fluorescence intensity decreases with the addition of Cu^{2+} ion the quantum yield was observed to be 0.05. This attributed to the selective sensing performance towards Cu^{2+} ion sensing.

Limit of detection

Limit of detection was calculated by $(\text{LOD} = 3\sigma/S)$, where σ is the standard deviation of the blank sample and S is the absolute value of the slope between absorption intensity and concentration of Cu^{2+} . The detection limit of DTBPA 1 was found to be $0.789 \mu\text{M}$ which is found to be very low as compared to WHO guidelines which is $20 \mu\text{M}$.

Density Functional Theory (DFT)

The results of using the Gaussian 16 *ab initio*/DFT quantum chemical simulation package.^[1] The geometry optimization of all possible conformations 1C-M, 2C-M, 3C-M, 4C-M) of molecule N,N-diphenyl-4-(6-(thiophen-2-yl)-[2,2'-bipyridin]-4-yl)aniline is carried out at B3LYP/6-31+g(the computational calculations performed are obtained d) level, further to investigate their interaction with Cu^{2+} , all possible conformations of molecule after complexation with Cu^{2+} ($1\text{C-M} + \text{Cu}^{2+}$, $2\text{C-M} + \text{Cu}^{2+}$, $3\text{C-M} + \text{Cu}^{2+}$, $4\text{C-M} + \text{Cu}^{2+}$) were optimized at the B3LYP/LANL2DZ/6-31+g(d) level (Figure 5). Analysis of the energies before and after complexation of Cu^{2+} concludes that the 2C-M upon interaction with Cu^{2+} forms $1\text{C-M} + \text{Cu}^{2+}$, with the rotation of C–C bond connecting central and side substituted pyridine rings. The Conformational analysis for the compound DTBPA 1 as represented in Table S2.

Crystal Study

The crystal DTBPA 1 was prepared by slow diffusion method using chloroform and methanol solvent system kept for 8 days. The crystal was analysed and found to be suitable for single

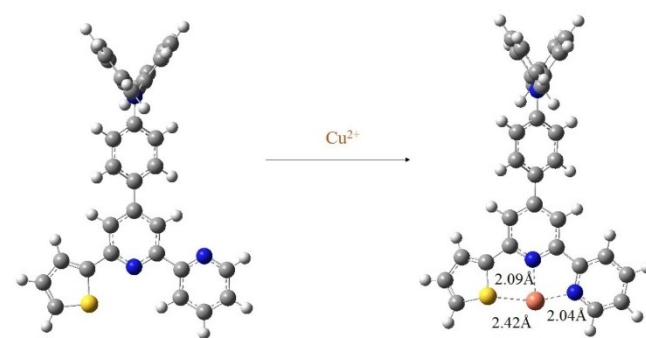


Figure 5. DFT study performed for DTBPA 1 probe on Gaussian 16 *ab initio*/DFT quantum chemical simulation.

crystal X-ray diffraction (SCXRD) study. The Crystal structure and parameters are as tabulated in Table 1 (ESI) with CCDC 2234448. The space group observed for the crystal is monoclinic space group P21/c Z=4. The crystal was successfully determined by using Bruker D8Quest Eco X-ray diffractometer (Figure 6). Finally, intensity data collection was performed at room temperature using monochromated (MoKa=0.71073 Å) radiation. In order to integrate frames program suit APEX3 (Version 2018.1) was used for absorption correction and unit cell determination. Further refinements are performed with SHELXS. All hydrogens are refined anisotropically.

Practical Application

Water analysis

The probe was further used for practical application for detecting trace amount of Cu²⁺ ion in real water sample. Herein we have collected two water sample river water and tap water and was pre-treated before analysis. River water sample was collected from River Mandovi Goa and Drinking water was taken from the tap source. The river water was spiked with 2.5 µL of 1 mM Cu²⁺ ion and tap water was spiked with 6.5 µL of 1 mM Cu²⁺ ion and to the above solution 10 µL of probe was added, mix the solution thoroughly and record the emission after 5 minutes. The emission intensity was plotted against the standard plot of fluorescence intensity. Thus, the pre-spiked Cu²⁺ ion concentration could be easily detected by probe in

the contaminated water sample with 98 to 104% recovery as shown in table below.

Conclusions

In summary we have reported the fluorescent DTBPA 1 molecule for detection of Cu²⁺ ion in a solution. The molecule was showed quick and high selectivity for Cu²⁺ ion in presence over other common metal ions. The molecule was successfully synthesized and characterized by ¹HNMR, ¹³CNMR, elemental analysis, single crystal XRD, ESI mass spectrometry. The DFT calculation were performed by using ab initio Gaussian software Gaussian 16 *ab initio*/DFT quantum chemical simulation. The fluorescent sensor reached lower detection limit of 0.789 µM very low given by environmental protection agency. The developed molecule was successfully utilized for determination of copper in in water sample.

Experimental Section

Materials and methods

4-(diphenylamino)benzaldehyde, acetyl thiophene and other solvents such as ammonium hydroxide, acetic acid, KOH required for the synthesis was purchased from Sigma-Aldrich, Alfa Aesar chemicals. All metal salts were used from the available analytical grade. ¹HNMR spectra and ¹³CNMR were recorded on 400 MHz and 100 MHz Bruker spectrometer respectively using deuterated CDCl₃ solvent and tetramethylsilane as an internal standard. Absorption studies were performed on Shimadzu spectrophotometer 2500 and followed simultaneous fluorescence studies on Agilent spectrophotometer 1800. While the ground state geometries studies for the probe was performed by density functional theory (DFT) studies performed on Gaussian 16 *ab initio*/DFT quantum chemical simulation package.^[27,28,29]

Synthesis and Characterization

Synthesis of (E)-3-(4-(diphenylamino)phenyl)-1-(thiophene-2-yl)prop-2-en-1-one (4)

To the reaction mixture of 4-(diphenylamino) benzaldehyde 2 and 2-acetyl thiophene 3 (0.20 gm, 0.002 mol) and (0.5 gm, 0.002 mol) in 15 ml ethanol 5% potassium hydroxide (0.5 gm dissolved in 10 ml ethanol) was added dropwise over 10 min. The reaction mixture was allowed to stir at room temperature for 24 hours (Scheme 1). The orange solid product formed was filtered and washed with water which was further recrystallized using ethanol to give compound 4 (0.51 gm, 64.4%). ¹HNMR (400 MHz, CDCl₃) δ ppm: 6.99 (d, 2H), 7.14 (m, 7H), 7.24 (5H, td, J=7.5, 18.8 Hz), 7.48 (2H, d, J=8.4 Hz), 7.63 (1H, d, J=3.5 Hz), 7.81 (2H, t, J=10.3 Hz). ¹³CNMR (100 MHz, CDCl₃) δ ppm: 182.057, 150.262, 146.829, 145.984, 143.904, 133.415, 131.375, 129.822, 129.557, 128.197, 127.650, 125.532, 124.202, 121.540, 118.925, 77.413, 77.095, 76.777. Elemental analysis: Calcd. (%): C, 78.71; H, 5.02; N, 3.67; Found (%): C, 78.12; H, 5.13; N, 3.45.

Sr.No	Sample	Concentration of Cu (II) ion found	Concentration of Cu (II)ion added	Recovery % RSD
1	Drinking Water	3.40×10 ⁻⁶	3.25×10 ⁻⁶	104.61%
2	River Water	1.23 x10 ⁻⁶	1.25×10 ⁻⁶	98.40%

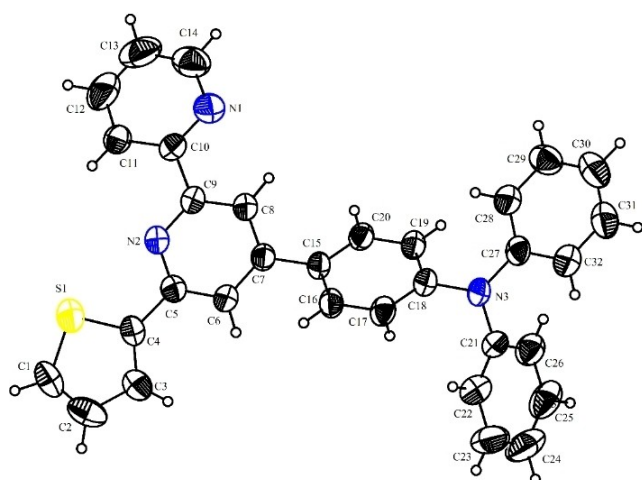
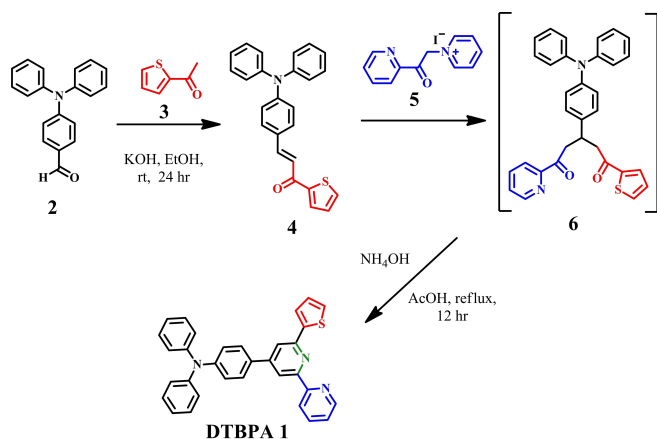


Figure 6. Crystal structure of the compound DTBPA 1.



Scheme 1. Synthetic pathway for synthesis of DTBPA 1.

Synthesis of 1-(2-(thiophene-2-yl)-2-oxoethyl)pyridin-1-ium (5)

The reaction mixture containing 2-acetyl thiophene **3** (2.2 gm, 0.02 mol) and iodine (5.1 gm, 0.02 mol) mixed in 25 ml of pyridine was refluxed for 3 hrs. The intermediate **5** was prepared by following reported literature. Allow the reaction mixture to cool after completion the precipitate formed was filtered. The solid product formed was washed thoroughly with cold pyridine. The product formed was directly used for next step reaction without any purification. (yield: 6.02 gm, 80%).

Synthesis of probe DTBPA 1

The intermediate **6** was formed by refluxing the mixture of **4** (0.3 gm, 0.001 mol) and **5** (2.1 gm, 0.007 mol) in presence of ammonium hydroxide and 10 ml acetic acid at at 90 °C for 12 hrs. the reaction improvement was monitored by thin layer chromatography (TLC). After completion of the reaction allow the mixture to cool to room temperature and add 30 ml of cold water. The solid formed then washed with cold methanol dried and impurities were removed by eluting on column chromatography with ethyl acetate and Pet ether solvent. greenish yellow solid was obtained Yield (1.4gm, 58%). ¹H NMR (CDCl₃, 400 MHz): δ_H 8.62 (1H, d, *J*=4.6 Hz), 8.55 (1H, d, *J*=8.2 Hz), 8.46 (1H, d, *J*=1.8 Hz), 7.79 (2H, m, *J*=2.9, 5.8, 5.8 Hz), 7.63 (3H, m, *J*=2.4, 6.9, 10.0 Hz), 7.36 (1H, q, *J*=2.0 Hz), 7.09 (9H, m, *J*=4.4, 8.7 Hz), 7.01 (9H, t, *J*=7.4 Hz). ¹³C NMR (100 MHz, CDCl₃) δ ppm: 154.913, 151.291, 148.7607, 147.915, 147.878, 146.295, 144.435, 135.973, 130.547, 128.386, 126.988, 126.931, 126.512, 123.847, 123.481, 122.831, 122.456, 122.034, 120.534, 115.714, 114.923, 76.307, 75.990, 75.672. ESI-MS calculated. (M)⁺, 481.16, obs. 481.61 (M+1)⁺. Elemental analysis: Calculated (%): C,79.80; H,4.81; N,8.72 Found (%): C,79.62; H,4.79; N,8.34.

¹H NMR Spectra of DTBPA 1 and in presence of Cu²⁺

The ¹H NMR spectra for probe DTBPA 1 was recorded with and without addition of Cu²⁺ ion in DMSO-*d*₆. From H NMR spectrum it can be concluded that spectrum labelled as a which is without Cu²⁺ showed well defined peaks while with the addition of Cu²⁺ all peaks shifted towards upfield region as shown in Figure S8 this indicates that when receptor binds with copper ion which is paramagnetic in nature influences the peaks in the spectrum.

Supporting Information

Job plot, spectroscopic characterisation, detail of DFT and crystal data for this article is given via a link at the end of the document.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: diphenylamine donor · sensing · single crystal · Density functional theory · water analysis

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