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A Receptor Based on Diphenylaniline Donor Connected with Difuran and Pyridine as Acceptors: Synthesis, Crystal Structure and Selective Detection of Iron Ion

Geeta A. Zalmi[+], Dinesh N. Nadimetla[+], Sarvesh S. Harmalkar, Kedar U. Narvekar, and Sheshanath V. Bhosale*[a]

In this work, the fluorescent receptor 4-(2,6-di(furan-2-yl)pyridin-4-yl)-N,N-diphenylaniline (DFPDA) was successfully synthesized overall in three steps, which bears three acceptor moieties one pyridine and two furans connected to a donor triphenylamine The DFPDA was fully characterized through ^{1}H-NMR, ^{13}C-NMR, ESI mass and elemental analysis. Further, single X-ray structure confirm the intermediate and final DFPDA molecules. When we employed DFPDA molecule for sensing of metal ion, it shows selective detection of Fe^{3+} over other metal ions (Cu^{2+}, K^{+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Ca^{2+}, Fe^{2+} as their respective salts) dissolving in 1:1 water/DMSO solution with the binding constant 3.75×10^{-5} M. The limit of detection of DFPDA was found to be 52 nM which is much lower than the environmental protection agency guidelines (5.37 μM). Therefore, we believe that the DFPDA 1 fluorescent receptor may become outstanding chromophore for practical applications. **Competing financial interests**: The authors declare no competing interests.

Introduction

Iron (Fe^{3+}) is the most crucial transition metal ion in the body as it plays a very important role in maintaining the life of an organism and has significance in many biochemical processes at a cellular level. Many enzymes need Fe^{3+} as a catalyst and play significant role in electron transport through red blood cells, oxidoreductase catalysis, oxygen metabolism as well as RNA and DNA synthesis.[1,2] Its overdose and deficiency lead to hypoferremia or hyperferremia accordingly.[3] The deficiency of Fe^{3+} induces imbalance in iron transport and its storage may lead to a various pathological disorder such as diabetes, anaemia, and kidney damages. In particular deficiency of iron leads in human body leads to anaemia, which may lead to death by deprivation of oxygen in various organs in the body.[4] In the human body, liver and spleen are the richest organs that need to have a sufficient amount of iron, as approximate iron content in the well-nourished human body contains nearly 4 g (70% in Hgb, 25% in storage).[5,6] Iron meets the natural water bodies by weathering, industrial waste or corrosion of metals which results in to change in taste of water and promotes the bacteria proliferation in water.[7] Recently Fe^{3+} detection have attracted the attention of many researchers and is very effective not only in environmental monitoring but also in biomedical applications.[8,9] Currently there are several instrumentation techniques such as atomic absorption/emission spectrometry, spectrophotometry and electrochemical methods used for the detection of Fe^{3+}.[10] However, due to their sophisticated instrumentation which requires a long detection time, and needs sample treatment procedures restricts their use for practical application. Thus, a few of these methods have several disadvantages which need complex technologies, costly devices, and time-consuming in operation of the instruments. Hence, recently fluorescence molecules have gained considerable attention of many researchers and proved to be advantageous over instrumental techniques for monitoring and detection of toxic ions, environmental and biological samples.[11,12,13,14] Since last two decades designing and construction of fluorescent molecules for transition metal ions have attracted significant interest in sensing metal ions.[15–17]

Earlier work by our group demonstrated the design and synthesis of novel donor-acceptor system i.e. 4-(2,6-di-(dithiophen-2-yl)pyridin-4-yl)-N,N-diphenylaniline (DTPDA) which is shown to be highly selective towards Pb^{2+} and Fe^{3+} ion.[18] In similar directions, recently, we designed tetraphenylethylene aggregation-induced emissive active molecule (AIE) comprising of thiophene and bipyridine molecule as receptor sites, which shows selective sensing for Cu^{2+} ion.[19] Learning from our recent work, herein, we have synthesized a donor-acceptor system which consists of diphenylaniline (DA) as a donor which is fused with acceptors i.e. one pyridine (P) and difuran (DF) moieties, which act as receptors (Scheme 1). The newly synthesized DFPDA **1** receptor shows highly selective and sensitive towards Fe^{3+} ions over other metal cations such as Cu^{2+}, K^{+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Ca^{2+}, Fe^{2+} as their respective salts. The selective sensing can be monitored by colorimetric changes in visible as well as under UV-light (365 nm).[20]

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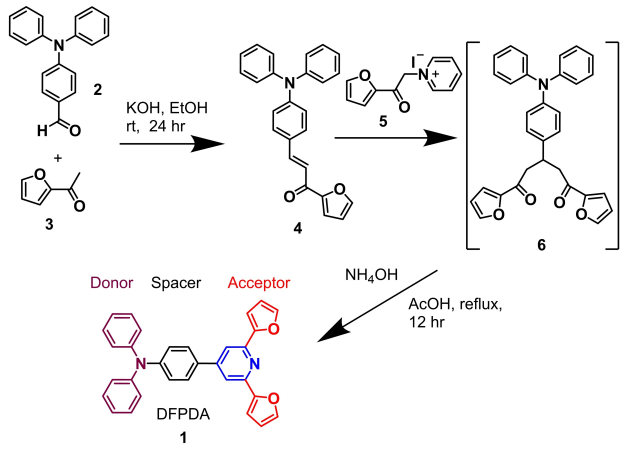

Scheme 1. Synthesis of DFPDA 1.

Results and Discussion

Absorption and emission spectra in different solvents

The DFPDA **1** was further characterized by UV-Vis absorption and fluorescence spectroscopy. The absorption and fluorescence studies of the DFPDA **1** was carried out in different organic solvents such as acetonitrile, dimethyl sulphoxide (DMSO), hexane, methanol, chloroform and tetrtahydrofuran (THF) as shown in Figure 1. It was observed that DFPDA **1** showed different absorption peaks with different absorption wavelengths upon a change in polarity of solvents (Figure 1a). Further emission studies were performed in the above solvents, which display emission properties DFPDA **1** (2.5×10^{-5} M) upon excitation at ($\lambda_{ex}=330$ nm) in various solvents exhibited a shift in fluorescence emission band with change in intensity (Figure 1b). Nevertheless, in polar solvent red-shift was observed, however, in non-polar solvents such as chloroform and THF blue-shift of emission was observed. It can be seen that the emission intensity in hexane shows non-emission, whereas the emission band for DFPDA **1** in DMSO appeared at 495 nm with the quantum yield (ϕ) found to be 0.49. Thus, it can be concluded that the emission peak position and quantum yield of DFPDA **1** depends on the polarity of the solvents. The DFPDA **1** shows to be producing good absorption and emission band in DMSO solvent, thus, we have used DMSO for further study.

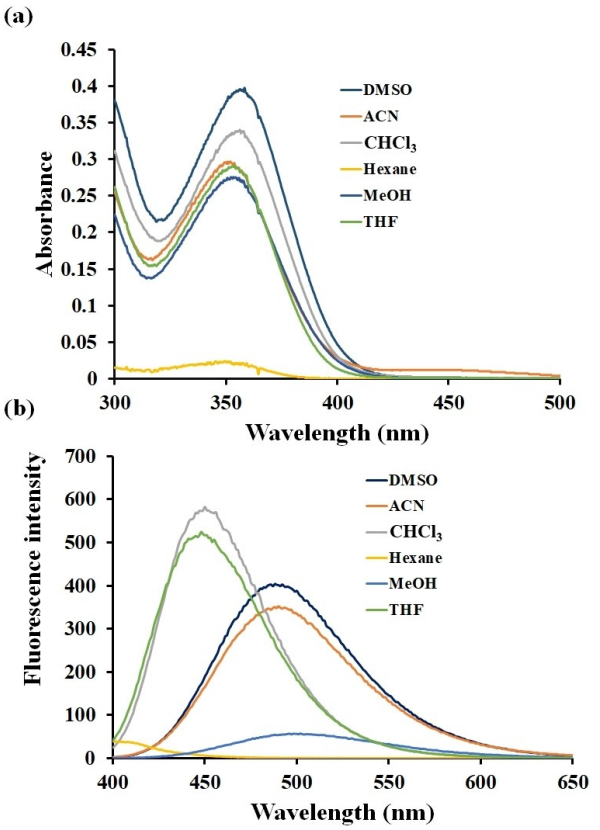

Figure 1. (a) UV-Vis absorption spectra and (b) fluorescence emission ($\lambda_{ex}=375$ nm) of DFPDA 1 ($2.5\times10^{<M->5}$M) in various solvents.

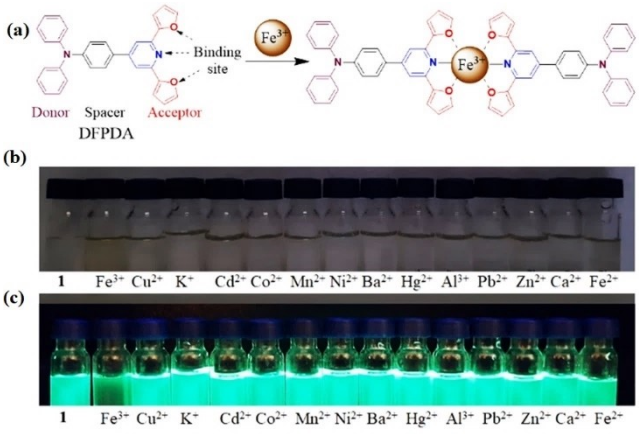

Figure 2. (a) Schematic illustration of binding site for Fe^{3+} ion. Solutions of DFPDA **1** ($2.5\times10^{<M->5}$M) in DMSO, upon addition of 2.5 equiv. of (Fe^{3+}, Cu^{2+}, K+, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Ca^{2+}, Fe^{2+} of metal ion solution (b) under visible light and (c) under UV-light 365 nm.

Sensing performance of DFPDA receptor 1

The selectivity and sensitivity for the DFPDA **1** (2.5×10^{-5} M) was studied by adding different metal ions such as (Fe^{3+}, Cu^{2+}, K^{+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Ca^{2+}, Fe^{2+}). The color change was observed under visible light and UV-Vis (365 nm) as represented in Figure 2a and 2b. However, it can be noted that under visible light the DFPDA **1** is colorless in DMSO but upon the addition of Fe^{3+} metal ion the color of the solution changes in presence over other metal ions. Under visible light the color of the DFPDA **1** changes from colorless to light yellow indicating the selectivity towards the Fe^{3+} metal ion. Instead to further confirm its selectivity the same solution containing different metal ions was placed under UV light at 365 nm and it was observed that the green fluorescence color of the solution changes to yellow-brown which further confirms the fluorescence quenching. The remarkable color

change under the naked eye thus indicates that the DFPDA **1** has high selectivity towards Fe^{3+} metal ion. Hence, the DFPDA **1** can be used for naked-eye colorimetric and fluorescent sensor for Fe^{3+} ion.

UV-Vis absorption study

Furthermore, the color change observed in the naked eye was confirmed by absorption study and fluorescence study. The UV-Vis absorption spectra were recorded for DFPDA **1** with the addition of different cations. The absorption maxima were observed at 357 nm for DFPDA **1** in DMSO (2.5×10^{-5} M). The UV-Vis absorption studies revealed that upon addition of different cations to the solution of the DFPDA **1** it shows a significant change in absorption towards Fe^{3+} ion in the presence of other metal ions The significant absorption increase was observed for the DFPDA **1** on the addition of Fe^{3+} ion compared to other metal ions at 357 nm as shown in Figure 3a. The following optical and photophysical properties are mostly affected by photoinduced electron transfer (PET). Thus, it can be concluded that the DFPDA **1** has high selectivity for Fe^{3+} ion over other metal species. In addition, absorption titration studies were performed for the DFPDA **1** (Figure 3b). The absorption studies revealed that the upon incremental addition of Fe^{3+} ion from (0–2.5 Equiv.) to the DFPDA **1** (1.37×10^{-5} M) solution in DMSO, the absorption band at 375 nm increases. The following spectral changes in absorption reveal

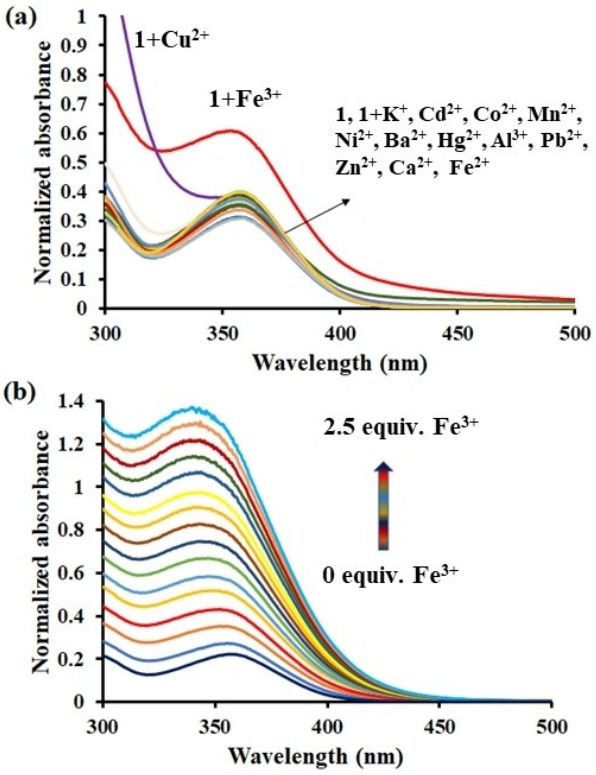

Figure 3. (a) UV-Vis absorption spectra of 1 (2.5×10^{-5} M) in presence of different cations and (b) absorption spectra with incremental addition of Fe^{3+} (0–2.5 equiv., 1.37×10^{-5} M) in DMSO.

that the DFPDA **1** is highly selective towards Fe^{3+} ion in the presence of other metal ions.

Fluoresence emission study

The detection of the metal ion was further investigated and confirmed by fluorescence emission for the DFPDA **1** towards Fe^{3+} ion in DMSO. When the solution DFPDA **1** was excited at 350 nm the appearance of the emission band was at 495 nm. Different metal ions were added to the solution of the DFPDA **1** and it was observed that in the presence over all metal ion only Fe^{3+} ion showed high selectivity. As can be seen in the figure 4a upon the addition of Fe^{3+} ion there is a quenching of fluorescence observed for the solution of the DFPDA 1. However, initially it was observed that upon adition of Fe^{3+} with there is a change in fluorescence color change but upon incremental addition of Fe^{3+} ion there is complete quenching of fluorescence. Further to study the sensing

the ability of the DFPDA **1** fluorescence titration was carried out which showed that upon incremental addition of Fe^{3+} ion in the DFPDA **1** there is a quenching of fluorescence observed.

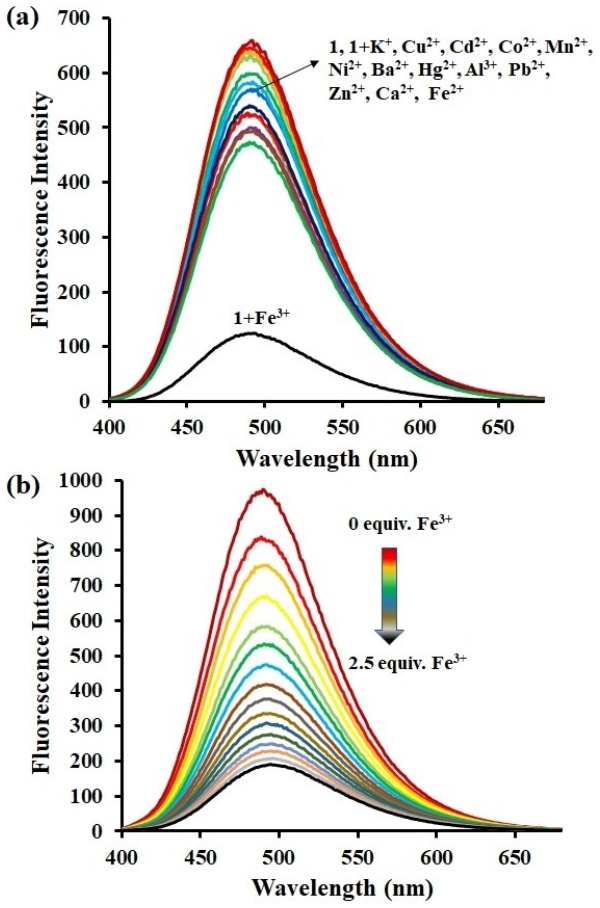

Figure 4. (a) Fluorescence emission spectra of **1** (2.5×10^{-5} M) in presence of different cations (2.5×10^{-3} M, $\lambda_{ex}=350$ nm, $\lambda_{em}=495$ nm) (excitation slit = 5 nm emission slit = 5 nm) and (b) Emission spectra with the incremental addition of Fe^{3+} from (0–2.5 equiv. of 1.37×10^{-5} M) in DMSO ($\lambda_{ex}=350$ nm, $\lambda_{em}=495$ nm) (excitation slit = 10 nm, emission slit = 2.5 nm).

However, the estimated fluorescence quantum yield of the DFPDA **1** was found to be (49%) in DMSO at room temperature. As shown in Figure 4b, the fluorescence intensity gradually decreases upon the addition of Fe^{3+} (0–2.5 equiv.). The decrease in fluorescence intensity is ascribed due to the electron-donating nature of diphenyl rings and the participation of the lone pair of electrons present on nitrogen and difuran moiety from the receptor towards the coordination of the Fe^{3+} ion and which represents the turn-off emission with a decrease in the quantum yield of the DFPDA 1:Fe^{3+} representing PET transfer process. Thus fluorescence emission behavior showed the selective detection of Fe^{3+} ion. The quenching constant (Ksv) was found to be ($Ksv = 4.96 \times 10^{4}$).

Stoichiometry analysis and binding constant

The stoichiometry and binding constant of the complex formed between the DFPDA **1** and Fe^{3+} were investigated by performing Jobs Plot and Benesi Hildebrand plot respectively.[21,22] The jobs plot was represented between the fluorescence emission intensity against the mole fraction [1]/[1 + Fe^{3+}]. The Jobs plot showed that the stoichiometry of the complex formed between DFPDA **1** is 2:1 complex (1:Fe^{3+}) Figure 5a. However, the binding constant for the Fe^{3+} to DFPDA **1** was further confirmed by Benesi-Hildebrand plot which was found to be 3.75×10^{-5} M Figure 5b.

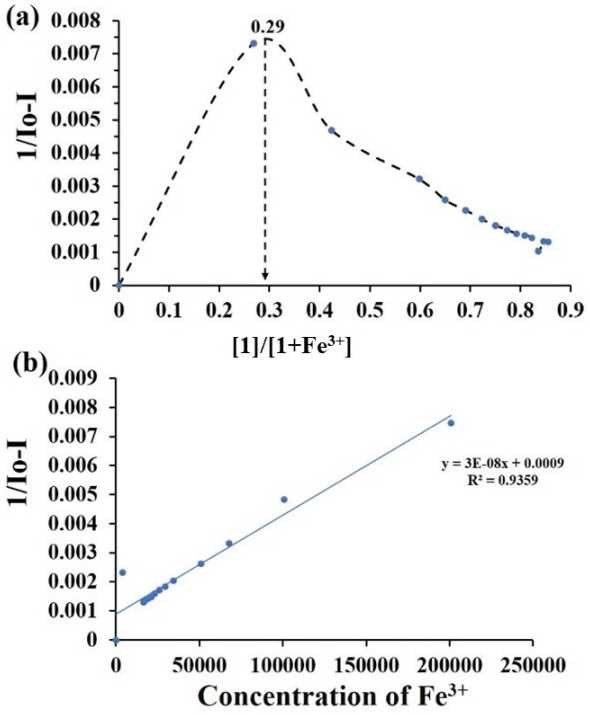

Figure 5. (a) Job's plot and (b) Benesi-Hildebrand plot of probe DFPDA **1** with Fe^{3+} ion in DMSO. The solution containing DFPDA **1** was excited at 330 nm and emission was observed at 495 nm. the stoichiometry of the complex is DFPDA **1**:Fe^{3+} (2:1) while the binding constant was observed to be $3.75 \times 10^{<M->5}$M.

Limit of detection

The Limit of detection can be calculated by (LOD = 3σ/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 Fe^{3+}. The DFPDA **1** showed detection limit to 52 nM which is found to be very low as compared to the permissible limit suggested by World Health Organization (WHO) agency guidelines is 5.37 μM. Thus, suggest that DFPDA **1** can be employed as a sensitive fluorescent DFPDA **1** for the detection of Fe^{3+} metal ion.

Competitive Fe^{3+} ion binding

The competitive binding study was performed for the DFPDA **1** by adding different metal ions as the interfering ions (Fe^{3+}, Cu^{2+}, K^{+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Ca^{2+}, Fe^{2+}). As represented in (Figure S1) the blue bar depicts the DFPDA **1** along with all other cations while the red bar represents the DFPDA **1** with metal ion in the presence over Fe^{3+} metal ion. It can be observed that the absorption band intensities of DFPDA did not show much change upon the addition of 2.5 equivalent of metal ions. However, there was a remarkable increase in absorption change observed upon the addition of Fe^{3+} metal ion. The increase in absorption peak at 357 nm indicates that the DFPDA 1 is highly selective and sensitive towards Fe^{3+} metal ion over other tested cations. Hence the DFPDA **1** may employ as an excellent fluorescent chemosensor for selective detection of Fe^{3+}.

Reversibility and reusability

The synthesized DFPDA **1** was further checked for the reversibility and it was observed that the DFPDA **1** showed reversible nature. The absorption and fluorescence spectra was recorded at room temperature for the DFPDA **1**. Initially, DFPDA **1** (2.5×10^{-5} M) was taken in the cuvette in 2 ml DMSO and to that 50 μL of Fe^{3+} was added and to the same solution, NaOH was added. It was observed that upon the addition of NaOH the fluorescence reappears where in ferric hydroxide $Fe(OH)_3$ precipitates out. The solution was centrifuged and its absorbance and fluorescence spectra were recorded as shown in Figure S2. The absorption and fluorescence were recorded for the DFPDA **1**. Thus the DFPDA **1** was reversible for 3 cycles as shown in Figure S3.

Crystal study

3.1. Crystal structure of the (E)-3-(4-(diphenylamino)phenyl)-1-(furan-2-yl)prop-2-en-1-one (4): We were able to grow crystals suitable for SCXRD of 4 by slow diffusion of chloroform/methanol solution for 8 days. It crystallises in monoclinic space group $P2_1/c$ Z4 The technical details of data collection and selected refinement parameters for the compound 4 are given in supporting information Table S1. The single-crystal structure of the compounds was determined using Bruker D8 Quest Eco X-ray diffractometer. Intensity data were collected at room

temperature (RT) using monochromated (MoKα = 0.7107 Å) radiation. The program suite APEX3 (Version 2018.1) was used to integrate the frames, to perform absorption correction and to determine unit cell. The structures were solved with SHELXS and subsequent refinements were performed with SHELXL.[23] All non-hydrogen atoms were refined anisotropically. The H atoms attached to the aromatic ring were introduced in the calculated positions and included in the refinement by riding on their respective parent C atoms. The structural analysis further confirms compound forms one dimensional network resulting from intermolecular hydrogen C–H-π interactions separated by 2.718 Å. The H-bonding interactions are represented in ESI Figure S10.

Crystal structure of the compound 4-(2,6-di(furan-2-yl)pyridin-4-yl)-N,N-diphenylaniline (DFPDA) 1: The compound DFPDA **1** crystalizes by slow diffusion of Chloroform/methanol solution for 8 days and suitable for SCXRD. The compound crystalizes in monoclinic space group $P2_1/c$ Z = 4. The single crystal structure of the compounds was determined using Bruker D8 Quest Eco X-ray diffractometer. Intensity data were collected RT using monochromated (MoKα = 0.7107 Å) radiation. The program suite APEX3 (Version 2018.1) was used to integrate the frames, to perform absorption correction and to determine unit cell. The structures were solved with SHELXS and subsequent refinements were performed with SHELXL. All non-hydrogen atoms were refined anisotropically. The H atoms attached to the aromatic ring were introduced in the calculated positions and included in the refinement by riding on their respective parent C atoms. The packing interaction as represented in supporting information the structural analysis further confirms that the compound forms one-dimensional network resulting from intermolecular C–H-π interactions separated by 3.383 Å leading to a helical structure. The H-bonding interactions are shown in ESI Figure S11 for the compound DFPDA 1.

The crystallographic data for compound **4** and DFPDA **1** reported in this paper have been deposited to the Cambridge crystallographic data center with CCDC numbers 2149520 and 2149521, respectively (Figure 6 and Figure 7).

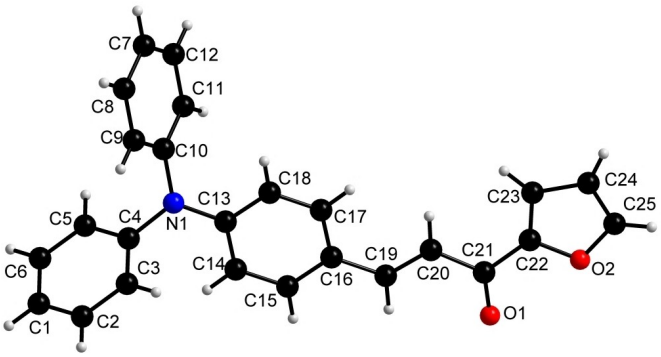

Figure 6. Crystal structure of the compound (E)-3-(4-(diphenylamino)phenyl)-1-(furan-2-yl)prop-2-en-1-one (4) (CCDC No. 2149520).

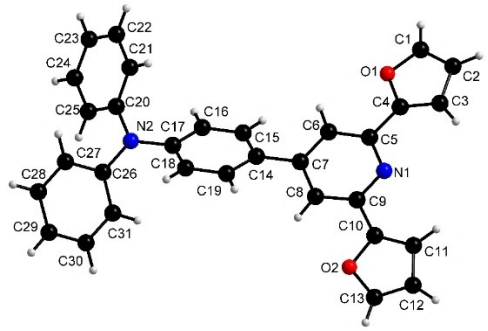

Figure 7. Crystal structure of the compound 4-(2,6-di(furan-2-yl)pyridin-4-yl)-N,N-diphenylaniline DFPDA 1. (CCDC No.2149521).

Conclusions

In summary, we successfully report the synthesis of a DFPDA **1** and employed it for fluorescent sensing of metal ions. The DFPDA **1** is utilized for colorimetric and fluorescent sensing of Fe^{3+} metal ion. In addition, the DFPDA **1** is used for naked-eye detection of Fe^{3+} ion over other ions such as Cu^{2+}, K+, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Ca^{2+}, Fe^{2+} salts. The synthesized DFPDA **1** shows high selectivity and sensitivity towards Fe^{3+} ion with the lowest detection limit (LOD) of 52 nM. However, the stoichiometry of the complex formed between DFPDA **1** and metal ion (1:Fe^{3+}) is 2:1. The compound 4 and the DFPDA **1** were crystalized in the methanol/chloroform diffusion method and characterized further by SXRD. The DFPDA **1** was studied for reversibility by using simple base NaOH and thus optical studies revealed that the DFPDA **1** was reversible for 3 cycles.

Experimental details

Chemical and Reagents

All solvents and reagents were commercially available AR grade and used without any treatment. All metal ionic solution of respective sulfate and chloride solution which includes $CuSO_4.5H_2O$, $FeCl_3$, $ZnSO_4.7H_2O$, $Fe(SO_4)_2(NH_4)_2.6H_2O$, $Al_2(SO_4)_3.16H_2O$, $CaCl_2.2H_2O$, $NiSO_4.6H_2O$, $HgCl_2$, $CdCl_2$, KCl, $BaCl_2$, $MnCl_2.4H_2O$, $Pb(OAC)_2$. Dimethyl sulfoxide (DMSO) was purchased from Sigma-Aldrich. ^{1}HNMR spectra were recorded on 400 MHz and ^{13}CNMR using 100 MHz Bruker spectrometer. Tetramethylsilane (TMS) was used as an internal standard. The $CDCl_3$-*d* and DMSO-d_6 solvents were used for NMR studies. Mass spectrometric data were obtained by positive electron spray ionization (ESI-MS) technique on an Agilent Technologies 1100 Series (Agilent Chemistation Software) mass spectrometer. IR spectra were recorded on a Perkin Elmer FT-IR 400 spectrometer. UV-Vis absorption spectra were recorded by UV-Vis 1800 Shimadzu spectrophotometer and fluorescence emission measured on RF-6000 (Shimadzu, Japan) spectrofluorophotometer.

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

In 50 mL round bottom flask, 4-(diphenylamino) benzaldehyde 2 and 2-acetyl furan 3 (0.20 gm, 0.002 mol) and (0.5 gm, 0.002 mol) was added in 15 ml ethanol. To the above reaction mixture 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. Yellow precipitate formed was filtered and washed with cold water, and recrystallized from ethanol to give compound 4 (0.36 gm, 51.64%). IR (cm^{-1}): 3152, 3055, 3027, 2631, 1658, 1578, 1503, 1485, 1324, 1048, 753, 704. ^{1}HNMR (400 MHz, $CDCl_3$) δ ppm: 6.60 (m, J = 1.6 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 7.17 (m, 6H), 7.36 (m, 6H), 7.52 (d, J = 8.4 Hz, 2H), 7.65 (s, 1H), 7.88 (d, J = 1.6 Hz, 1H); ^{13}CNMR (100 MHz, $CDCl_3$) δ ppm: 178.1, 154.0, 150.3, 146.8, 146.3, 143.8, 129.9, 129.5,127.7, 125.5, 124.2, 121.5, 118.5, 117.0, 112.5. ESI-MS calcd. 365.14 $(M)^+$, obs. 366.3 $(M+1)^+$. Elemental analysis: Calcd. (%): C, 82.17; H, 5.24; N, 3.83. Found (%): C, 82.24; H, 5.28; N, 3.90. Melting point 162 °C

Synthesis of 1-(2-(furan-2-yl)-2-oxoethyl)pyridin-1-ium (5)[14]

The intermediate 5 was prepared by following literature method.[14] To a mixture of 2-acetyl furan 3 (2.2 gm, 0.02 mol) and iodine (5.1 gm, 0.02 mol) mixed in 25 ml of pyridine then the reaction mixture was refluxed for 3 hrs. After completion of reaction allow the reaction mixture to cool at room temperature. The precipitate formed was filtered and washed thoroughly with cold pyridine which was then used for next reaction step without purification (yield: 1.17 gm, 73%).

Synthesis of 4-(2,6-di(furan-2-yl)pyridin-4-yl)-N,N-diphenylaniline (DFPDA) receptor 1.

A mixture of 4 (0.3 gm, 0.001 mol) and 5 (2.1 gm,0.007 mol) was heated under reflux to form intermediate 6 in presence of ammonium hydroxide and 10 ml acetic acid. Further, the reaction mixture was refluxed at 90 °C for 12 hrs. After completion of reaction allow the reaction mixture to cool at room temperature and added 30 ml of cold distilled water. The formed precipitate was then filtered and washed with cold methanol dried and purified by column chromatography eluting column with ethyl acetate and PET ether mixture gives 1.3 gm (57% yield) of brown solid. IR (cm^{-1}): 3441, 3063, 2961, 2849, 1583, 1484, 1427, 1322, 1269, 1175, 1090, 1025, 803, 755, 695, 619. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm): 6.48-6.49 (dd, J = 4 Hz, 2H), 7.03 (t, J = 7.4 Hz, 2H), 7.10 (m, 3H), 7.14 (m, 2H), 7.25-7.19 (t, J = 8.4 Hz, 4H), 7.4 (m, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.70 (s, 2H,).^{13}CNMR (100 MHz, $CDCl_3$) δ ppm: 153.2,149.5, 149.1, 147.6, 147.2,147.0,143.4, 138.5, 138.4, 130.9, 129.7, 129.4, 129.0, 127.8, 126.3, 125.1, 125, 124.4, 123.9, 123.6, 122.8, 119.3, 119, 114.2, 112.1, 109.74. ESI-MS calculated. 454.168 $(M)^+$, obs. 455.100 $(M+1)^+$. Elemental analysis: Calculated (%): C, 81.92; H, 4.88; N, 6.16; Found (%): C, 81.38; H, 4.96; N, 6.23.

UV-Vis experiments

UV-Vis absorption spectra of the DFPDA **1** upon addition of different cations. The stock solution of the DFPDA **1** (10^{-3} M) was prepared by dissolving 4 mg in 10 ml of DMSO. The stock solution of various metal ions was prepared (10^{-3} M) including Fe^{3+}, Cu^{2+}, K^+, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Ca^{2+}, Fe^{2+} in 1:1 water/DMSO mixture. The selectivity towards different metal ions was investigated for the receptor by adding 50μL of DFPDA **1** in 2 ml DMSO solvent. To the series of solutions 20 μL of metal ions solution was added, mix the solution properly before spectral measurement and the change in absorption was recorded. The absorption maxima were found to be 357 nm.

UV-Vis titration of the DFPDA **1** *upon addition of* Fe^{3+}*:* The stock solution of the DFPDA **1** was prepared by dissolving 4 mg in 10 ml DMSO solvent (10^{-3} M). Since the DFPDA **1** was highly selective towards Fe^{3+} metal ion the stock solution of metal ion was prepared (0.001 M). The stock solution 50μL was placed in a quartz cell containing 2 ml DMSO and to that Fe^{3+} metal ion solution was added in incremental fraction and absorption spectra were recorded upon each addition of metal ion.

Fluorescence experiments

Fluorescence spectra for the DFPDA **1** performed upon addition of different metal ions (10^{-3} M) such as Fe^{3+}, Cu^{2+}, K^+, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Ca^{2+}, Fe^{2+} in 1:1 water/DMSO mixture. To the solution of the DFPDA **1** (12.5 μL) of stock solution in 2 ml DMSO solvent followed by the addition of 20 μL of metal ions solution, allow the solution to mix properly before the spectral measurement. The emission spectra were recorded with observed emission at 495 nm.

Fluorescence titration of the DFPDA **1** *upon addition of* Fe^{3+}*:* Further the fluorescence emission spectral studies were performed by taking the 12.5 microliters from a stock solution of 1 (10^{-3} M) in quartz cuvette containing 2 ml DMSO. To the above solution, incremental Fe^{3+} metal ion solution of (0.001 M) concentration was added. Mix the solution properly and record the fluorescence emission spectra of the solution upon each incremental addition at room temperature.

Crystal study

Crystal structure of (E)-3-(4-(diphenylamino)phenyl)-1-(furan-2-yl)prop-2-en-1-one (4): The crystal of a 4 was prepared by slow diffusing methanol in chloroform for 7 days and was characterized by X-ray crystallography. Crystal data: $C_{25}H_{19}NO_2$, Monoclinic, a = 11.2990(5), b = 10.2751(5), c = 16.5433(7), α = 90, β = 98.4830, γ = 90, V = 1899.64(15) A^0, T = 293(2)K, Space group = $P2_1/c$, Z = 4, Collected reflections = 23205, Independent reflections = 4700, F-(000) = 786, R1 = 0.06, Goodness of fit = 1.073.

Crystal structure of receptor 4-(2,6-di(furan-2-yl)pyridin-4-yl)-N,N-diphenylaniline (DFPDA) *1*: The crystal of a DFPDA **1** was prepared by slow diffusing methanol in chloroform for 3 days and was characterized by X-ray crystallography. Crystal structure determination of DFPDA 1, Crystal data: $C_{31}H_{22}N_2O_2$, Monoclinic, a = 15.2782(6), b = 8.4305(3), c = 18.5467(7), α = 90, β = 101.928, γ = 90, V = 2337.29(15) A^0, T = 293(2)K, Space group = $P2_1/c$, Z = 4, Collected reflections = 33674, Independent reflections = 5806, F(000) = 952, R_1 = 0.06, Goodness of fit = 1.0338.

Summary Supporting Information: supporting ifnromation contains all the spectra of all the characterized compound (^{1}HNMR ^{13}CNMR, ESI-mass and IR), competitive study plot, crystal data and reversibility study.

Author Contributions

G.Z. performed synthesis and sensing properties by means of UV-Vis absorption and fluorescence properties along with prepared first draft of the manuscript. D.N.N. perform the NMR and help G.Z. S.S.H. and K.U.N. performed single X-ray crystallography. S.V.B. designed the experiments, directed, interpreted and analyses the data and finalize the manuscript. All co-authors reviewed the manuscript.

Supporting Information

Provides further information about the characterization and sensing performance of 1 stacking of 1 and 4 by SXRD. The sensing performance, and comparative detection limit is available in the supplementary information.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: Chemosensor · donor-acceptor · Fe^{3+} ion · optical sensor · 'Turn-On' fluorescence

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