Chromogenic and fluorogenic detection of selected anions by bis-terpyridine Fe(II) complex through displacement approach

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Abstract. This paper deals with synthesis, characterization and anion recognition properties of a homoleptic bis-terpyridine Fe(II) complex covalently coupled with diarylethene unit. The recognition event was examined in both organic as well as mixed aqueous–organic medium through different optical channels and spectroscopic techniques by taking advantage of metal–ligand interaction in the complex. The complex acts as sensor for F^- , OAc^- and CN^- among the other studied anions (F^- , Cl^- , Br^- , I^- , CN^- , OAc^- , $H_2PO_4^-$, SCN^- , BF_4^- and ClO_4^-) without selectivity. In contrast to acetonitrile, the complex acts as highly selective chromogenic and fluorogenic sensor for only CN^- in water. Detection limit of the metalloreceptor towards CN^- was determined from the absorption and emission titration data and the observed values lie in the order of 10^{-9} M in acetonitrile and 10^{-8} M in mixed aqueous–organic media.

Keywords. Iron complex; terpyridine ligand; diarylethylene; anion sensing; cyanide ion.

1. Introduction

Supramolecular chemistry of anion recognition and sensing continues to be a vibrant area of research as few of them play crucial roles in biological, aquatic, environmental and industrial processes.^{1–4} Among the anions, detection of cyanide ion as well as its quantification is a crucial task for the scientist because it is extremely toxic to the environment and also for human health and other living organisms.^{5,6} Sincere efforts have been devoted for designing effective sensors for cyanide ion^{7–11} and most of the chemosensors usually recognize cyanide based on three well known strategies: (i) the ‘binding site-signaling subunit’ approach where the binding sites and the optical signaling moieties are covalently connected in such a manner that the interaction of CN^- with the binding site(s) induces electronic reorganization of the signaling subunit resulting in change of their optical spectral behaviours,^{12–15} (ii) the ‘chemodosimeter’ approach whereby anion-induced chemical reactions usually occur resulting in changes

in fluorescence or color^{7,8,16–19} and (iii) the ‘displacement’ strategy wherein the binding sites and signaling subunits are not usually covalently connected but form a molecular adduct and upon coordination of CN^- to the binding site leads to the displacement of the signaling subunit, which is usually accompanied with optical spectral changes.^{20–26} Each strategy has its own merits as well as demerits. In the first strategy, the chemosensors usually detect CN^- by means of hydrogen bonding interaction and most of the reported sensors suffer from the lack of selectivity. Both ‘displacement’ and ‘chemodosimeter’ strategies have also some drawbacks such as lack of reversibility, and requirement of energy (heat or light) to overcome the activation barrier for the addition of cyanide to the active site of the chemosensors and usually irreversible in nature. In addition, majority of the small molecule chemosensors for CN^- are based on organic molecules and show their sensing abilities mainly in organic media which in turn are major deterrent for their use in practical application.

Compared with pure organic hosts, the receptors based on coordination compounds of transition met-

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Chart 1. Molecular structure of the terpyridine ligand (tpy-pvp-Cl) and its Fe(II) complex of composition $[\text{Fe}(\text{tpy-pvp-Cl})_2]^{2+}$ (1).

als having wide variety of geometries and very rich photophysical and electrochemical properties are relatively less in the literature.^{27–30} Metal fragment in the complex usually acts as the reporter unit by modulating optical and/or electrochemical signal as a result of host–guest interaction.^{27–30} A few low spin d^6 transition metal complexes (such as Ru(II), Os(II), Rh(III) and Ir(III)) derived from polyheterocyclic ligands were designed as anion sensors by virtue of their outstanding photo-redox behaviors and in majority of cases the incoming anionic guest interacts with suitable binding group located in the secondary coordination sphere in the complex.^{31–40} Although the platinum group metals are very efficient in detecting selected anions because of their unique combination of photophysical and electrochemical properties, but the main disadvantage is their high cost which is a major problem for their practical applications. To this end, we designed in this work, an Fe(II) complex derived from a terpyridine ligand functionalized with a diarylethylene moiety at the 4'-position of the terpyridine ring (Chart 1). Owing to the lower energy metal-to-ligand charge transfer band in the visible region, the complex offers both chromogenic and fluorogenic detection of selected anions. In this work, we investigate the anion sensing behavior of the bis-terpyridine Fe(II) complex in both organic as well as mixed aqueous–organic media through multiple optical channels and spectroscopic techniques.

2. Experimental

2.1 Materials

Reagent grade chemicals obtained from commercial sources were used as received. Solvents were purified and dried according to standard methods. 4-Chloro benzaldehyde and

tetrabutylammonium (TBA) salt of the anions were purchased from Sigma-Aldrich. 4'-(p-methylphenyl)-2,2':6',2''-terpyridine (tpy-PhCH₃), 4'-(p-bromomethylphenyl)-2,2':6',2''-terpyridine (tpy-PhCH₂Br), and [4'-(p-triphenyl phosphoniummethylphenyl)-2,2':6',2''-terpyridine]Bromide (tpy-PhCH₂PPh₃Br) were synthesized according to the literature procedures.^{41,42}

2.2 Preparation of the ligand,

4'-{4-[2-(4-Chloro-phenyl)-vinyl]-phenyl}-[2,2':6',2''] terpyridine (tpy-pvp-Cl)

A mixture of 4'-(p-triphenylphosphonium methylphenyl)-2,2':6',2''-terpyridine]bromide (tpyPhCH₂PPh₃Br) (332 mg, 0.5 mmol) and 4-chlorobenzaldehyde (71 mg, 0.5 mmol) was thoroughly dissolved in dry dichloromethane and was cooled to $\sim 5^\circ\text{C}$ under nitrogen protection. To the mixture, t-BuOK (115 mg, 1.0 mmol) was added slowly and the resulting mixture was stirred magnetically for ~ 12 h. The volume of the mixture was reduced and dichloromethane was completely removed by the addition of methanol. The crude product was washed with water, dried in air and purified by silica gel column chromatography using 10:1 (v/v) CHCl₃–MeOH mixture. The compound was finally purified by recrystallization from CHCl₃–MeOH (1:2, v/v) mixture. Yield: 120 mg (54%). Elemental anal. Calcd. (%) for C₂₉H₂₀N₃Cl: C, 78.10; H, 4.52; N, 9.42. Found: C, 78.05; H, 4.57; N, 9.38. ¹H NMR (300 MHz, CDCl₃, δ / ppm): 8.76 (s, 2H, H3'), 8.72 (nr, 2H, H6), 8.69–8.65 (m, 2H, H3), 7.94–7.89 (m, 2H, H8), 7.88 (t, 1H, $J = 2.1$, H4), 7.85 (t, 1H, $J = 2.2$, H4), 7.79 (d, 1H, $J = 8.3$, H7), 7.64 (d, 1H, $J = 8.3$, H7), 7.47 (d, 1H, $J = 8.5$, H11), 7.37–7.32 (m, 3H, 1H11+2H5), 7.26 (nr, 1H, H12), 7.21 (nr, 1H, H12), 7.13 (nr, 1H, H10), 6.70–6.57 (m, 1H, H9). ESI-MS (positive, CHCl₃): $m/z = 446.09(100\%)$ [(tpy-pvp-Cl+H)⁺].

2.3 Synthesis of the Fe(II) complex,

[Fe(tpy-pvp-Cl)₂](ClO₄)₂ (1)

To a stirred CHCl₃–MeOH (1:2, v/v) solution (25 mL) of tpy-pvp-Cl (110 mg, 0.25 mmol), a MeOH solution of Fe(ClO₄)₂·6H₂O (44 mg 0.12 mmol) was added. The colorless solution immediately changed into blue-violet and during stirring at room temperature for ~ 1 h microcrystalline compound deposited. The compound was filtered, washed with water, and dried in a vacuum. The crude compound was washed with chloroform and then purified by alumina column chromatography using 1:10 (v/v) toluene–MeCN mixture. The compound was finally recrystallized from MeCN–MeOH (1:2, v/v) mixture when a violet microcrystalline compound was obtained; yield 100 mg (76%). Elemental anal. Calcd. (%) for C₅₈H₄₀N₆Cl₄O₈Fe: C, 60.75; H, 3.51; N, 7.329. Found: C, 60.71; H, 3.53; N, 7.34. ¹H NMR (300 MHz, CD₃CN, δ / ppm): 9.22 (s, 2H, H3'), 9.17 (s, 2H, H3'), 8.64–8.6028 (nr, 4H, H6), 8.36 (d, 2H, H8, $J = 7.5$), 8.23 (d, 2H, H7, $J = 7.92$), 7.99 (d, 2H, H4, $J = 9.0$), 7.90 (m, 4H, H4+H8), 7.69–7.62 (m, 4H, H11), 7.48–7.46 (nr, 2H, $J = 6.0$, H7), 7.36 (s, 6H, H3+H10), 7.19 (d, 4H, H12), 7.08 (nr, 4H, H5), 6.86

(d, 2H, H9, $J = 6.0$). ESI-MS (positive, CH_3CN): $m/z = 473.03(100\%) [\text{Fe}(\text{tpy-pvp-Cl})_2]^{2+}$.

Caution! Perchlorate salt of the Fe(II) complex used in this study is potentially explosive and therefore should be handled in small quantities with care.

2.4 Physical measurements

Elemental analyses of the compounds were performed with a Vario-Micro V2.0.11 elemental (CHNSO) analyzer. ^1H and $\{^1\text{H}-^1\text{H}\}$ COSY NMR spectra were obtained on a Bruker Avance DPX 300 spectrometer using CDCl_3 , CD_3CN or $\text{DMSO}-d_6$ solutions. High resolution mass spectroscopy was performed on a Waters Xevo G2 QTOF mass spectrometer. The UV-Vis absorption spectral measurements were performed with a Shimadzu UV 1800 spectrometer. Steady state luminescence spectra were acquired by a Horiba Fluoromax-4 spectrofluorimeter. All the UV-Vis absorption and emission measurements were carried out at room temperature. Luminescence quantum yields were determined by using literature method taking quinine sulphate as the standard. Luminescence lifetime measurements were carried out by using time-correlated single photon counting (TCSPC) set up working in nanosecond time domain from Horiba Jobin-Yvon. The luminescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBH DAS6 software. Anion sensing studies of the receptor were carried out in acetonitrile as well as in $\text{MeCN}-\text{H}_2\text{O}$ (1:100 v/v). For a typical titration experiment, 2 μL aliquots of a given anion (2.0×10^{-2} M) were added to a 2.5 mL solution of the Fe(II) receptor (1.0×10^{-5} M). Either TBA or Sodium salts of different anions were used for titration experiments.

3. Results and Discussion

3.1 Synthesis and characterization

The terpyridine ligand (tpy-pvp-Cl) was obtained in reasonably good yield (54%) by reacting 4'-(2,2':6',2''-terpyrididyl-4)-benzyltriphenyl phosphonium bromide (tpy- $\text{PhCH}_2\text{PPh}_3\text{Br}$) with 4-chloro benzaldehyde in dichloromethane solvent at ~ 0 to 5°C under nitrogen protection. Upon treating a $\text{MeOH}-\text{CHCl}_3$ (2:1, v/v) solution of tpy-pvp-Cl with $\text{Fe}(\text{ClO}_4)_2$ in 2:1 molar ratio, a deep violet colored solution results which on stirring for few minutes produces a dark violet microcrystalline solid of composition $[\text{Fe}(\text{tpy-pvp-Cl})_2]^{2+}$. Purification of the ligand was performed by silica gel column chromatography followed by recrystallization from $\text{MeOH}-\text{CHCl}_3$ (2:1, v/v). The Fe(II) complex, on the other hand, was purified by alumina column chromatography followed by recrystallization from $\text{MeCN}-\text{MeOH}$ (1:2, v/v) mixture. Both compounds were thoroughly characterized by their elemental (C, H and N) analyses, high

resolution mass and NMR spectroscopic measurements and the results are given in the Experimental Section. The ESI mass spectrum of the Fe(II) complex in CH_3CN exhibits one abundant peak at $m/z = 473.03$ (Figure S1, in Supplementary Information). The isotopic distribution pattern of the peak at $m/z = 473.03$ (100%) separated by 0.5 Da matches nicely to the pattern simulated for $[\text{Fe}(\text{tpy-pvp-Cl})_2]^{2+}$.

The ^1H NMR spectrum of tpy-pvp-Cl as well as its Fe(II) complex, $[\text{Fe}(\text{tpy-pvp-Cl})_2]^{2+}$ are presented in Figure 1. Both compounds exhibit a number of resonances in the aromatic region and tentative assignment of the proton resonances were done by taking advantage of their $\{^1\text{H}-^1\text{H}\}$ COSY NMR spectra. The terpyridine (H3–H6) protons as well as the protons associated with diarylethylene unit (H9–H12) lying in the region between 7.32 and 8.72 ppm have been assigned by taking into consideration the multiplicities of the peak, values of the coupling constants as well chemical shifts values.

Upon coordination with Fe^{2+} , the chemical shifts of the tpy-pvp-Cl protons are presented in Figure 1b. H3' proton of tpy moiety gets significantly downfield shifted while the other tpy protons (H7–H11) get moderately downfield shifted due to the drift of electron density from the heteroaromatic moieties to the Fe^{2+} center. The chemical shift of H9 and H10 protons associated with ethylenic double bond is also shifted towards downfield region. H3 proton resonance, on the other hand, shifted remarkably towards up-field region probably because of the ring current anisotropic effect induced by the adjacent terminal pyridine ring of the tpy moiety.

3.2 Absorption and emission spectral properties

Absorption spectrum of free ligand (tpy-pvp-Cl) in acetonitrile consists of a band at 318 nm which arises mainly due to intra-ligand charge transfer transition (ILCT) and the next higher energy band at 284 nm, assignable predominantly due to $\pi - \pi^*$ transitions within the aromatic moieties of the ligand. Upon excitation on either of the two absorption maxima, an intense emission band was observed at 407 nm whose quantum yield (Φ) is 0.030 and lifetime ($\tau = 1.0$ ns). The absorption spectrum of acetonitrile solution of $[\text{Fe}(\text{tpy-pvp-Cl})_2]^{2+}$ shows an intense band at 572 nm which is due to $\text{Fe}^{\text{II}}(\text{d}\pi) - \pi^*(\text{tpy})$ MLCT transition. The spectrum of the complex also exhibits a series of higher energy absorptions arising from ligand centered $\pi - \pi^*$ and $n - \pi^*$ transitions. Upon excitation at any of the absorption band, the complex does not exhibit any emission at room temperature. Literature reports suggest that the

Figure 1. ^1H NMR (300 MHz) spectra of (a) tpy-pvp-Cl in CDCl_3 and (b) $[\text{Fe}(\text{tpy-pvp-Cl})_2]^{2+}$ in CD_3CN .

photophysics of the polypyridine Fe(II) complex is complicated by the presence of low lying ligand field (LF) excited states.^{43–45} These states arise from population of the empty metal $d\sigma^*$ orbitals. Although optical transitions to yield the LF excited states are not dipole-allowed and are therefore of low probability, the LF states can become populated by crossing from the MLCT states. This occurs readily in polypyridine Fe(II) complexes where the LF state lies below the MLCT state.^{43–45}

3.3 Anion sensing studies of the metalloreceptor through different optical channels and spectroscopic techniques

The sensing ability of the metalloreceptor was initially investigated on a qualitative basis by visual inspection of its anion-induced color changes in both acetonitrile and water. Tetrabutylammonium salts of F^- , Cl^- , Br^- , I^- , CN^- , OAc^- , H_2PO_4^- , SCN^- , BF_4^- and ClO_4^- were

used for the sensing studies. It was observed that upon addition of 12 equiv. of various anions in acetonitrile, the bright violet colored solution of the Fe(II) complex became colorless in presence of F^- and OAc^- ions, while the color changes to light green in presence of CN^- (Figure 2).

In contrast to acetonitrile, the deep violet color of the metalloreceptor became faint in mixed aqueous-acetonitrile only in presence of CN^- among the other studied anions (Figure 3).

Upon irradiation of UV light of wavelength 365 nm, bright bluish-green fluorescence color was observed in the presence of F^- , OAc^- and CN^- ions in acetonitrile (Figure 2), while similar fluorescence color was observed in presence of only CN^- in mixed aqueous-acetonitrile medium (Figure 3). Thus, visual color change of the metalloreceptor can be useful for the “naked-eye” detection of the said anions in both organic as well as aqueous medium. In addition, selectivity is

Figure 2. Color changes that are observed in naked eye (a), and in presence of UV light (b), when acetonitrile solutions of the metalloreceptor (5×10^{-5} M) are treated with various anions (5.0×10^{-3} M).

Figure 3. Color changes that are observed in naked eye (a), and in presence of UV light (b), when the H_2O – MeCN (100:1, v/v) solutions of the metalloreceptor (5×10^{-5} M) are treated with various anions (5.0×10^{-3} M).

increased significantly in water where the metalloreceptor exclusively sense CN^- in presence of the other studied anions. This prompted us to investigate the anion sensing behavior of the metalloreceptor through various spectroscopic techniques.

UV-Vis absorption and emission spectra of the metalloreceptor in presence of various anions are presented in Figure 4. The MLCT band at 572 nm gets significantly affected compared with the other bands in the UV region in both media. In acetonitrile, upon addition of 12 equiv.

of the anions, the MLCT band is completely disappeared in presence of F^- , while substantial diminution of the MLCT band along with evolution of weak and broad band in the longer wavelength region are observed for OAc^- and CN^- (Figure 4a). In contrast to neat acetonitrile, the diminution of the MLCT band occurs only with CN^- in mixed-aqueous medium (Figure 4b). Free metalloreceptor is non-luminescent at room temperature but addition of the various anions, substantial emission enhancement at ~ 407 nm was observed for each of F^- ,

Figure 4. UV-Vis absorption (a and b) and photoluminescence (c and d) spectral changes of 1.0×10^{-5} M solutions of the metalloreceptor in acetonitrile and water–acetonitrile (100:1, v/v) mixture upon addition of different anions (100 μL) as their TBA and sodium salts (5.0×10^{-3} M). Excitation wavelength for recording emission is 330 nm.

OAc^- and CN^- , albeit in different extent (Figure 4c). In line with the absorption spectra, the enhancement of emission occurs only with CN^- in mixed-aqueous medium (Figure 4d).

To have quantitative information about the receptor–anion interaction process, absorption and emission titration of the metalloreceptor was carried out with incremental addition of the anions. It was observed that the MLCT band at 572 nm in acetonitrile medium gradually decreased in intensity and finally completely disappeared upon addition of 12 equiv. of either F^- or OAc^- with concomitant disappearance of the violet color of the solution (Figure 5a and Figure S2a, in Supplementary Information) and the final spectrum at saturation looks very similar to that of the free ligand. In contrast to F^- or OAc^- , saturation occurs upon addition of 6 equiv. of CN^- and color of the resultant solution became light green with weak and broad band spanning in the range between 540 nm and 620 nm (Figure 6a). In each case, successive absorption curves pass through several well-defined isosbestic points. We are not very sure about the actual species that formed at saturation but to the best of our expectation, the composition

of the final product may be $[\text{Fe}(\text{tpy-pvp-Cl})(\text{CN})_3]^-$. The result of the blank experiment involving titration of $\text{Fe}(\text{ClO}_4)_2$ with incremental addition of CN^- does not impart any green color in the final solution which can rule out the probable formation of $[\text{Fe}(\text{CN})_6]^{4-}$ as in the case of F^- or OAc^- .

Emission titrations of $[\text{Fe}(\text{tpy-pvp-Cl})_2]^{2+}$ as a function of the said anions were also carried out. Incremental addition of the said ions gives rise to gradual emission enhancement at 407 nm and finally saturated upon addition of 12 equiv. of F^- or OAc^- (Figure 5b and Figure S2b, in Supplementary Information). It is of interest to note that the extent of emission enhancement is little less in case of CN^- compared with F^- or OAc^- (Figure 4c). Thus, both absorption and emission titration data clearly indicate that addition of the said anions lead to sequester Fe^{2+} from the complex to form a more stable ion-pair or complex cation (such as $[\text{FeF}_6]^{4-}$) and excess anions (except CN^-) lead to regenerate the free terpyridine ligand.

In aqueous-acetonitrile medium, the titration profiles in presence of CN^- differ from those in neat acetonitrile. It may be mentioned here that absorption and emission

Figure 5. UV-Vis absorption (a), and photoluminescence (λ_{ex} : 330 nm) (b) spectral changes of the metal-loreceptor (1.0×10^{-5} M) in acetonitrile upon incremental addition of F^- (5.0×10^{-3} M). The insets show the equivalent plot of the experimental absorbance and luminescence data.

Figure 6. UV-Vis absorption (a), and photoluminescence (λ_{ex} : 330 nm) (b) spectral changes of the metal-loreceptor (1.0×10^{-5} M) in acetonitrile upon incremental addition of CN^- (5.0×10^{-3} M). The insets show the equivalent plot of the experimental absorbance and luminescence data.

Figure 7. UV-Vis absorption (a), and photoluminescence (λ_{ex} : 330 nm) (b) spectral changes of the metal-loreceptor (2.0×10^{-5} M) in water-acetonitrile (100:1, v/v) mixture upon incremental addition of CN^- (5.0×10^{-3} M). The insets show the equivalent plot of the experimental absorbance and luminescence data.

Figure 8. ^1H NMR (300 MHz) spectral titration of the metalloreceptor in $\text{DMSO-}d_6$ (2.5×10^{-3} M) upon gradual addition of F^- ion (0–12 equiv.).

spectral titrations of the metalloreceptor were conducted in HEPES buffer solution at pH 7.2 to exclude the disturbance from hydroxide ion which may be produced from the hydrolysis of cyanide in water. Gradual reduction of absorbance along with small red-shift of the MLCT band and enhancement of emission intensity at 410 nm was also observed upon incremental addition of 12.0 equiv. of CN^- but the extent of change is much less compared with neat acetonitrile (Figure 6). Further addition of CN^- gives rise to gradual precipitation of the resulting complex (Figure 7).

To prove the interaction of metalloreceptor with various anions, ^1H NMR titration experiments were conducted upon incremental addition of F^- and OAc^-

in $\text{DMSO-}d_6$ as well as with CN^- in CD_3CN (Figure 8 and Figure S3, in Supplementary Information). 5.0×10^{-3} M solution of the complex was employed in the titration experiment. Upon addition of both F^- and OAc^- , the chemical shifts of $\text{H}3'$ and $\text{H}6$ are found to be remarkably up-field shifted, $\text{H}7$ – $\text{H}10$ protons moderately up-field shifted, while $\text{H}5$ and $\text{H}11$ protons shifted to small down-field region. Assignments of the different protons in the final spectrum indicate that the spectrum is of that of the free ligand, although small variation of spectral pattern is observed between the spectrum recorded in CDCl_3 and $\text{DMSO-}d_6$. Thus, both F^- and OAc^- induce complete decoordination of Fe(II) center from the complex yielding the free ligand. The

Table 1. Spectrophotometric and fluorimetric detection limits of $[\text{Fe}(\text{tpy-pvp-Cl})_2]^{2+}$ in acetonitrile and water–acetonitrile (100:1, v/v) mixture.

Compound	Detection Limit (M) in acetonitrile		Detection Limit (M) in acetonitrile		Detection Limit (M) in water–acetonitrile (100:1, v/v) mixture	
	Abs	Emission	Abs	Emission	Abs	Emission
$[\text{Fe}(\text{tpy-pvp-Cl})_2]^{2+}$	F^-		CN^-		CN^-	
	$(1.18 \pm 0.03) \times 10^{-9}$	$(1.19 \pm 0.04) \times 10^{-9}$	$(2.00 \pm 0.04) \times 10^{-9}$	$(1.18 \pm 0.06) \times 10^{-9}$	$(2.20 \pm 0.02) \times 10^{-8}$	$(1.90 \pm 0.06) \times 10^{-8}$

spectral profile in presence of CN^- is quite different from both F^- and OAc^- (Figure S3, in Supplementary Information). It is observed that complete displacement of $\text{Fe}(\text{II})$ ion from the complex does not occur. Instead, one terpyridine ligand is still coordinated with $\text{Fe}(\text{II})$, while the second one is probably displaced by three incoming CN^- ligands. In addition, some small but finite change in spectral pattern and/or chemical shift of selected terpyridine protons (H6, H5 and H4) occurs upon displacement of one ligand moiety from the $\text{Fe}(\text{II})$ center. UV-Vis absorption spectral titrations also indicate the same conclusion. Even after addition of excess CN^- to the acetonitrile solution of the complex, clear broad (most probably MLCT) bands in the visible range (between 540 nm and 620 nm) are observed indicating the coexistence of both the ligand as well as $\text{Fe}(\text{II})$.

For practical applicability, the limit of detection and selectivity of the metalloreceptor are very important parameters. To this end, we have determined the detection limit of the metalloreceptor by utilizing the absorption and emission titration data in both media and the values are provided in Table 1. The calculated values (lying in the range between $(1.18 \pm 0.03) \times 10^{-9}$ M and $(1.19 \pm 0.04) \times 10^{-9}$ M for F^- and between $(1.18 \pm 0.06) \times 10^{-9}$ M and $(2.20 \pm 0.02) \times 10^{-8}$ M for CN^-) indicate that the complex provides extremely low limit detection of CN^- , even in mixed aqueous–organic medium (Figures S4–S9, in Supplementary Information). The selectivity of the metalloreceptors towards a particular ion such as F^- or CN^- in presence of other studied anions was also investigated. UV-Vis absorption and emission measurements were performed by treating the aqueous solution of the complex ($c \sim 2 \times 10^{-5}$ M) with any of the two anions (F^- or CN^-) in the presence of each of the other studied anions. In the competition experiments, we are still able to observe color as well as spectral changes in presence of each of F^- , CN^- and OAc^- in acetonitrile while the color and spectral change occurs only with CN^- in water. Likewise, enhancement of emission also occurs with F^- or CN^- in acetonitrile whereas only in presence of CN^- in water. Once a particular ion among the two (F^- or CN^-) is added, the other anion was unable to make any further change. The inability of the complex to sense F^- and OAc^- in aqueous medium is due to the higher hydration energy of F^- ($\Delta G_h^\circ = -465$ kJ/mol) and OAc^- ($\Delta G_h^\circ = -465$ kJ/mol) compared with CN^- ($\Delta G_h^\circ = -295$ kJ/mol). In addition, higher pK_a value for HCN in water ($pK_a = 9.0$) compared with HF ($pK_a = 3.17$) and HOAc ($pK_a = 4.75$) shows more basic character of CN^- compared with F^- and OAc^- in water.³⁴ The results clearly indicate that the

metalloreceptor possesses very high selectivity towards CN^- over the other anions in predominantly aqueous medium.

4. Conclusions

In this work, we report an unprecedented homoleptic bis-terpyridine Fe(II) complex for multichannel sensing of selective anions in both organic and aqueous medium by taking advantage of metal–ligand interaction *via* displacement approach. In acetonitrile medium, the metalloreceptor functions as sensor for F^- , OAc^- and CN^- without selectivity, but in water it acts as chromogenic and fluorogenic sensor for only CN^- ion. One of the most important observations of this work is that the Fe(II) complex exhibits very high selectivity and sensitivity towards CN^- in water with very low detection limit up to 10^{-8} M and thus may be useful for practical applications.

Supplementary information (SI)

Characterization data of the ligand as well as the metal complexes, UV-Vis absorption and emission titration profiles as a function of different anions and the plots for determination of the detection limits of the complexes towards different anions are available at www.ias.ac.in/chemsci.

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References

1. Sessler J L, Gale P A and Cho W S 2006 *Anion receptor chemistry* (Cambridge, UK: Royal Society of Chemistry)
2. *Supramolecular Chemistry of Anions* 1997 A Bianchi, K Bowman-James and E Garcia-España (Eds.) (New York: Wiley-VCH)
3. Bowman-James K 2005 Alfred Werner Revisited: The coordination chemistry of anions *Acc. Chem. Res.* **38** 671
4. Beer P D 1996 Anion selective recognition and optical/electrochemical sensing by novel transition-metal receptor systems *Chem. Commun.* 689
5. Kulig K W 1991 *Cyanide toxicity* (Atlanta: U.S. Department of Health and Human Services)
6. Taylor J, Roney N, Fransen M E and Swarts S 2006 *Toxicological profile for cyanide* (Atlanta: DIANE Publishing)
7. Xu Z, Chen X, Kim H N and Yoon J 2010 Sensors for the optical detection of cyanide ion *Chem. Soc. Rev.* **39** 127
8. Kaur K, Saini R, Kumar A, Luxami V, Kaur N, Singh P and Kumar S 2012 Chemodosimeters: an approach for detection and estimation of biologically and medically relevant metal ions, anions and thiols *Coord. Chem. Rev.* **256** 1992
9. Wang F, Wang L, Chen X and Yoon J 2014 Recent progress in the development of fluorometric and colorimetric chemosensors for detection of cyanide ions *Chem. Soc. Rev.* **43** 4312
10. Kubik S 2010 Anion recognition in water *Chem. Soc. Rev.* **39** 3648
11. Sun W, Guo S, Hu C, Fan J and Peng X 2016 Recent development of chemosensors based on cyanine platforms *Chem. Rev.* **116** 7768
12. Gunnlaugsson T, Glynn M, Tocci G M, Kruger P E and Pfeffer F M 2005 Anion recognition and sensing in organic and aqueous media using luminescent and colorimetric sensors *Coord. Chem. Rev.* **250** 3094
13. Sun S-S and Lees A J 2000 Advanced concepts in fluorescence sensing: part A: small molecule sensing *Chem. Commun.* 1687
14. Saha S, Ghosh A, Mahato P, Mishra S, Mishra S K, Suresh E, Das S and Das A 2010 Specific recognition and sensing of CN^- in sodium cyanide solution *Org. Lett.* **12** 3406
15. Lee K-S, Kim H-J, Kim G-H, Shin I, Hong J-I 2008 Fluorescent chemodosimeter for selective detection of cyanide in water *Org. Lett.* **10** 49
16. Santos-Figueroa L E, Moragues M E, Climent E, Agostini A, Martínez-Máñez R and Sancenón F 2013 Chromogenic and fluorogenic chemosensors and reagents for anions. A comprehensive review of the years 2010–2011 *Chem. Soc. Rev.* **42** 3489
17. Chung S-Y, Nam S-W, Lim J, Park S and Yoon J 2009 A highly selective cyanide sensing in water via fluorescence change and its application to in vivo imaging *Chem. Commun.* 2866
18. Bhalla V, Singh H and Kumar M 2012 Triphenylene based copper ensemble for the detection of cyanide ions *Dalton Trans.* **41** 11413
19. Lou X, Zhang L, Qin J and Li Z 2008 An alternative approach to develop a highly sensitive and selective chemosensor for the colorimetric sensing of cyanide in water *Chem. Commun.* 5848
20. Nguyen B T and Anslyn E V 2006 Indicator-displacement assays *Coord. Chem. Rev.* **250** 3118
21. Lou X, Ou D, Li Q and Li Z 2012 An indirect approach for anion detection: the displacement strategy and its application *Chem. Commun.* **48** 8462
22. Divya K P, Sreejith S, Balakrishna B, Jayamurthy P, Anees P and Ajayaghosh A 2010 A Zn^{2+} -specific fluorescent molecular probe for the selective detection of endogenous cyanide in biorelevant samples *Chem. Commun.* 6069
23. Shaily K A and Ahmed N 2017 Indirect approach for CN^- detection: development of “Naked-Eye” Hg^{2+} -induced turn-off fluorescence and turn-on cyanide sensing by the Hg^{2+} displacement approach *Ind. Eng. Chem. Res.* **56** 6358

24. La M, Hao Y, Wang Z, Han G-C and Qu L 2016 Selective and sensitive detection of cyanide based on the displacement strategy using a water-soluble fluorescent probe *J. Anal. Methods Chem.* **2016** 1
25. Chow C-F, Ho P-Y, Wong W-L and Gong C-B 2015 A multifunctional bimetallic molecular device for ultrasensitive detection, naked-eye recognition, and elimination of cyanide ions *Chem. Eur. J.* **21** 12984
26. Maurya N, Bhardwaj S and Singh A K 2017 Selective colorimetric and fluorescence 'turn on' sensor for Ag^+ and in-situ sensing of CN^- (off-on-off) via displacement approach *Mater. Sci Eng. C* **74** 55
27. Martínez-Máñez R and Sancenón F 2003 Fluorogenic and chromogenic chemosensors and reagents for anions *Chem. Rev.* **103** 4419
28. Beer P D and Bayly S R 1998 Transition-metal receptor systems for the selective recognition and sensing of anionic guest species *Acc. Chem. Res.* **31** 71
29. Pérez J and Riera L 2008 Stable metal-organic complexes as anion hosts *Chem. Soc. Rev.* **37** 2658
30. Amendola V and Fabbri L 2009 Anion receptors that contain metals as structural units *Chem. Commun.* 513
31. Paul B D, Szemes F, Balzani V, Salà, Drew M G B, Dent S W and Maestri M 1997 Anion selective recognition and sensing by novel macrocyclic transition metal receptor systems. ^1H NMR, electrochemical, and photophysical investigations *J. Am. Chem. Soc.* **49** 11864
32. Cui Y, Niu Y-L, Cao M L, Wang K, Mo H-J, Zhong Y-R and Ye B-H 2008 Ruthenium(II) 2, 2'-bibenzimidazole complex as a second-sphere receptor for anions interaction and colorimeter *Inorg. Chem.* **47** 5616
33. Mo H-J, Shen Y and Ye B-H 2012 Selective recognition of cyanide anion via formation of multipoint NH and phenyl CH hydrogen bonding with acyclic ruthenium bipyridine imidazole receptors in water *Inorg. Chem.* **51** 7174
34. Bar M, Maity D, Das K and Baitalik S 2017 Asymmetric bimetallic ruthenium(II) complexes selectively sense cyanide in water through significant modulation of their ground and excited state properties *Sens. Actuat. B* **251** 208
35. Mardanya S, Karmakar S, Bar M and Baitalik S 2015 Pyrene-biimidazole based Ru(II) and Os(II) complexes as highly efficient probes for the visible and near infrared detection of cyanide in aqueous media *Dalton Trans.* **44** 21053
36. Maity D, Das S, Mardanya S and Baitalik S 2013 Synthesis, structural characterization, and photophysical, spectroelectrochemical, and anion-sensing studies of heteroleptic ruthenium(II) complexes derived from 4'-polyaromatic-substituted terpyridine derivatives and 2,6-bis(benzimidazol-2-yl)pyridine *Inorg. Chem.* **52** 6820
37. Maity D, Bhaumik C, Mondal D and Baitalik S 2014 Photoinduced intramolecular energy transfer and anion sensing studies of isomeric $\text{Ru}^{\text{II}}\text{Os}^{\text{II}}$ complexes derived from an asymmetric phenanthroline-terpyridine bridge *Dalton Trans.* **43** 1829
38. Mardanya S, Karmakar S, Maity D and Baitalik S 2015 Ruthenium(II) and Osmium(II) mixed chelates based on pyrenyl- pyridylimidazole and 2,2'-bipyridine ligands as efficient DNA intercalators and anion sensors *Inorg. Chem.* **54** 513
39. Chowdhury B, Sinha S and Ghosh P 2016 Selective sensing of phosphates by a new bis-heteroleptic Ru^{II} complex through halogen bonding: A superior sensor over its hydrogen-bonding analogue *Chem. Eur. J.* **22** 18051
40. Chowdhury B, Dutta R, Khatua S and Ghosh P 2016 A cyanuric acid platform based tripodal bis-heteroleptic Ru(II) complex of click generated ligand for selective sensing of phosphates via C-H anion interaction *Inorg. Chem.* **55** 259
41. Pott K T, Usifer D A and Abruna H D 1987 4-Vinyl-, 6-Vinyl-, and 4'-Vinyl-2,2':6',2'' terpyridinyl ligands: their synthesis and the electrochemistry of their transition-metal coordination complexes *J. Am. Chem. Soc.* **109** 3961
42. Spahni W and Calzaferri G 1984 Synthese von para-substituierten phenyl-terpyridin liganden *Helv. Chim. Acta* **67** 450
43. Winker J R and Sutin N 1987 Lifetimes and spectra of the excited states of cis dicyanobis(2,2'-bipyridine)iron(II) and -ruthenium(II) in solution *Inorg. Chem.* **26** 220
44. Creutz C, Chou M, Netzel T L, Okumura M and Sutin N 1980 Lifetimes, spectra, and quenching of the excited states of polypyridine complexes of iron(II), ruthenium(II), and osmium(II) *J. Am. Chem. Soc.* **102** 1309
45. Bergkamp M A, Guetlich P, Netzel T L and Sutin N 1983 Lifetimes of the ligand-to-metal charge-transfer excited states of iron(III) and osmium(III) polypyridine complexes. Effects of isotopic substitution and temperature *J. Phys. Chem.* **87** 3877