Supporting Information

Stimuli-Responsive Near Infrared Emissive Os(II)-Terpyridine Complexes with a Sense of Logic

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**Physical Measurements.** UV-vis absorption spectra were recorded using a Shimadzu UV 1800 spectrometer. Steady state luminescence spectra were acquired either by a Perkin–Elmer LS55 or a Horiba Fluoromax-4 spectrofluorometer. Luminescence quantum yields were determined using literature method taking $[\text{Ru(bpy)}_3]^{2+}$ as the standard. Luminescence lifetime measurements were carried out by using time-correlated single photon counting set up from Horiba Jobin-Yvon. The samples were excited with 450 nm Nanoled. The luminescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBH DAS6 software. ESI mass spectra were recorded on a Waters Xevo G2 QTOF mass spectrometer. NMR spectra of the compounds were acquired on either Bruker 400 or 500 MHz spectrometer.

To determine the ground state p$K_a$ values of the complexes, spectrophotometric titrations were carried out with a series of aqueous solutions and pH adjusted in the range of 2.5-12. Robinson-Britton buffer was used in the study. The pH measurements were made with a Beckman Research Model pH meter. The pH data and the titration data and using eqn (S1).$^{S1}$

$$\text{pH} = \text{p}K_a - \log \frac{A - A_0}{A_f - A_0}$$  \hspace{1cm}  (S1)

Excited-state p$K_a$ values of the complexes were also calculated by using lifetimes (τ) vs. pH data and with the help of the following equation S2.$^{S2}$

$$pK_a^* = \text{pH} + \log \frac{\tau_{\text{acid}}}{\tau_{\text{base}}}$$  \hspace{1cm}  (S2)

where pH is the inflection point of the curve of emission intensity as a function of pH. $\tau_{\text{acid}}$ and $\tau_{\text{base}}$ correspond to the lifetimes of the protonated and deprotonated states, respectively. The lifetime values are experimentally obtained at pH levels well above and well below the midpoint, where $\tau$ is relatively invariant with pH.

The sensing studies of the receptors with different anions and cations were carried out in acetonitrile as well as in water medium. Tetrabutylammonium (TBA) salts of different anions and hydrated perchlorate salts of the metals were used for titration experiments. The binding/equilibrium constant towards the ions were evaluated from the absorbance data using equation (S3).$^{S3}$

$$A_{\text{obs}} = (A_0 + A_{\infty}K[G]_T)/(1 + K[G]_T)$$  \hspace{1cm}  (S3)
where $A_{\text{obs}}$ is the observed absorbance, $A_0$ is the absorbance of the free receptor, $A_\infty$ is the maximum absorbance induced by the presence of a given ionic guest, $[G]_T$ is the total concentration of the guest, and $K$ is the binding/equilibrium constant of the host–guest entity. Binding constants were performed in duplicate, and the average value is reported.

**Anion Sensing Behaviors of the Complexes in Acetonitrile.** Experiments were performed in MeCN by taking tetrabutylammonium salts of $F^-$, $\text{Cl}^-$, $\text{Br}^-$, $I^-$, $\text{AcO}^-$, $\text{CN}^-$, $\text{SCN}^-$, and $\text{H}_2\text{PO}_4^-$. Absorption and emission spectra in presence of 10 equiv of various anions are presented in Figure S7. The extent of change in the absorption spectrum of 2 is greater than 1. Only $F^-$ and $\text{CN}^-$ induces change in the MLCT band in 1, while each of $F^-$, $\text{AcO}^-$, $\text{CN}^-$, and $\text{H}_2\text{PO}_4^-$ leads to red-shift of the MLCT band in 2, although the extent varies with the nature of the anions. In line with the absorption spectral behavior, visual colour change was also observed in presence of aforementioned anions (Figure S7). For both compounds emission quenching were observed in presence of the excess of the anions.

Titration measurements were also done to get quantitative data for the complex-anion interaction process (Figures S8-S11). Both complexes exhibit two-step changes in their absorption and emission spectra. In case of 1, addition of the anions primarily leads to change in the intensity of the different bands with small shift of their position. By contrast, for 2, the change of absorbance occurs along with larger red-shift of the band (particularly for MLCT). Almost 10 equiv of the anions were consumed to reach the saturation points. Despite the presence of only one NH proton, 1 exhibits two-steps changes (Figures S8-S9), while in spite of the presence of three NH protons, 2 shows only two-step changes with $F^-$, $\text{CN}^-$, $\text{AcO}^-$ and $\text{H}_2\text{PO}_4^-$ (Figures S10-S11). The first change in 1 is probably associated with anion-induced removal of a proton from the protonated pyridine moiety which most likely results during recrystallization of the complexes in presence of $\text{HClO}_4$ medium, while the second change is due to the removal of the proton from the neutral imidazole ring on the bridge. The presence of protonated tri-positive ion was also evident in the ESI mass spectrum of 1 (Figure 2a). In case of 2, NH proton associated with protonated pyridine-imidazole initially removed in the first step, while in the second step two NH protons of $\text{H}_3\text{pbbzim}$ moiety are dissociated with excess of the anions. Each spectral change is accompanied by the appearance of
isosbestic points. Equilibrium constants of the receptor-anion interaction process were estimated by using absorption titration data and the estimated values are presented in Table 3 and found to lie in order of $10^6 \text{M}^{-1}$.

In line with UV-vis absorption spectra, two-steps changes are also seen in the emission spectra for both compounds. The first step change in 1 is associated with enhancement of emission, while the second-step change is accompanied with almost complete emission quenching with $\text{F}^-$, $\text{CN}^-$, and $\text{AcO}^-$. In contrast to 1, substantial emission quenching occurs in two successive steps in 2 accompanied by blue-shift of the band in each steps. Small variation in the spectral responses observed is due to the difference in their charge density, size, and the basicity of the anions. The equilibrium constants estimated from emission titration data were found to correlate well with the absorption data (Table 3). Limits of detection of the selected anions were also calculated from the UV-vis absorption and emission titration data (Figures S12-S15) and were found to lie in the range of $2.00 \times 10^{-9} \text{M}-6.00 \times 10^{-9} \text{M}$ for $\text{F}^-$ (Table 4).

Luminescence lifetime were also acquired as function of $\text{F}^-$ and $\text{H}_2\text{PO}_4^-$ and decay curves and values of lifetimes associated with each decay were shown in Figures S16-S18. In contrast to their steady state spectra, the lifetime of both complexes changed in one step. For 1, the extent of decrease is less with $\text{F}^-$ (105 ns $\rightarrow$ 93 ns) than $\text{H}_2\text{PO}_4^-$ (105 ns $\rightarrow$ 72 ns). In case of 2, lifetime increases with $\text{F}^-$ (48 ns $\rightarrow$ 22 ns and 90 ns) while decrease with $\text{H}_2\text{PO}_4^-$ (48 ns $\rightarrow$ 24 ns). It is of interest to note that initial mono-exponential decay of 2 gradually converted to bi-exponential with overall increase of lifetime in presence of $\text{F}^-$. The red-shift of the MLCT band can be attributed to the second-sphere donor-acceptor interactions (hydrogen bonding and/or proton transfer) between the imidazole NH proton(s) and the anions resulting in increased negative charge on the metal center.$^{54-56}$ Emission enhancement for 1 in the first step is probably due to increased electron delocalization arising out of removal of a proton from protonated pyridine moiety in the complex. Quenching of emission, on the other hand, is probably because of photo-induced intramolecular electron transfer from deprotonated imidazole unit to the photo-excited Os(II)-terpyridine unit.
It is interest to note that 1 equiv of F\textsuperscript{−}, AcO\textsuperscript{−}, and H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−} lead to ~2-fold emission enhancement, while addition beyond 1 equiv lead to ~88-fold emission quenching in 1. Thus, 1 can function as selective "turn on" type of emission sensor for the said anions up to 1 equiv, while "turn off" type emission sensor in presence of excess anions. On the other hand, nearly complete emission quenching occurs in 2 by F\textsuperscript{−}, CN\textsuperscript{−}, AcO\textsuperscript{−} and H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−} and hence functions as only "turn off" type emission sensor for the said anions.
Figure S1. \(^{1}H-^{1}H\) COSY NMR spectrum of \([(\text{dipy-Hbzim-tpy})\text{Os(tpy-PhCH}_3)](\text{ClO}_4)\_2\) (I) in DMSO-\(d_6\).
Figure S2. (1H-1H) COSY NMR spectrum of \([(dipy-Hbzim-tpy)Os(H_2pbbzim)](ClO_4)_2\) (2) in DMSO-\(d_6\).
Figure S3. UV-vis absorption and emission ($\lambda_{ex}$: 490 nm) spectra of 2 (a and b, respectively) in few solvents.

Figure S4. Change in time-resolved luminescence decay of 1 (a) and 2 (b) in few solvents. Insets to the figures show the lifetimes. Excitation wavelength is 450 nm.
Figure S5. Luminescence spectra (λ<sub>ex</sub>: 490 nm) (a) and lifetime (b) of the complexes in EtOH-MeOH (4:1, v/v) at 77K. Excitation wavelength for acquiring lifetime is 450 nm.

Table S1 Redox data<sup>[a]</sup> for 1 and 2 in acetonitrile

| Compds | Oxidation<sup>b</sup> | Reduction<sup>c</sup> |
|--------|----------------------|----------------------|
|        | E<sub>1/2</sub>(ox), V | E<sub>1/2</sub>(red), V |
| 1      | 0.91                 | -0.86, -1.11, -1.45  |
| 2      | 0.80                 | -1.00, -1.41, -1.55  |

<sup>[a]</sup> All potentials are referenced against Ag/AgCl electrode with E<sub>1/2</sub> = 0.36 V for the Fc/Fc<sup>+</sup> couple.<sup>[b]</sup> Reversible electron -transfer process with a Pt working electrode. <sup>[c]</sup> E<sub>1/2</sub> values obtained SWV with glassy carbon electrode.
Figure S6. Two-step changes in the excited state lifetimes of 1 (a and b, respectively) with variation of pH of the solution. Inset shows the decay profiles of 1 as a function of pH. pK$_{a}^{*}$ values are also given in the figure. Excitation wavelength for acquiring lifetime is 450 nm.
Figure S7. UV-vis absorption and emission ($\lambda_{ex}=490$ nm) spectral changes of 1 (a and c, respectively) and 2 (b and d, respectively) in MeCN upon addition of different anions. The visual color changes are shown in the insets of figure a and b.
**Figure S8.** UV-vis absorption (a and b) and photoluminescence ($\lambda_{ex}$: 490 nm) (c and d) spectral changes of 1 (1.0×10⁻⁵ M) in acetonitrile upon addition of F⁻ (5×10⁻³ M). The insets show the fit of the experimental absorbance and luminescence data to a 1:1 binding profile.
Figure S9. UV-vis absorption (a and b) and photoluminescence (λ<sub>ex</sub>: 490 nm) (c and d) spectral changes of 1 (1.0×10<sup>-5</sup> M) in acetonitrile upon addition of H<sub>2</sub>PO<sub>4</sub> (5×10<sup>-3</sup> M). The insets show the fit of the experimental absorbance and luminescence data to a 1:1 binding profile.
Figure S10. UV-vis absorption (a and b) and emission ($\lambda_{ex} = 490$ nm) (c and d) spectral changes of 2 (1.0×10^{-5} M) in acetonitrile upon addition of H$_2$PO$_4^-$ (5×10^{-3} M). The insets show the fit of the experimental absorbance and luminescence data to a 1:1 binding profile.
Figure S11. UV-vis absorption (a and b) and photoluminescence ($\lambda_{\text{ex}}$: 490 nm) (c and d) spectral changes of 2 (1.0×10^{-5} M) in acetonitrile upon addition of F$^-$ (5×10^{-3} M). The insets show the fit of the experimental absorbance and luminescence data to a 1:1 binding profile.
Figure S12. (a) Absorption spectral changes during the titration of the receptor 1 (1.0 × 10⁻⁵ M) with F⁻ in acetonitrile medium, inset: Normalized absorbance between the minimum absorbance and the maximum absorbance. (b) A plot of (A-A_{min})/(A_{max}-A_{min}) vs Log([F⁻]), the calculated detection limit of receptor is 2.0 × 10⁻⁹ M.

Figure S13. (a) Emission spectral (λ_{ex}: 490 nm) changes during the titration of the receptor 1 (1.0 × 10⁻⁵ M) with F⁻ in acetonitrile medium, inset: Normalized intensity between the minimum intensity and the maximum intensity. (b) A plot of (I-I_{min})/(I_{max}-I_{min}) vs Log([F⁻]), the calculated detection limit of receptor is 4.0 × 10⁻⁹ M.
Figure S14. (a) Absorption spectral changes during the titration of the receptor 2 (1.0 × 10⁻⁵ M) with F⁻ in acetonitrile medium, inset: Normalized absorbance between the minimum absorbance and the maximum absorbance. (b) A plot of \((A-A_{\text{min}})/(A_{\text{max}}-A_{\text{min}})\) vs \(\log([F^-])\), the calculated detection limit of receptor is 5.0 × 10⁻⁹ M.

Figure S15. (a) Emission spectral \((\lambda_{\text{ex}}: 490 \text{ nm})\) changes during the titration of the receptor 2 (1.0 × 10⁻⁵ M) with F⁻ in acetonitrile medium, inset: Normalized intensity between the minimum intensity and the maximum intensity. (b) A plot of \((I-I_{\text{min}})/(I_{\text{max}}-I_{\text{min}})\) vs \(\log([F^-])\), the calculated detection limit of receptor is 6.0 × 10⁻⁹ M.
Figure S16. Change in time-resolved luminescence decay of 1 (a and b) in acetonitrile solution at room temperature upon incremental addition of F⁻ and \( \text{H}_2\text{PO}_4^- \) ion. Insets show the lifetimes of the complex. Excitation wavelength for acquiring lifetime is 450 nm.

Figure S17. Change in time-resolved luminescence decay of 2 (a and b) in acetonitrile solution at room temperature upon incremental addition of F⁻ ion. Insets show the lifetimes of the complex. Excitation wavelength for acquiring lifetime is 450 nm.
Figure S18. Change in time-resolved luminescence decay of 2 (a and b) in acetonitrile solution at room temperature upon incremental addition of H$_2$PO$_4^-$ ion. Insets show the lifetimes of the complex. Excitation wavelength for acquiring lifetime is 450 nm.

Figure S19. Changes in UV–vis absorption (a) and luminescence ($\lambda_{ex}$: 490 nm) spectra (b) of 1 in aqueous solution (2.0 × 10$^{-5}$ M) upon incremental addition of CN$^-$ ion (0.1M). The insets show the change of absorbance and luminescence with equivalent of CN$^-$ ion.
Figure S20. Change in luminescence decay profiles of 1 (a and b) in aqueous solution (2.0 × 10^{-5} M) at room temperature upon incremental addition of CN\(^{-}\) and SCN\(^{-}\) (0.1 M). Insets show the lifetimes of the complex. Excitation wavelength for acquiring lifetime is 450 nm.

Figure S21. Change in luminescence decay profiles of 2 in aqueous solution (2.0 × 10^{-5} M) at room temperature upon incremental addition of CN\(^{-}\) (0.1 M). Insets show the lifetimes of the complex. Excitation wavelength for acquiring lifetime is 450 nm.
Figure S22. (a) Absorption spectral changes during the titration of the receptor 1 (2.0 × 10^{-5} M) with CN⁻ in aqueous solution, inset: Normalized absorbance between the minimum absorbance and the maximum absorbance. (b) A plot of (A-A_{min})/(A_{max}-A_{min}) vs Log([CN^-]), the calculated detection limit of receptor is 5.4 × 10^{-8} M.

Figure S23. (a) Absorption spectral changes during the titration of the receptor 1 (2.0 × 10^{-5} M) with SCN⁻ in aqueous solution, inset: Normalized absorbance between the minimum absorbance and the maximum absorbance. (b) A plot of (A-A_{min})/(A_{max}-A_{min}) vs Log([SCN^-]), the calculated detection limit of receptor is 1.7 × 10^{-8} M.
Figure S24. (a) Emission ($\lambda_{ex}: 490$ nm) spectral changes during the titration of the receptor 1 ($2.0 \times 10^{-5}$ M) with CN$^-$ in aqueous medium, inset: Normalized intensity between the minimum intensity and the maximum intensity. (b) A plot of ($I_{imin}/(I_{max}-I_{min})$) vs Log([CN$^-$]), the calculated detection limit of receptor is $8.7 \times 10^{-8}$ M.

Figure S25. (a) Emission ($\lambda_{ex}: 490$ nm) spectral changes during the titration of the receptor 1 ($2.0 \times 10^{-5}$ M) with SCN$^-$ in aqueous medium, inset: Normalized intensity between the minimum intensity and the maximum intensity. (b) A plot of ($I_{imin}/(I_{max}-I_{min})$) vs Log([SCN$^-$]), the calculated detection limit of receptor is $1.1 \times 10^{-8}$ M.
Figure S26. (a) Absorption spectral changes during the titration of the receptor 2 (2.0 × 10⁻⁵ M) with CN⁻ in aqueous solution, inset: Normalized absorbance between the minimum absorbance and the maximum absorbance. (b) A plot of (A-Aₘᵢₙ)/(Aₘₐₓ-Aₘᵢₙ) vs Log([CN⁻]), the calculated detection limit of receptor is 6.9 × 10⁻⁸ M.

Figure S27. (a) Emission (λₑₓ: 490 nm) spectral changes during the titration of the receptor 2 (2.0 × 10⁻⁵ M) with CN⁻ in aqueous medium, inset: Normalized intensity between the minimum intensity and the maximum intensity. (b) A plot of (I-Iₘᵢₙ)/(Iₘₐₓ-Iₘᵢₙ) vs Log([CN⁻]), the calculated detection limit of receptor is 7.9 × 10⁻⁸ M.
Figure S28. UV-vis absorption (a and b, respectively) and emission (λ<sub>ex</sub> = 490 nm) (c and d, respectively) spectral changes of 1 in MeCN upon addition of HClO<sub>4</sub>. The insets show the fit of the experimental absorbance and luminescence data to a 1:2 binding profile.

Figure S29. UV-vis absorption and emission (λ<sub>ex</sub>: 490 nm) spectral changes of 1 (a and b, respectively) in MeCN upon addition of different cations. The visual color changes upon addition of different cations are shown in the insets of Figure (a).
Figure S30. UV-vis absorption and emission ($\lambda_{ex}$: 490 nm) spectral changes of 2 (a and b, respectively) in MeCN upon addition of different cations. The visual color changes upon addition of different cations are shown in the insets of Figure (a).

Figure S31. UV-vis absorption (a and b) and photoluminescence ($\lambda_{ex}$: 490 nm) (b) spectral changes of 1 ($1.0 \times 10^{-5}$ M) in acetonitrile upon addition of Fe$^{2+}$ ($5 \times 10^{-3}$ M). The insets show the fit of the experimental absorbance and luminescence data to a 1:2 binding profile.
Figure S32. UV-vis absorption (a and b) and photoluminescence ($\lambda_{\text{ex}}$: 490 nm) (c and d) spectral changes of 1 (1.0×10^{-5} M) in acetonitrile upon addition of Zn$^{2+}$ (5×10^{-3} M). The insets show the fit of the experimental absorbance and luminescence data to a 1:2 binding profile.
**Figure S33.** UV-vis absorption (a) and photoluminescence (λex: 490 nm) (b) spectral changes of 2 (1.0×10⁻⁵ M) in acetonitrile upon addition of Cu²⁺ (5×10⁻³ M). The insets show the fit of the experimental absorbance and luminescence data to a 1:2 binding profile.

**Figure S34.** UV-vis absorption (a) and photoluminescence (λex: 490 nm) (b) spectral changes of 2 (1.0×10⁻⁵ M) in acetonitrile upon addition of Fe²⁺ (5×10⁻³ M). The insets show the fit of the experimental absorbance and luminescence data to a 1:2 binding profile.
REFERENCES

S1. D. D. Perrin and B. Dempsey, *Buffers for pH and Metal Ion Control*, Chapman and Hall, London, 1974.

S2. J. F. Ireland and P. A. Wyatt, Acid-Base Properties of Electronically Excited States of Organic Molecules. *Adv. Phys. Org. Chem.* **1976**, *12*, 131-159.

S3. H-J. Schneider, A. Yatsimirsky, Principles and methods in supramolecular chemistry; John Wiley & Sons: England (*2000*) p 142.

S4. Cui, Y.; Mo, H. J.; Chen, J. C.; Niu, Y. L.; Zhong, Y. R.; Zheng K. C.; Ye B. H., Anion-Selective Interaction and Colorimeter by an Optical Metalloreceptor Based on Ruthenium(II) 2,2-Biimidazole: Hydrogen Bonding and Proton Transfer. *Inorg. Chem.* **2007**, *46*, 6427–6436.

S5. Mo, H. J.; Niu, Y. L.; Zhang, M.; Qiao, Z. P.; Ye, B. H. Photophysical, Electrochemical and Anion Sensing Properties of Ru(II) Bipyridine Complexes with 2,2'-Biimidazole-like Ligand. *Dalton Trans.* **2011**, *40*, 8218-8225.

S6. Zheng, Z.-B.; Duan, Z.-M.; Ma Y.-Y.; Wang, K.- Z.; Highly Sensitive and Selective Difunctional Ruthenium(II) Complex-Based Chemosensor for Dihydrogen Phosphate Anion and Ferrous Cation. *Inorg. Chem.* **2013**, *52*, 2306-2316.