# Supporting Information

# A highly sensitive redox-active monolayer for “signal-on” optical detection of iron(II)

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**Materials and Methods:** Most of the metal salts were purchased from BDH Chemicals Ltd and used as received. $RuCl_3 \cdot 3H_2O$, 3-iodo-n-propyl-trimethoxysilane, 2,2'-bipyridine, 4,4'-dimethyl, 2,2'-bipyridine and ammonium hexafluorophosphate were purchased from Aldrich and used as received. $Ce(SO_4)_2 \cdot 4H_2O$ was purchased from BDH Chemicals Ltd and used as received. Anhydrous $FeCl_3$ and $FeCl_2$ were purchased from Merck and Aldrich respectively. Methanol and ethanol were purchased from Merck and was distilled over activated magnesium turnings and iodine before use. 30% aq. Ammonia, $H_2O_2$, dry n-pentane, toluene, dichloromethane and acetonitrile (All AR grade) were purchased from s. d. fine chemicals (India). Dichloromethane (DCM) was purified with $H_2SO_4$ and distilled under $N_2$ over $P_2O_5$, degassed and was stored over activated 4 Å molecular sieves in brown bottle. Deuterated solvents were purchased from Aldrich. Glass slides having thickness ~1.0-1.2 mm were purchased from Pearl India and single-crystal silicon [100] substrates were purchased from Beschichtungen (Silz, Germany). Indium tin oxide coated glass was purchased from Environ sales (India). Hydrothermal bombs (25mL & 50mL) were purchased from Prakash Scientific Works (India). Water used for the experiment was double distilled.

Si(100) and ITO coated glass were cleaned by sonication in hexane followed by acetone, then ethanol and dried under an $N_2$ stream. Soda-lime glass was cleaned by immersion in a "piranha" solution (7:3 v/v, $H_2SO_4$/30% $H_2O_2$) for 1 h. (*Caution: Piranha is an extremely dangerous oxidising agent and all protective measures must be adopted to prevent any harm*). Subsequently, this was rinsed with deionized water followed by RCA cleaning protocol: 1:5:1 (v/v) $NH_3 \cdot H_2O/H_2O$/30% $H_2O_2$ at room temperature for 45 min. The substrates were washed with ample amount of deionized water and were dried under an $N_2$ stream. All substrates were dried in an oven for 2 h at 130°C. The monolayer formation was carried out under an inert atmosphere using standard Schlenk/cannula techniques. 4'-Methyl-4-(2-pyridin-4-yl-vinyl)-[2,2']bipyridinyl and $Ru(bipyridine)_2Cl_2 \cdot 2H_2O$ were prepared according to published procedures[S1,S2] and characterized by $^1H$ NMR.

UV-Vis spectroscopy was carried out using a JASCO UV-Vis-NIR spectrophotometer (670D). Elemental analyses were performed on a GMbH VarioEL elemental analyzer. Mass spectra were recorded on THERMO Finnigan LCQ Advantage max ion trap mass spectrometer (MSAIF, CDRI, Lucknow, India). Atomic force microscopy (AFM) images were recorded using a Solver P47 (NTMDT) operated in the tapping mode. OTESP-type Si SPM probes were used with a resonance frequency of tip ~250 kHz and a tip radius of ~10 nm. Roughness data were extracted from 1000 nm × 1000 nm images. CHI-660D electrochemical analyzer was used to carry out electrochemical measurements. pH meter was calibrated before each measurements using standard buffer solution of pH 4 and pH 10. All $^1$H NMR spectra were recorded on Jeol JNMECX 400P spectrometer. All chemical shifts ($\delta$) are reported in ppm, and coupling constants ($J$) are in Hz. The $^1$H NMR chemical shifts are relative to tetramethylsilane; the resonances of the residual protons of the solvent were used as an internal standard for $^1$H. All measurements were carried out at 298 K, unless otherwise stated.

**Preparation of Precursor Complex:** The precursor complex of **1** were synthesized by the method as reported earlier[S3,S4]. The reaction of Ru(bipyridine)$_2$Cl$_2$.2H$_2$O (200 mg; 0.385 mmol) with 4'-methyl-4-(2-pyridin-4-yl-vinyl)-[2,2']bipyridinyl (126 mg; 0.46 mmol) under reflux in 50 mL ethanol-water (1:1, v/v) for 7h gives dark brown color solution this was concentrated to 10 mL under vacuum. The desired complex was precipitated by adding saturated aqueous solution of ammonium hexafluorophosphate [163 mg (1.0 mmol) in 3 mL] and filtered off. This was washed with an excess of water, then ether and purified by column chromatography using alumina (neutral, activity G-III) column and toluene-acetonitrile (80:20 v/v) as eluent. The first dark brown fraction was collected and dried under *vacuo*. Yield: 233 mg (62%). Anal. Found (%): C, 46.86; H, 3.19, Calc. (%) for $RuC_{38}H_{31}F_{12}N_7P_2$: C, 46.73; H, 3.20. $^1$H NMR ($CD_3CN$): $\delta$ 8.58 (3H, m), 8.50 (5H, d), 7.77 (4H, m), 7.71-6.87 (14H, m), 7.64 (1H, d; J = 16.4 Hz), 7.53 (1H, d, J = 16.4 Hz), 2.56 (3H, s). ES MS: m/z: 343.64 ($M^{2+}$-2PF$_6$). UV-vis ($CH_3CN$), $\lambda$, nm ($\varepsilon$, M$^{-1}$cm$^{-1}$): 456 (17831), 329 (18145), 285 (66397), 242 (25940).

**Preparation of Complex 1:** An excess of 3-iodo-n-propyl-1-trimethoxysilane (81 mg, 0.28 mmol) was added to a dry THF/acetonitrile (90:10 v/v) solution (20 mL) of precursor complex (55 mg, 0.056 mmol) under N$_2$ in a pressure vessel. The reaction mixture was stirred and heated at 90 °C for 48h. Subsequently, the volume was reduced to ~2 mL. The addition of dry pentane (15 mL) at 25 °C to reaction mixture resulted in the precipitation of the desired product. The solvent was decanted and the precipitate was washed with dry pentane up to 3 times then dried under vacuum to get the desired product (complex **1**). Yield: 60 mg (85%). Anal. Found (%): C, 41.83; H, 3.69, Calc. (%) for $RuC_{44}H_{46}F_{12}IN_7O_3P_2Si$: C, 41.71; H, 3.66. $^1$H NMR

(400 MHz, $CD_3CN$): δ 8.79–7.15 (26H, m; ArH and 2H, d; -CH=CH-), 4.45 (2H, t; -$CH_2$-), 3.53 (9H, s; -$OCH_3$), 2.59 (3H, s; -$CH_3$), 0.89 (2H, m; -$CH_2$-), 0.65 (2H, t; -$CH_2$-). UV/vis ($CH_3CN$), $\lambda$, nm ($\varepsilon$, $M^{-1}cm^{-1}$): 459 (21326), 335 (24731), 282 (90740), 239 (36439).

**Scheme S1.** Schematic representation for the preparation of complex **1**.

**Formation of Monolayer:** Under $N_2$, freshly cleaned quartz, glass, ITO and silicon substrates were loaded into a hydrothermal bomb equipped with home-made Teflon holder and immersed in dry acetonitrile/toluene (3:7 v/v) solutions (0.5 mM) of complex **1** and heated for 52h at 80 °C with the exclusion of light. The functionalized substrates were then rinsed with dichloromethane, acetonitrile and sonicated gently for 5 min each in acetonitrile and isopropanol. The samples were then wiped with a task wipe then dried under a stream of $N_2$. Finally, the samples were cleaned with $CO_2$ snow jet cleaning system and stored in the dark.

**Reversibility tests: alternating treatment of the sensors with Fe(II) and Ce(IV) in air.** The double-side coated **1**-based monolayers on glass were chemically activated with [$Ce(SO_4)_2.4H_2O$] (1.0 mM, in water containing 0.01 M $H_2SO_4$, 3 min) in air to yield the ruthenium(III) chromophore-based monolayer. The oxidized monolayer was fully reduced with $FeCl_2$ to yield Ru(II)-based monolayer. Several oxidation/reduction cycles were obtained by immersion of the functionalized glass substrates for 3 min in a 0.01 M solution of $H_2SO_4$ (10 mL) containing 1.0 mM [$Ce(SO_4)_2.4H_2O$], and 2 min in a $FeCl_2$ (1.0 ppm in $CH_2Cl_2$) solution (10 mL), respectively. The substrates were rinsed with dry $CH_3CN$, gently cleaned with task paper and dried at room temperature under a gentle stream of $N_2$ before recording the absorption spectrum. The experiment was repeated for eight Ru(II)/Ru(III) cycles (Figure 2).

**Preparation of $CH_2Cl_2$ samples with ppb/subppm-levels of $FeCl_2$.** A stock solution of 400 ppm of $FeCl_2$ in dry MeCN was made by dissolving 8 mg $FeCl_2$ in 20 mL dry MeCN, which was further diluted several times with $CH_2Cl_2$ to generate solutions containing 1, 0.5, 0.3, 0.2, 0.1, 0.05, 0.02, 0.01 and 0.005 ppm of $FeCl_2$ respectively. The sample preparation was carried out using silanized glassware.

**Sensing of subppm-levels of $FeCl_2$ in $CH_2Cl_2$.** Precautions were taken to exclude the presence of water throughout the experiment. The activated ruthenium(III)-based monolayers on glass substrates were tested in series of $CH_2Cl_2$ samples containing 1, 0.5, 0.3, 0.2, 0.1, 0.05, 0.02, 0.01 and 0.005 ppm of $FeCl_2$, respectively. In a particular set of experiments, the substrates were immersed in a $CH_2Cl_2$ solution containing 0.1 ppm of $FeCl_2$ for 2 min, rinsed with dry $CH_2Cl_2$ and carefully wiped with task paper before recording the UV-Vis spectra. Subsequently the monolayer was activated with $[Ce(SO_4)_2.4H_2O]$ (1.0 mM, in water containing 0.01 M $H_2SO_4$, 3 min), wiped with task paper and fully dry under $N_2$ flow. The full recovery of the system was confirmed by UV-Vis analyses. This procedure was repeated using same monolayers and $CH_2Cl_2$ samples containing 1, 0.5, 0.3, 0.2, 0.05, 0.02, 0.01 and 0.005 ppm of $FeCl_2$, respectively (Figure 3). In another set of experiment, the reduction of the **1**-based monolayers on glass (1 cm × 2.5 cm) with 0.01 ppm $FeCl_2$ was followed as a function of time and monitored *ex-situ* with UV/Vis spectrophotometer (Figures 3, inset).

**Selectivity test in organic and aqueous matrix.** The solutions of the metal salts (NaCl, KCl, $CaCl_2$, $MgCl_2$, $NiCl_2$, $ZnCl_2$, $CuCl_2$, $FeCl_3$, $RhCl_3$, $FeCl_2$) and solvents ($C_6H_6$, $CH_3CN$, $H_2O$) used for selectivity study were made by dissolving the corresponding salt in dry $CH_2Cl_2$, $CH_2Cl_2$/DMF (3:1 v/v) or deionized $H_2O$ ($1 \times !0^{-4}$ M each). The pH ($\approx$1) of the aqueous solutions of metal salts was adjusted using 32 % HCl. The **1**-based monolayer was immersed in the above solutions for 3 min each followed by washing in dry $CH_2Cl_2$ and drying under $N_2$ stream before recording UV-Vis spectra.

**Stability test of the 1-based monolayer.** **1**-based monolayer was subjected to thermal stress. The samples were placed inside a sealed glass pressure tube under air. The thermal stability was monitored by *ex-situ* UV-Vis measurements at 200 ± 5 $^{o}$C for varying time intervals (1, 3, 6, 10, 22, 29 and 49 h). The temporal stability was monitored by keeping the samples for >1h at various temperatures (i.e., 25, 80, 100, 120, 180, 200, and 230 °C). Before each temperature increase, the samples were allowed to attain room temperature, rinsed with $CH_3CN$, gently wiped with task paper and analyzed by UV-Vis spectrophotometry (Figure 5). After thermal stress experiment the sample was tested for sensing/resetting experiments for four cycles (Figure 5, inset).

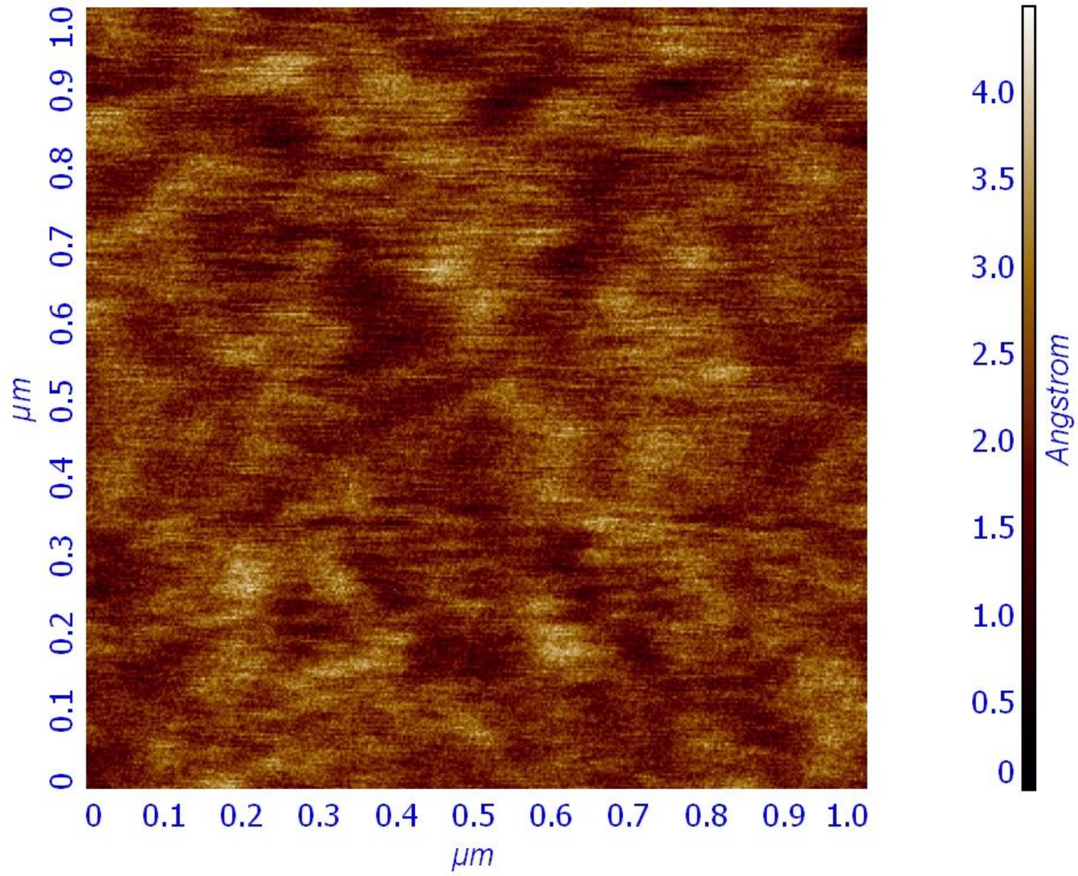

**Figure S1.** AFM image of **1**-based monolayer on Si(100) operated in tapping mode using a Si OTESP-type SPM probe with a resonance frequency of 346.4 kHz. Scan speed 1.6 Hz. No pinholes or other defects were observed, though there is some evidence of interaction between the films and the tip. Root-mean-square surface roughness (Rq) on Si = 0.097 nm for 1000 × 1000 nm scan area.

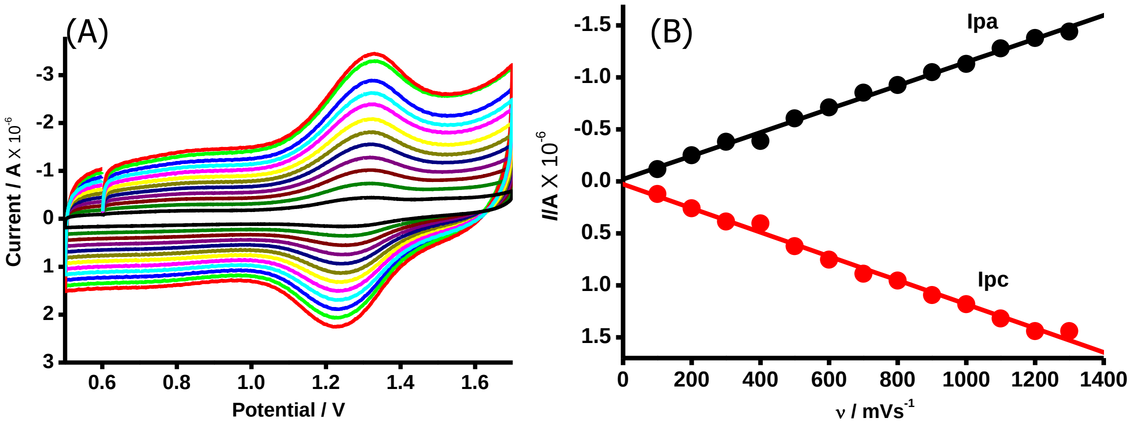

**Figure S2.** (A) Representative cyclic voltammetric responses at different scan rates of the **1**-based monolayer on ITO-coated glass, which operates as the working electrode. Pt wires were used as reference and counter electrodes. The electrochemical (EC) experiments were carried out at room temperature in dry $CH_3CN$ containing $^tBu_4NPF_6$ (20 mM) with a CHI660D potentiostat. The voltage scan rate was varied from 100 to 1300 $mVs^{-1}$. $E_{1/2}$ = 1.27 V *vs* Pt; 0.90 vs Fc/Fc$^+$, $\Delta E$ = 50 mV. Footprint calculated using area under the peak was 80 – 100 $Å^2$/molecule. (B) Linear correlation of the peak current $I_pa$ and $I_pc$ versus the scan rate ν for scan rates starting from 100 mV/s to 1300 mV/s, ($R^2 \approx 0.99$).

## References.

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