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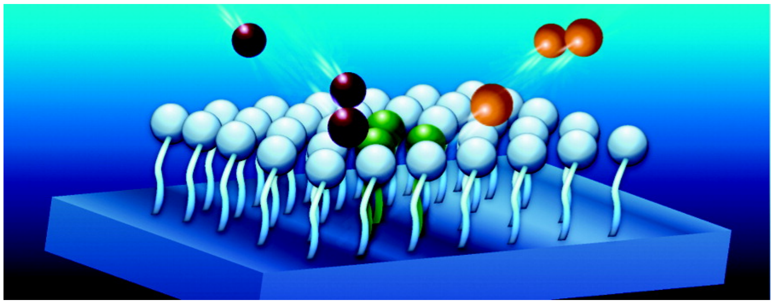
J. Am. Chem. Soc., **2007**, 129 (40), 12296-12303• DOI: 10.1021/ja074134p • Publication Date (Web): 19 September 2007



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ARTICLES

Monolayer-Based Selective Optical Recognition and Quantification of $FeCl_3$ *via* Electron Transfer

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Abstract: Reagentless optical recognition and parts-per-million (ppm) quantification of $FeCl_3$ in CH_3CN was demonstrated using a redox-active Os(II)-chromophore-based monolayer on glass. The Fe^{3+}-induced oxidation of the monolayer is fully reversible and can be monitored optically with a conventional UV/vis spectrophotometer (260−800 nm). The system can be reset with water within <1 min. Selectivity of the sensor toward $FeCl_3$ is not affected by the presence of representative alkali metals, alkaline earth metals, and other transition-metal salts. Sensing of Fe^{3+} and concurrent generation of Fe^{2+} can be also observed with the naked eye by adding 2,2′-bipyridyl (bipy) to the solution to generate $[Fe(bipy)_3]^{2+}$. Validation of the analytical performance characteristics of the sensor was performed including reversibility, reproducibility, stability, and the detection range (0.5−162 ppm of $FeCl_3$ in CH_3CN, 100−1000 ppm in water). The monolayer is sensitive and specifically responsive to its target ion. In addition, a blind test was conducted to probe the reproducibility and reproducibility variances of the system. The reaction of the monolayer with a CH_3CN solution containing 5 ppm of $FeCl_3$ follows pseudo first-order kinetics in the monolayer with $\Delta G^{\ddagger}_{298K} = 21.6 \pm 0.1$ kcal/mol, $\Delta H^{\ddagger} = 10.2 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger} = -38.3 \pm 4.9$ eu.

Introduction

Molecular recognition[1] with monolayer assemblies[2] is a vast and rapidly emerging area that offers a novel and powerful route to molecular-based nanoscale systems that might have various applications, including chemical sensors,[3−10] optical/electronic switches,[11−17] and memory elements.[18−20] In particular, optical detection and quantification of parts-per-million (ppm) levels of various chemicals, gases, and biologically relevant metal ions have recently gained much scientific interest, since their greatest advantage is that the organic sensing devices do not need to be directly wired with large-scale electronics.[7,8,21−27] For instance, the large design flexibility and stability of porphyrins and fullerenes has been exploited by Gulino, Fragalà, Schwartz, and others to assemble functional monolayers capable of detecting acids and gases, including NO_x, NH_3, and O_2.[21−25,28] In another recent example, Reinhoudt and co-workers showed that siloxane-based monolayers consisting of amino-capped functionalities operate as optical sensors for ppm-level detection of bivalent metal ions, including Pd, Ca, Zn, Cu, Co, and Pb.[4,26,27] Interestingly, most monolayer-based sensor systems are based on relatively weak but selective and reversible noncovalent host−guest interactions. Operation of electron-transfer based systems[7,8,29,30] differs from coordination and lock-

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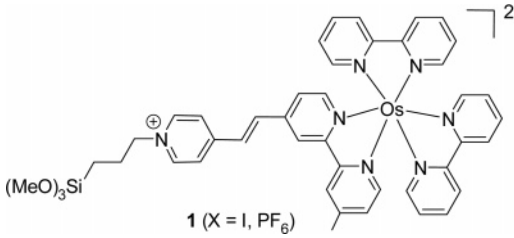
10.1021/ja074134p CCC: \$37.00

and-key principle-based sensors,[31] since the former offers selectivity based on the oxidizing/reducing ability of the analyte−monolayer couple.[1,6]

Direct and rapid quantitative monitoring of $Fe^{2+/3+}$ levels constitute important environmental[32−35] and biomedical objectives,[36] since effective monitoring is crucial for elucidating a wide variety of cell functions, including oxygen metabolism, electron-transfer processes, and the formation of RNA and DNA.[37−39] Direct detection of corrosion rates is another important challenge.[40,41] Recent state-of-the-art approaches adopted for the detection of $Fe^{2+/3+}$ are based on selective host−guest interactions either in solution or at the surface of polymer-based electrodes.[42−49] To the best of our knowledge, robust monolayer-based sensors for selective optical detection and quantification of ppm levels of Fe^{3+} in solution are still unknown.[10,27,42]

Metal coordination complexes such as the known chromophore **1**,[7,8,20] which contain bipyridyl-based ligands having low-lying π^* orbitals, are often intensely colored due to the presence of a characteristic metal-to-ligand charge-transfer (MLCT) band in the visible region of the absorption spectrum. Since the MLCT band is highly dependent on the formal metal oxidation state, such structurally well-defined complexes can be used as molecular (nonlinear) optical switches/memory elements and sensors.[7,8,15−17,20] The physicochemical properties of osmium and ruthenium bipyridyl complexes as well as structurally related complexes have been studied extensively in solution,[11,50−66] in polymer/sol−gel and metal oxide mesoporous matrices,[48,67−73] and as molecular building blocks for the formation of mono- and multilayer assemblies.[15−17,74−84]



1 (X = I, PF_6)

We present here the direct optical detection and quantification of ppm levels of Fe^{3+} in organic and aqueous solutions using a previously reported **1**-based monolayer on glass.[7,8,20] The robust **1**-based monolayer can be utilized to detect $FeCl_3$ in the presence of representative alkali metals, alkaline earth metals, and transition-metal salts. In addition, $FeCl_3$ can be detected and quantified in the presence of $FeCl_2$ and structurally well-defined Fe^{3+} complexes. The straightforward $FeCl_3$ detection system is based on a nondestructive surface-to-solution one-electron transfer process. This redox process changes the formal oxidation state of the Os^{2+}-based monolayer, which can be read out optically with a commercially available UV/vis spectrophotometer in the transmission mode (260−800 nm). The monolayer sensor can be reset by simply washing with water for <1 min. Monitoring of the Fe^{3+} induced one-electron oxidation of the immobilized Os^{2+} complexes (**1**) can be achieved by either *ex situ* or *in situ* follow-up UV/vis measurements, whereas the

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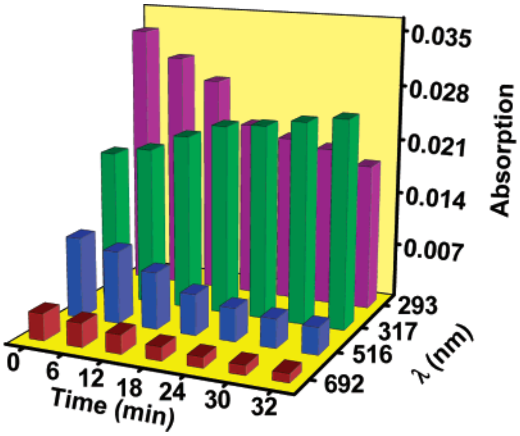

Figure 1. Representative absorption spectral changes of the **1**-based monolayer as a function of immersion time observed during a sensing experiment with 2.0 ppm of $FeCl_3$ in dry CH_3CN (~94% oxidation, 32 min).

formed Fe^{2+} can be trapped by 2,2′-bipyridyl (bipy). The resulting $[Fe(bipy)_3]^{2+}$ complex can be detected and quantified optically in solution. In addition, the amount of Fe^{3+} in water can be quantified as well.

Results and Discussion

Chromophore **1** forms covalently bound siloxane-based monolayers on glass, silicon, and indium-tin-oxide (ITO)-coated glass substrates at evaluated temperatures from dry solutions under N_2.[7,8,20] These reported monolayers are thermally robust in air and have been characterized by aqueous contact angle measurements, ellipsometery, UV/vis spectroscopy, atomic force microscopy (AFM), cyclic voltammetry, and synchrotron X-ray reflectivity (XRR).[7,8,20] In addition, DFT calculations indicated that chromophore **1** has a bent structure as a result of the pyridinium moiety.[8] The UV/vis properties of the **1**-based monolayer on transparent substrates such as glass or quartz are similar to the optical characteristics of complex **1** in solution and can be used to read out the formal metal oxidation state.[7,8,20]

The three characteristic absorption bands at $\lambda = 692$, 516, and 293 nm of the **1**-based monolayer on glass exhibit very strong hypochromic shifts upon exposure to a dry CH_3CN solution containing only ppm levels of $FeCl_3$ within ~30 min, whereas no optical changes are observed upon exposure of the monolayer to the solvent for prolonged periods. In addition, a new band at $\lambda = 317$ nm appears, which can be assigned to the ligand-to-metal charge transfer (LMCT) band. These gradually occurring optical changes are indicative of a change in the formal metal oxidation from Os^{2+} to Os^{3+} and can be monitored *ex situ* with a standard UV/vis spectrophotometer in the transmission mode.[8,20] The changes in optical properties of the monolayer-based sensor with time after exposure to a CH_3CN solution containing only 2 ppm of $FeCl_3$ at room temperature are shown in Figure 1. Saturation of the sensor is observed after 32 min (for ~94% oxidation) by *ex situ* UV/vis measurements, since no further changes are observed after prolonged exposure to the solution with $FeCl_3$. Importantly, the gradual optical changes allow quantification of the amount of $FeCl_3$. The oxidation process can be interrupted at any given time, resulting in the formation of mixed monolayers, which is a topic of much current interest.[78,85−87] To the best of our knowledge, well-defined monolayers consisting of metal-based chromophores having a formally different oxidation state are rare.[7,8,20]

$[Os(bipy)_3]^{2+}$ is known to reduce Fe^{3+} in solution with concurrent oxidation of the Os^{2+} center.[50,66,88] Indeed, complex **1** undergoes one-electron transfer with Fe^{3+} in solution. For instance, treating a dry CH_3CN solution of complex **1** for 30 min with 1.5 equiv of $FeCl_3$ resulted in an optical response similar to the absorption changes of the **1**-based monolayer. The large optical changes upon oxidation of complex **1** in solution

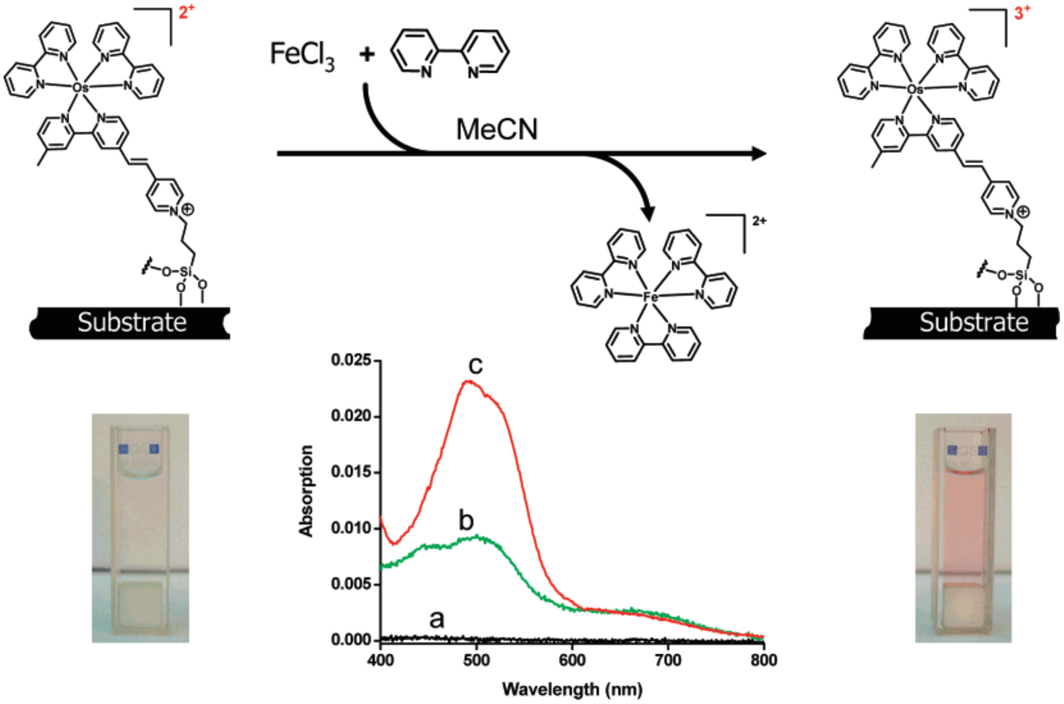

Figure 2. *In situ* absorption spectral change after treating the **1**-based monolayer on glass with 5 ppm of $FeCl_3$ in dry CH_3CN and subsequently trapping the formed Fe^{2+} with excess bipy to afford $[Fe(bipy)_3]^{2+}$: (a) baseline (black), (b) **1**-based monolayer in dry CH_3CN with bipy (green), (c) *in situ* generation of $[Fe(bpy)_3]^{2+}$ (red) (a, b, c in figure).

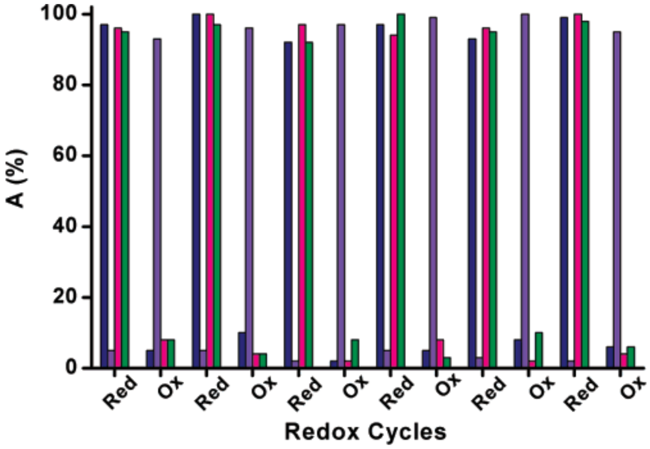

Figure 3. Optical changes as a result of FeCl$_3$ in CH$_3$CN, and water-induced oxidation and reduction, respectively, of the **1**-based monolayer with $\lambda = 293$ nm (blue), 317 nm (violet), 516 nm (pink), and 692 nm (olive). Absorption (relative response, %) vs the number of sensing/recovery cycles. Detection of Fe^{3+} was carried out with a dry CH$_3$CN solution of FeCl$_3$ (162 ppm, 2 min), whereas regeneration of the sensor was carried out in water (<1 min).

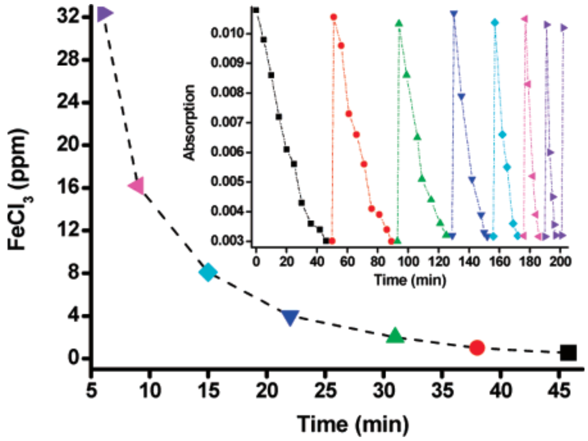

Figure 4. Saturation of sensor vs time for the detection of FeCl$_3$ content in dry CH$_3$CN. The inset shows *ex situ* UV/vis followup experiments for the ^{1}MLCT band at $\lambda = 516$ nm in dry CH$_3$CN containing 0.5 (black), 1.0 (red), 2.0 (green), 4.0 (blue), 8.1 (light blue), 16.2 (pink), and 32.4 ppm (purple) of FeCl$_3$, respectively, followed by the recovery of the Os^{2+}-based monolayers with H$_2$O (<1 min). The lines serve as guides for the eyes.

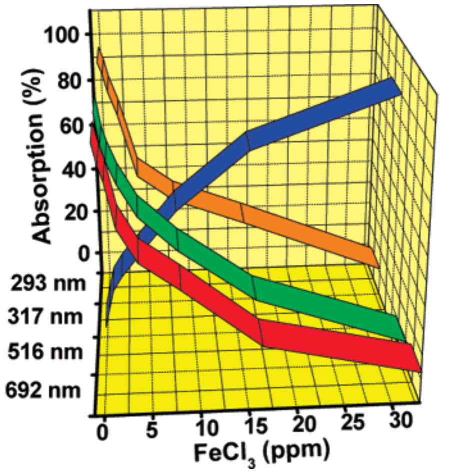

Figure 5. Graphical representation of absorption intensity changes at $\lambda =$ 692 nm (red), 516 nm (green), 317 nm (blue), and 293 nm (orange) after a 5 min of exposure to FeCl$_3$ (range: 0.5−32.4 ppm) in dry CH$_3$CN.

or as a surface-confined monolayer are typical in the generation of [Os(bipy)$_3$]$^{3+}$-type complexes.[7] Generation of Fe^{2+} by the immobilized complex **1** is unambiguous. Addition of excess bipy (~5 equiv) to a CH$_3$CN solution containing 5 ppm of FeCl$_3$ resulted in the formation of [Fe(bipy)$_3$]$^{2+}$ upon reaction of the analyte with the **1**-based sensor (Figure 2). The UV/vis spectrum of the product solution shows the characteristic absorption intensities of [Fe(bipy)$_3$]$^{2+}$ at $\lambda = 520$, 359, and 297 nm after a 25-min exposure time. No [Fe(bipy)$_3$]$^{2+}$ formation was observed by UV/vis measurements in the absence of the **1**-based monolayer. FeCl$_2$ and related Fe^{2+} compounds are known to react readily with 2,2′-bipyridyl to afford [Fe(bipy)$_3$]$^{2+}$.[48] The intense MLCT band with $\epsilon_{520\text{nm}} \approx 11.2 \times 10^3$ indicated that $\sim 3.8 \times 10^{-9}$ mol of [Fe(bpy)$_3$]$^{2+}$ was generated.[61] Thus, the **1**-based monolayer mediates the formation of nanomole quantities of Fe^{2+}, which is accessible in solution for complexation with bipy. The intense and distinct color change of the solution from light yellow to pink allows even naked-eye detection of the formed [Fe(bpy)$_3$]$^{2+}$.

The monolayer performance is demonstrated for six alternating cycles by exposing the system to a solution of CH$_3$CN containing 162 ppm of FeCl$_3$ for 2 min followed by rinsing with H$_2$O for <1 min (Figure 3). Os^{3+} and Ru^{3+} complexes are known to undergo reduction in solution with H$_2$O.[7,8,51,63,64,89] Recently we reported that the chemical oxidation of the **1**-based monolayer with a Ce(IV) salt results in the formation of an Os^{3+} sensor platform capable of oxidizing ppm levels of H$_2$O while concurrently regenerating the Os^{2+} system.[7] The FeCl$_3$ sensing system also exhibits excellent reversibility, since no hysteresis was observed during sensing and the subsequent recovery cycles. For both the Os$^{2+/3+}$ oxidation states, the shape and peak position of the absorption maxima remain unchanged. The observed on/off ratios for the Os$^{2+/3+}$ monolayer and the large spectral window (260−800 nm)[8] allow accurate ppm-level detection of Fe^{3+} (on/off ratios: $\lambda = 293$ nm, 2:1; $\lambda = 317$ nm, 2:3; $\lambda = 516$ nm, 3:1; $\lambda = 692$ nm, 4:1). Because of the monolayer's stability and nondestructive optical readout, data can be averaged over repeated measurements. Furthermore, one can choose to integrate over the entire absorption window (400−800 nm) instead of monitoring only a specific wavelength (*vide infra*).

The **1**-based monolayer was exposed to a series of CH$_3$CN solutions containing ppm levels of FeCl$_3$ ranging from 0.5 to 32.4 ppm in order to gain insight into the operation range and response time as a function of analyte concentration. The optical changes were recorded *ex situ* as a function of time in order to determine the response properties (Figure 4). Saturation of the sensor depends on the FeCl$_3$ concentration and takes 6−46 min. Importantly, saturation of the monolayer to determine the FeCl$_3$ content in a given sample is not necessary. The large optical absorbance differences between the Os$^{2+/3+}$ couple allow accurate determination of the FeCl$_3$ content within a range of

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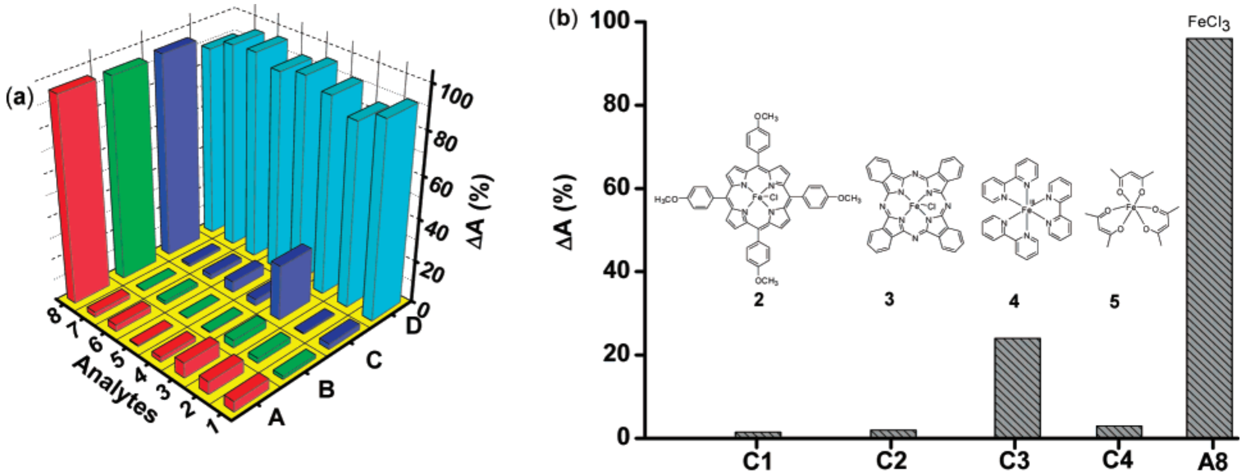

Figure 6. (a) Graphical representation of the data shown in Table 1. Relative *ex situ* UV/vis absorption intensity changes at $\lambda = 516$ nm after treating the monolayer with 5×10^{-4} M (CH_3CN or CH_3CN/DMF = 1:1 v/v) solutions of transition metals, alkali metals, alkaline metals, and Fe^{3+} complexes (**2**−**5**) in the presence of $FeCl_3$ (102 ppm) for 5 min. For matrices containing different metal salts, the same solvents were used as for the solutions containing only one analyte. (b) Reactivity of Fe^{3+} complexes (**2**−**5**) and $FeCl_3$ with the **1**-based monolayer (see also: C1−4 and A8 in Figure 6a and Table 1).

Table 1. Summary of Analytes and Matrices, and the Corresponding Absorption Intensity Changes (ΔA) at $\lambda = 516$ nm in % of the **1**-Based Monolayer

	A (ΔA %)	**B** (ΔA %)	**C** (ΔA %)	**D** (ΔA %)
1	$HgCl_2$[a] (4.9)	KCl[b] (1.5)	**2**[a] (2.5)	$FeCl_3$, $FeCl_2$ (92)
2	$ZnCl_2$[a] (6.0)	NaCl[b] (2.4)	**3**[a] (0.5)	$FeCl_3$, $CuCl_2$ (86)
3	$CuCl_2$[a] (7.0)	LiCl[b] (3.6)	**4**[a] (26)	$FeCl_3$, $ZnCl_2$ (92)
4	$CoCl_2$[a] (2.2)	CsCl[b] (0.5)	**5**[a] (3.0)	$FeCl_3$, $HgCl_2$ (96)
5	$FeCl_2$[a] (0.5)	$MgCl_2$[b] (0.2)	$RhCl_3$[b] (5.0)	$FeCl_3$, $MnCl_2$ (93)
6	$MnCl_2$[b] (3.0)	$CaCl_2$[b] (1.5)	$CrCl_3$[a] (2.0)	$FeCl_3$, $NiCl_2$ (97)
7	$NiCl_2$[b] (2.3)	$BaCl_2$[b] (0.2)	$AlCl_3$[a] (1.3)	$FeCl_3$, $CaCl_2$ (96)
8	$FeCl_3$[a] (96)	$FeCl_3$, KCl, NaCl, LiCl, CsCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, (95)	$FeCl_3$, **2**, **3**, **5**, $RhCl_3$, $CrCl_3$, $AlCl_3$ (96)	$FeCl_3$, $FeCl_2$, $CuCl_2$, $ZnCl_2$, $HgCl_2$, $MnCl_2$, $NiCl_2$, $CaCl_2$ (90)

[a] CH_3CN. [b] CH_3CN/DMF (1:1 v/v).

0.5−32.4 ppm in CH_3CN within only a 5-min exposure time, as shown in Figure 5. A blind test was performed for four samples containing a given amount of $FeCl_3$ in CH_3CN with a monolayer calibrated with a series of five $FeCl_3$-containing CH_3CN solutions (range: 0−32.4 ppm). The monolayer-derived $FeCl_3$ concentrations listed here between brackets are in excellent correlation with the expected values in ppm: 3.0 (4.4 ± 0.8), 4.5 (5.7 ± 0.9), 15 (14.0 ± 1.3), 30.0 (27.6 ± 1.8)

Generation of practical monolayer-based sensing devices requires many stringent criteria. For instance, the sensor response for a given analyte often needs to be consistent in the presence of a matrix containing many other compounds. The optical properties of the **1**-based monolayer do not change upon exposure to a series of solutions (CH_3CN or CH_3CN/DMF, 1:1 v/v) containing one or a mixture of representative alkali metals (Li^+, Na^+, K^+, and Cs^+), alkaline earth metals (Mg^{2+}, Ca^{2+}, and Ba^{2+}), other transition metal cations (Hg^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Rh^{3+}, and Cr^{3+}) or well-defined Fe^{3+} complexes such as iron(III) 5,10,15,20-tetrakis-(4-methoxyphenyl)porphyrin chloride (**2**), iron(III) phthalocyanine chloride (**3**), and iron(III) tris(acetylacetonate) (**5**). Exposing the **1**-based monolayer to solutions of the above mentioned salts in the presence of $FeCl_3$ results in optical responses nearly identical to the responses observed for solutions containing only $FeCl_3$ (Figure 6 and Table 1).

It is expected that compounds that can undergo redox chemistry with the $Os^{2+/3+}$ couple of compound **1** will interfere with the $FeCl_3$ chemistry. Interestingly, we only observed a relatively weak optical reponse (∼25% decrease in absorption intensity) upon exposing the **1**-based monolayer to a solution containing 480 ppm of $[Fe(bipy)_3](PF_6)_3$ (**4**), whereas this complex undergoes readily electron transfer in solution with Os^{2+} tripyridyl complexes. The redox processes at the monolayer-solution interface and in solution may follow distinctly different mechanistic pathways. It is known that surface-confined organic compounds often show different reaction patterns and physicochemical properties than when in solution.[90−92] This suggests that functional monolayers may be developed that can selectively detect redox-active analytes.

The Os^{2+}/Fe^{3+} redox reaction at the surface−solution interface can also be conveniently monitored *in situ* by variable temperature UV/vis spectrometry. For example, Figure 7 shows the results of the reaction of the **1**-based monolayer with a CH_3CN solution containing 5 ppm of $FeCl_3$ at four different temperatures within the range 298−328 K. The reaction follows pseudo first-order kinetics in the **1**-based monolayer with $\Delta G^{\ddagger}_{298K} = 21.6 \pm 0.1$ kcal/mol, $\Delta H^{\ddagger} = 10.2 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger} = -38.3 \pm 4.9$ eu. Nearly identical activation parameters were observed upon reaction of the **1**-based monolayer on glass with 5 ppm of $NOBF_4$ in dry CH_3CN: $\Delta G^{\ddagger}_{298K} = 21.5 \pm 0.7$ kcal/mol, $\Delta H^{\ddagger} = 9.5 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -40.6 \pm 1.1$ eu.[8] This may suggest that the nature of the oxidant ($FeCl_3$ or $NOBF_4$) is not playing a significant role prior to and during the rate-determining step.

Coordinatively saturated complexes such as **1** are relatively inert to ligand substitution reactions;[50,66,88] therefore, electron transfer must occur *via* an outer-sphere mechanism with possible participation of the nitrogen-based ligands.[93−95] Ligand dissociation can be excluded because this would have resulted in the (irreversible) formation of $[Fe(bipy)_3]^{2+}$, which has not been observed by UV/vis spectroscopy. The overall process at the

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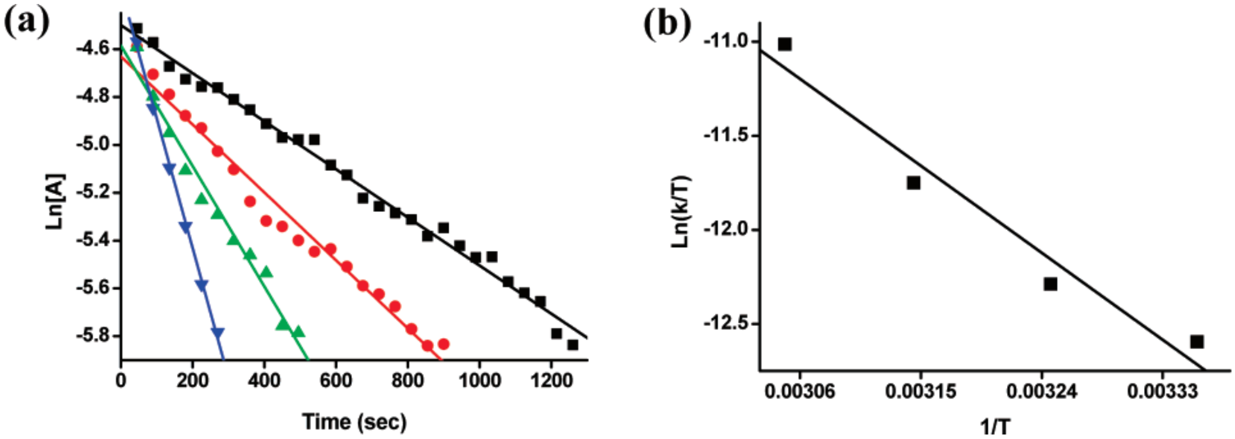

Figure 7. (a) *In situ* recorded absorption changes of the ^{1}MLCT band at $\lambda = 516$ nm at 298 K, $k = 1.01 \times 10^{-3}$ s^{-1}, $R^2 = 0.990$ (black); 308 K, $k = 1.42 \times 10^{-3}$ s^{-1}, $R^2 = 0.978$ (red); 318 K, $k = 2.51 \times 10^{-3}$ s^{-1}, $R^2 = 0.976$ (green); and 328 K, $k = 5.41 \times 10^{-3}$ s^{-1}, $R^2 = 0.996$ (blue). The solid lines show the linear fits that indicate a pseudo first-order process in the **1**-based monolayer. (b) Eyring plot for the reaction of 5 ppm of $FeCl_3$ in dry CH_3CN with the **1**-based monolayer with $R^2 = 0.956$.

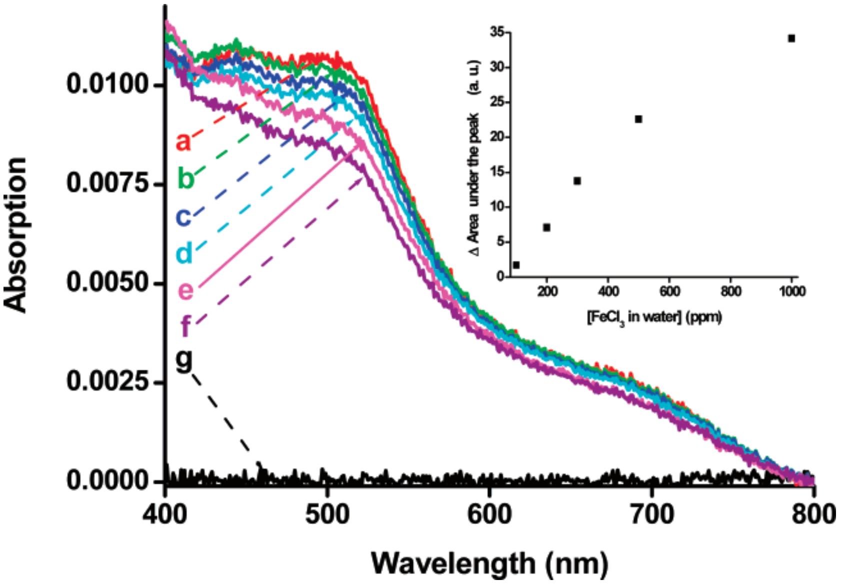

Figure 8. Relative intensity change of the visible region absorption bands (400−800 nm) observed for the detection of Fe^{3+} in water after a 5-min exposure: (a) 0 ppm, (b) 100 ppm, (c) 200 ppm, (d) 300 ppm, (e) 500 ppm, (f) 1000 ppm, and (g) baseline. The inset shows the change of the peak area in the visible region vs Fe^{3+} concentration after 5 min. $FeCl_3$ hydrolyzes to form insoluble hydroxide species upon aging.

surface−solution interface most likely involves four major steps: (I) approach/diffusion of the analyte to or into the monolayer structure, (II) relatively rapid one-electron transfer (e.g., $k_{298K} > 10^{-5}$ M^{-1} s^{-1} for electron transfer between Os^{2+} and Fe^{3+} trisbipyridyl complexes in solution),[51,66] (III) ion pairing to balance the positive charge of the Os^{3+} complexes, (IV) diffusion/release of the Fe^{2+} species, which can be trapped by bipy. No solvent effect was observed when 5 ppm of $FeCl_3$ were reacted with the **1**-based monolayer in CH_3CN ($k = 1.04 \times 10^{-3}$ s^{-1}) and in CH_2Cl_2 ($k = 0.96 \times 10^{-3}$ s^{-1}). The entropy decrease is in agreement with ion pairing/trapping of anions from the solution by the monolayer to balance the extra charge upon oxidation of the metal center by Fe^{3+}.

The reaction of the immobilized complex **1** and $FeCl_3$ is not limited to dry organic solvents, although the generated Os^{3+} system is known to be reduced back to Os^{2+} with ppm levels of H_2O in THF at room temperature.[7] Nevertheless, the monolayer was also exposed to a series of freshly prepared aqueous solutions containing 100−1000 ppm levels of Fe^{3+}. Note that at higher concentrations insoluble iron hydroxides are formed. Likewise, these hydroxides are also formed upon aging of the solution. However, the optical changes of the immobilized complex (**1**) on glass are clearly dependent on the Fe^{3+} concentration (Figure 8). For example, 1000 ppm of Fe^{3+} reduces the absorption intensity of the MLCT band at $\lambda = 516$ nm by ∼40%, whereas 100 ppm of Fe^{3+} induces a ∼6% decrease after 5 min. However, there was no effect after prolonged exposure times. The difference in peak area in the entire visible region (400−800 nm) was plotted vs the Fe^{3+} concentration in H_2O (Figure 8, inset). The saturation time ranges from 30 s for 1000 ppm to 5 min for 100 ppm of Fe^{3+} in water.

Stimuli-responsive organic monolayers are relatively rare, and there is often a fine balance among function, material stability, and processability. Regardless of the many practical/engineering challenges, siloxane-based assemblies have been used for the fabrication of first-generation electro-optical modulations,[96,97]

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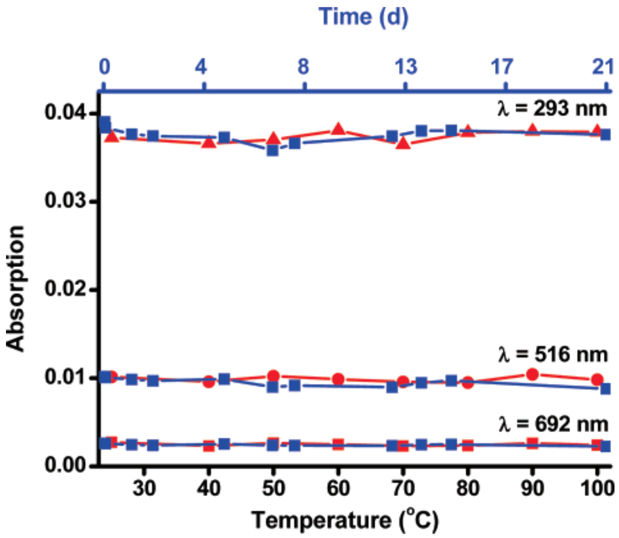

Figure 9. *Ex situ* UV/vis monitoring of the stability of the **1**-based monolayer on glass: (i) thermal treatment in water for 8 h (red), the sample was maintained at the indicated temperatures for 1 h and (ii) light sensitivity test at room temperature for 3 weeks (blue) (ambient light).

sensors,[7,8,21−27] waveguides,[98,99] organic light emitting diodes (OLEDs),[100−102] and organic field-effect transistors (OFETs).[103,104] Thermal stability is a key requirement for monolayer-based device development. The **1**-based covalently bound monolayers on glass are thermally stable up to 200 °C for 48 h[7] and remain fully functional even after 10 months of storage in air at room temperature with exclusion of light. *Ex situ* UV/vis monitoring of the temporal stability by gradually ramping up the temperature from 25 to 100 °C in water does not affect the optical properties of the system. UV/vis spectroscopy also revealed that the **1**-based monolayer is also stable in air under ambient light for at least 21 days (Figure 9).

Summary and Conclusions

In summary, exposure of an Os^{2+}-chromophore-based monolayer on glass to solvents containing 0.5−162 ppm of Fe^{3+} in CH_3CN and 100−1000 ppm of Fe^{3+} in water results in one-electron transfer from the covalently immobilized metal complexes to the inorganic analyte with concurrent optical changes. The sensor performance, including reversibility, response time, reproducibility, selectivity, stability, on/off ratio, and the ppm-level detection limit were investigated. In addition, the mechanism underlying the surface-confined redox chemistry was explored. The Fe^{3+}-induced oxidation of the molecular sensor generates Fe^{2+}, which can be detected within 5 min and monitored optically in the transmission mode with an of-the-self UV/vis spectrophotometer (260−800 nm). Bipy present in the reaction solution resulted in the formation of $[Fe(bipy)_3]^{2+}$, which is a rare example of monolayer-mediated solution chemistry.[105−110] Importantly, the redox-based Fe^{3+} nondestructive detection and quantification system can be easily reset with water within <1 min. The high stability of the **1**-based monolayer makes it a suitable candidate for device integration. The mode of operation involving reversible metal oxidation combined with optical reading is a largely unexplored route toward designing monolayer-based sensing devices.[7,8,20,21,23−25,29,111]

Experimental Section

Materials and Methods. The siloxane-based monolayer of chromophore **1** was synthesized and characterized as described earlier.[7,8,20] Iron(III) phthalocyanine chloride, iron(III) tetrakis-(4-methoxyphenyl)porphyrin chloride, $CrCl_3{\cdot}THF$, $MgCl_2$, and octadecyltrichlorosilane were purchased from Aldrich. Iron(III) acetylacetonate and $AlCl_3$ were purchased from Fluka. Most metal salts were purchased from BDH or Merck. CsCl was purchased from Fisher Scientific Company. All chemicals were used as received. Solvents (AR grade) were purchased from Bio-Lab (Jerusalem), Frutarom (Haifa), or Mallinckrodt Baker (Phillipsburg, NJ). Pentane was dried and purified using an M. Braun (Garching, Germany) solvent purification system. Anhydrous acetonitrile and *N*,*N*-dimethylformamide (sealed bottles) were purchased from Sigma-Aldrich and were stored in an M. Braun glovebox. Water was double distilled. All materials were stored in a glovebox with O_2 and H_2O levels < 2 ppm. All glassware was silanized to avoid the adsorption of water. The glassware was immersed in 1 mM solutions of octadecyltrichlorosilane in dry pentane for 2 h at room temperature in a N_2-filled glovebox. Subsequently, the glassware was rinsed with dry pentane and dried in an oven (120 °C for 2 h). UV/vis spectra were recorded on a Cary 100 spectrophotometer in transmission mode (200−800 nm) with the functionalized glass substrate fixed with a Teflon holder having a 1.5 cm × 0.75 cm window. An identical glass substrate without monolayer was used to compensate for the background absorption. All measurements were performed at room temperature (∼22 °C) unless stated otherwise. The reported values for the variable temperature experiments have an error of ±0.2 °C.

Preparation of CH_3CN/DMF Solutions with ppm-Levels of Analytes. A stock solution of 2.0 mM of $FeCl_3$ in dry CH_3CN was prepared by dissolving 16.2 mg of $FeCl_3$ in 50 mL of dry CH_3CN, which was further diluted to generate CH_3CN solutions containing 0.5−32.4 ppm of $FeCl_3$, respectively. Stock solutions of other analytes (chlorides of alkali metals, alkaline earth metals and transition metals, and iron(III) complexes) were prepared by dissolving the compounds in CH_3CN or CH_3CN/DMF (1:1 v/v). The sample preparation was carried out using silanized glassware in a N_2-filled glovebox with O_2 and H_2O levels < 2 ppm.

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Optical Sensing of ppm-Levels of FeCl$_3$ in CH$_3$CN. The **1**-based monolayer on glass was treated with a series of CH$_3$CN solutions containing 0.5−32.4 ppm of FeCl$_3$, respectively. The reaction of Fe^{3+} by the **1**-based monolayer on glass (1 cm × 2.5 cm) was monitored *ex situ* by UV/vis spectrophotometry in the transmission mode. In a particular set of experiments, monolayers on glass substrates were immersed in dry CH$_3$CN solutions containing 32.4, 16.2, 8.1, 4.0, 2.0, 1.0, and 0.5 ppm of FeCl$_3$ for 5 min. Next, the samples were rinsed with dry CH$_3$CN and carefully wiped with task paper in a N$_2$-filled glovebox before recording the UV/vis spectra. The **1**-based monolayer was reset to its original state by immersion of the sample in water for <1 min. Full recovery of the formal metal oxidation state was confirmed by UV/vis measurements. Saturation of the sensor was monitored by *ex situ* UV/vis measurements as a function of time.

Optical Sensing of ppm-Levels of FeCl$_3$ in Water. The **1**-based monolayers on glass substrates were exposed to air in a series of freshly prepared water samples containing 1000, 500, 300, 200, and 100 ppm of Fe^{3+}, respectively. Oxidation of the **1**-based monolayers on glass (1 cm × 2.5 cm) was *ex situ* monitored by UV/vis spectroscopy. The FeCl$_3$ solution in water was freshly prepared since the monolayer response is not linear at higher concentrations due to the formation of insoluble iron hydroxides. Likewise, these hydroxides are also formed upon aging of the solution.

Reversibility Test: Alternate Treatment of the Monolayer-Based Sensor with FeCl$_3$ and Water in Air. Alternate sensing/resetting cycles were obtained by immersion of glass substrates functionalized on both sides with a **1**-based monolayer for 2 min in dry CH$_3$CN solution of FeCl$_3$ (162 ppm) and water (<1 min), respectively. Next, the substrate was then rinsed with dry CH$_3$CN, gently cleaned with task paper, and then dried at room temperature under a gentle stream of N$_2$ before the absorption spectrum was recorded. The experiment was repeated for six alternating cycles of FeCl$_3$ exposure, and recovery was done with water.

***In situ* Detection of Fe^{2+} Formation in CH$_3$CN.** A glass substrate was placed in a quartz cuvette containing a solution of 5 ppm of FeCl$_3$ in 2 mL of dry CH$_3$CN. An excess of 2,2′-bipyridyl (∼5 equiv) was added to the reference and the monolayer-containing cuvette. Subsequently, the glass substrate from the sample cuvette was replaced by the **1**-based monolayer on glass and maintained for 30 min. Finally, the glass monolayer was again replaced by the same glass substrate, and the increase in absorbance at $\lambda = 528$ nm was recorded. In the sample cuvette solution the change in color from yellow to pink can be seen by the naked eye.

Variable Temperature UV/vis Follow-up Experiments. The **1**-based monolayer on glass was placed in a quartz cuvette containing 2 mL of dry CH$_3$CN. A glass substrate in dry CH$_3$CN was used as a reference. Subsequently, 20 μL of a freshly prepared FeCl$_3$ stock solution (2.5 mM; dry CH$_3$CN) was added to both cuvettes. The decrease in absorbance at $\lambda = 512$ nm was monitored as a function of time at 298, 308, 318, and 328 K until the sensor was saturated. Scan rate = 799.8 nm/min, cycle time = 45 s, data interval = 1.333 nm, average time = 0.100 s.

Acknowledgment. This research was supported by the Helen and Martin Kimmel Center for Molecular Design, NATO (SfP 981964), Henrich Gutwirth Fund for Research, YEDA, BMBF and the MJRG. M.E.vd.B. is the incumbent of the Dewey David Stone and Harry Levine Career Development Chair. T.G. wishes to thank the Sixth Framework Program (FP6) of the EU for an incoming Marie Curie fellowship.

JA074134P