Selective NO_x optical sensing with surface-confined osmium polypyridyl complexes

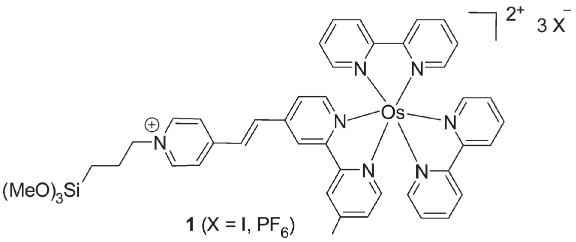
Antonino Gulino,*[ab] Tarkeshwar Gupta,[b] Placido G. Mineo[a] and Milko E. van der Boom*[b]

Received (in Cambridge, UK) 26th July 2007, Accepted 6th September 2007
First published as an Advance Article on the web 17th September 2007
DOI: 10.1039/b711400a

Optical detection of parts-per-million (ppm) levels of NO_2 (1–10 ppm) and NO_x (800–2550 ppm) by a structurally well-defined monolayer consisting of osmium polypyridyl complexes on glass substrates has been demonstrated.

Chemical reactivity, ligand coordination, and redox behavior of molecular monolayers are interesting phenomena because such films may be used for forming new patterned surfaces, memory devices, sensors, or switches.[1–6] Although many fundamental issues need to be addressed before device-quality functional monolayers become widely available, there is increasing scientific and technological interest in hybrid nanomaterials consisting of covalently bound organic compounds or metal complexes on inorganic surfaces.[6–14]

Formation of monolayer-based sensors, capable of selective detection and quantification of various chemical and biological substances at low concentrations is a challenging task.[2–5,15–29] For practical applications, the material must be robust, but react or interact selectively with a given analyte. For instance, covalently bound monolayers of osmium polypyridyl complexes (**1**) on float glass substrates are suitable interfaces for the optical detection of parts-per-million levels (ppm) of H_2O and NO^+ in organic solvents.[17,18,†] The high stability of **1**-based monolayers may also make them suitable candidates for detecting highly corrosive analytes such as NO_2 and NO_x in the gas phase. Monolayer chemistry/sensing with gaseous compounds is becoming increasingly important.[19–28] For instance, NO_x monitoring is strongly governed by environmental factors, since it can cause various environmental problems such as smog and acid rain.



1 (X = I, PF_6)

We demonstrate here the direct, reagentless optical detection of NO_2 and NO_x by a previously reported **1**-based monolayer on glass substrates.[14,17,18] The UV/Vis optical absorbance measurements of the molecular monolayer substrates exhibit the characteristic singlet and triplet states of the metal-to-ligand charge transfer (MLCT) bands at λ_{max} = 512 and 692 nm, respectively. The intensity of these distinct absorption bands can be used to monitor the formal metal oxidation state,[14,17,18] which can be controlled by NO_2 or NO_x. The sensor is selective because no reaction has been observed with air and a variety of other gases.

Exposure of the surface-confined osmium(II) polypyridyl complexes (**1**) to NO_2 in a N_2 stream results in one-electron oxidation of the metal center, as judged by UV/Vis spectroscopy in the transmission mode. Subsequently, reacting the functionalized substrates with H_2O results in regeneration of the optical properties of the system. This is exemplified by a series of reactions of the covalently bound **1**-based monolayer with a gentle stream of dry N_2 containing 1–10 ppm of NO_2, resulting in a decrease of the MLCT bands within the optical range of 350–800 nm. This behavior is typical of the formation of osmium(III) polypyridyl complexes.[14,17,18] The monolayer response time is dependent on the NO_2 concentration (*vide infra*).

In a representative *in-situ* continuous gas-flow experiment, the functionalized glass substrate (0.8 cm × 2.5 cm) is placed in a cuvette and exposed to a stream of N_2 containing only 1 ppm of NO_2. This results in relatively small but clearly observable optical changes ($\sim$20%), which reach a plateau after $\sim$12 min. No further decrease in the absorption intensity occurs upon prolonged NO_2 exposure. Accurate determination of the absorption intensity as a function of time is possible by integrating the entire absorption window. Subsequent treatment of the monolayer with a H_2O-saturated stream of N_2 for $\sim$1½ min results in complete recovery of the initial absorption intensities. The monolayer can be reused after drying under a stream of dry N_2 for 5 min. A more pronounced band variation is evident upon exposure of the monolayer to 5 ppm of NO_2 in N_2. All absorption band intensities decrease to 50% with respect to their saturated values within $\sim$22 min. Saturation of the monolayer is reached after $\sim$53 min (Fig. 1A). For the detection and quantification of an analyte it is not desirable to saturate a sensor. For instance, a pronounced decrease in absorption intensity is already evident after only 4 min (36% with respect to their saturated values), which can be used as the response time of the sensor for this concentration of NO_2. A similar optical behavior and a somewhat higher band intensity decrease rate have been observed upon monolayer exposure to a mixture of 10 ppm of NO_2 in dry N_2 (Fig. 1A). Apparently, the observed concentration dependent response may make it possible to quantify the amount of NO_2. Interestingly, several exposure/recovery cycles with alternating amounts of NO_2 (1, 5 and 10 ppm) in N_2 have been performed with no significant variation in the monolayer performance.

---

[a] *Dipartimento di Scienze Chimiche, Università di Catania, 95125, Catania, Italy. E-mail: agulino@dipchi.unict.it*
[b] *Department of Organic Chemistry, The Weizmann Institute of Science, 76100, Rehovot, Israel. E-mail: milko.vanderboom@weizmann.ac.il*

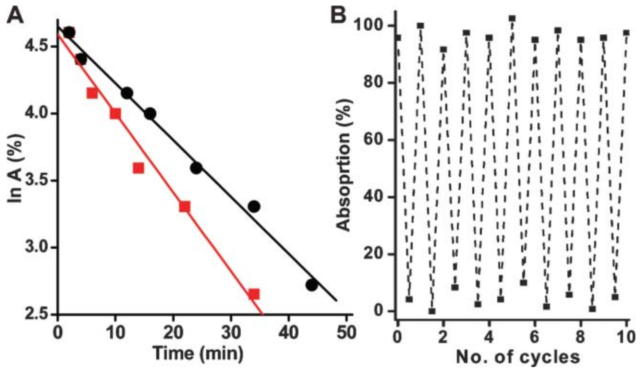


Fig. 1 (A) Intensity decrease of the optical absorbance band at λ = 512 nm of the **1**-based monolayer *vs.* time upon exposure to a gentle stream of 5 ppm (black line, ●; R^2 = 0.99), and 10 ppm (red line, ■; R^2 = 0.98) of NO_2 in N_2. (B) Chemical modulation of the optical absorbance band at λ = 512 nm by iterative exposure of the **1**-based monolayer to a stream of 5 ppm of NO_2 in N_2 for 53 min and to a H_2O-saturated N_2 stream for ~1½ min.

The optical monolayer responses, ΔA, exhibit low variances and are independent of the NO_2 exposure environment. As shown in Fig. 1B, the monolayer's performance/stability was demonstrated for 10 redox cycles. The monolayer is stable under the reaction conditions, as evident from optical absorption spectra. In fact, the entire system is remarkably stable: (i) no hysteresis was observed; the shape and peak position of the absorption maxima remain identical for both osmium oxidation states. (ii) No significant drift; a slow change in the output signal, independent of the input, has been observed. (iii) Almost no variations between the above-mentioned *in-situ* continuous gas-flow and *in-situ* static experiments with 5 ppm of NO_2 in dry N_2 were observed. (iv) In addition, no light-induced variation of the cuvette-containing monolayer was observed during solar lamp (60 W, ~15 cm distance) irradiation for 1 min with 5 ppm of NO_2 in dry N_2 inside the UV/Vis spectrophotometer. Water plays a key role in regenerating the osmium(II) setup.[17,18] The oxidized system is stable for prolonged periods of time under dry N_2. Recovery experiments by exposing the monolayer to the air resulted in a sluggish regeneration of the osmium(II) system with $t_{½} \approx 3$ h, which is more than two orders of magnitude slower than regeneration by exposure to a H_2O-saturated N_2 stream.

In addition to the above gas-flow experiments, using a calibrated N_2 cylinder containing ppm levels of NO_2, we also tested the sensor's behavior and stability toward NO_x in air. NO_x was generated by reacting nitric acid with Cu powder in air, and was trapped using Schlenk techniques.[30] This brown-colored gas mixture may also include other nitrogen oxide-based compounds, and reflects the possibility of environmental monitoring of NO_x. Injection of 2550 ppm of NO_x in air into a cuvette containing the **1**-based monolayer resulted in rapid oxidation (~10 s) of the immobilized metal complexes, as judged by UV/Vis analysis. Remarkably, no degradation of the monolayer's performance was observed for 10 redox cycles under these harsh reaction conditions (Fig. 2). Oxidation of the covalently bound osmium(II) complexes must involve trapping of newly generated anions (*e.g.*, NO_x^-) to balance the higher metal's oxidation state. Relatively small optical changes resulting from anion exchange may be masked due to the rather broad absorption signals.

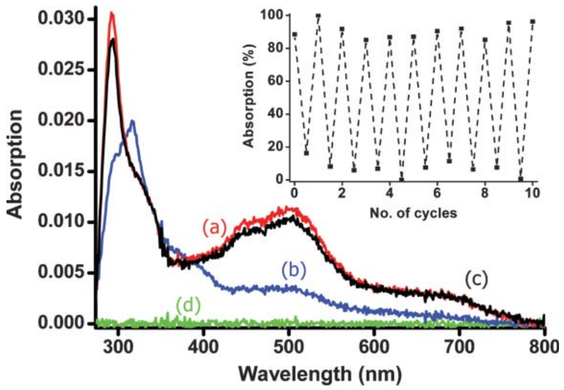


Fig. 2 Representative UV/Vis spectra of the **1**-based monolayer during an *ex-situ* sensing and recovery experiment with NO_x and water: (a) The red line represents the absorption spectrum of the monolayer prior to reacting with NO_x. (b) The blue spectrum was observed after 10 s of monolayer exposure to 2550 ppm of NO_x in air. (c) The black spectrum was observed after recovering the sensor with water (<1 min). (d) Baseline (green). The inset shows *in-situ* optical sensing and regeneration of the ^{1}MLCT band of the **1**-based monolayer at λ = 512 nm.

The output signal (A) of the **1**-based monolayer is inversely proportional to the value of the measured property [C] up to 2550 ppm upon stepwise increasing the NO_x concentration in air with 1 min intervals. The output signal does not clip and is saturated at higher NO_x concentrations for a 1 min exposure time (Fig. 3). The response time and the linear correlation of the gain (=A/[C]) are important characteristics and indicate the potential device performance.

Sensors should exhibit some sort of selectivity in order to have practical applications. Selectivity may be based on host–guest interactions, chemical reactivity, ligand coordination, *etc.*[1,2] Here, the introduced gas sensor exhibits selectivity based on redox properties. Indeed, the monolayer displays high selectivity for NO_x since only minor changes were observed by *in-situ* UV/Vis spectroscopy upon exposure to ~1 atm of pure CO, CO_2, H_2, N_2, O_2, N_2O, air, CH_4 and $CH_2{=}CH_2$ for at least 5 min as shown in Fig. 4. In addition, the monolayer is stable in concentrated HCl (36%, v/v) for 5 min, and in air for at least 6 months.

In summary, the device's performance and characteristics, including selectivity, gain, drift, stability, reversibility and range

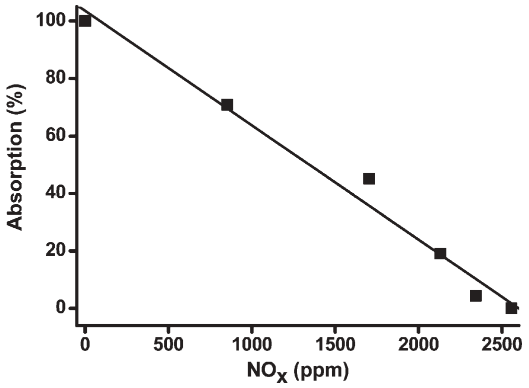


Fig. 3 UV/Vis absorption changes of the **1**-based monolayer at λ = 512 nm upon stepwise increasing the NO_x concentration from 0 to 2550 ppm with 1 min intervals in air (R^2 = 0.980).

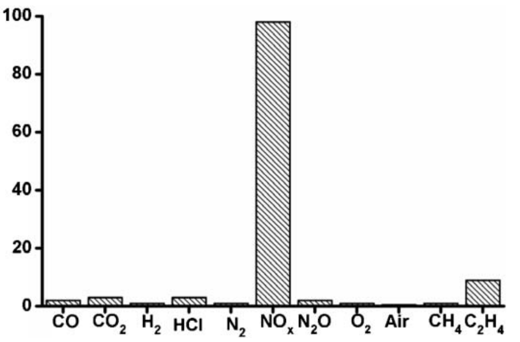


Fig. 4 Representative *in-situ* absorption intensity changes, ΔA, at λ = 512 nm after exposure of the **1**-based monolayer to various gases (~1 atm, at least 5 min) and HCl (36%, v/v; 5 min).

were explored. The **1**-based monolayer interface on float glass substrates is suitable for the selective optical detection of ppm-levels of NO_2 in N_2, and NO_x in air. The gas-triggered optical responses by NO_2 are independent of the flow rate. The redox chemistry is fully reversible and is straightforward to control because water can be used to reset the system within 1 min. The reactivity of the system with H_2O is a trade-off, because at high humidity levels the NO_2 detection limit may be affected. Nevertheless, the sensor is remarkably selective, since no reaction has been observed with air and with a variety of other gases. The well-defined molecular monolayer is a rare example of an optical sensor platform for highly toxic and corrosive gases. A good correlation for the gain within a large range (0–2550 ppm) was observed for NO_x. The full-scale range may be extended by using even shorter exposure times and/or different concentrations. The chemistry of organic interfaces can be rather complex because immobilized neighboring reactive sites can form a 2D network, which may respond differently to external triggers than in solution. In addition, structural inhomogeneities may make certain compounds less accessible to an incoming substrate/analyte, which can be observed optically.[20] However, such effects were not observed here. The monolayer structure and function are (photo)chemically and thermally robust (>200 °C),[17] making the monolayer a suitable candidate for device integration.

This research was supported by the Helen and Martin Kimmel Center for Molecular Design, NATO (SfP 981964), YEDA, and the Ministero Istruzione Università e Ricerca (MIUR, Roma; PRIN 2005 and FIRB 2003), BMBF and the MJRG. M. E. vd.B. is the incumbent of the Dewey David Stone and Harry Levine Career Development Chair. T. G. thanks the FP6 program for an incoming Marie Curie fellowship.

Notes and references

† Compound **1** and its monolayer were prepared as reported previously.[14] Robust siloxane-based monolayers are formed by covalent assembly of **1** from a dry CH_3CN–toluene (1 : 1 v/v) solution on glass substrates. Subsequently, the functionalized substrates were rinsed thoroughly and sonicated with CH_3CN and 2-propanol for 6 min to remove possible physisorbed material. UV/Vis measurements were performed using UV/Vis-1601 Shimadzu, Varian Cary 50 and 100 spectrophotometers. Cycles of 50 UV/Vis scans in the 350–800 nm range (scan frequency = 120 s, scan rate = 3.75 nm s^{-1}) were performed on the **1**-based monolayers during *in-situ* continuous leaking of 1–10 ppm of NO_2 in a dry N_2 gas stream (total flow rate = 100 sccm). Flow rates were controlled within ±2 sccm using MKS flow controllers and a MKS 147 Multi gas Controller. Controlled atmosphere measurements were performed by allowing the gas mixture to flow in a cuvette sealed with a Suba-seal septum equipped with two needles for gas in- and outlet. Recovery experiments were performed using a stream of H_2O-saturated N_2, followed by a flow of dry N_2 for 5 min. H_2O-saturated N_2 was prepared by guiding the gas through a H_2O-containing reservoir. Experimental uncertainty in the UV/Vis spectra is ±0.5 nm. Experiments with NO_x were performed using a sealable UV/Vis cuvette outfitted with a Teflon sample holder. **CAUTION**: NO_x and NO_2 are extremely toxic and highly corrosive gases.

1 L. Basabe-Desmonts, R. S. Zimmerman, D. N. Reinhoudt and M. Crego-Calama, *Springer Ser. Chem. Sens. Biosens.*, 2005, **3**, 169.
2 S. Flink, F. C. J. M. van Veggel and D. N. Reinhoudt, *Adv. Mater.*, 2000, **12**, 1315.
3 J. Kappler, U. Weimar and W. Goepel, *Adv. Gas Sens.*, 2003, 55.
4 R. M. Crooks and A. J. Ricco, *Acc. Chem. Res.*, 1998, **31**, 219.
5 D. C. Tully and J. M. J. Fréchet, *Chem. Commun.*, 2001, 1229.
6 S. Zhang, C. M. Cardona and L. Echegoyen, *Chem. Commun.*, 2006, 4461.
7 A. Facchetti, E. Annoni, L. Beverina, M. Morone, P. Zhu, T. J. Marks and G. A. Pagani, *Nat. Mater.*, 2004, **3**, 910.
8 Z. Liu, A. A. Yasseri, J. S. Lindsey and D. F. Bocian, *Science*, 2003, **302**, 1543.
9 J. Cui, A. Wang, N. L. Edleman, J. Ni, P. Lee, N. R. Armstrong and T. J. Marks, *Adv. Mater.*, 2001, **13**, 1476.
10 S. Sortino, S. Di Bella, S. Conoci, S. Petralia, M. Tomasulo, E. J. Pacsial and F. M. Raymo, *Adv. Mater.*, 2005, **17**, 1390.
11 H. Dacres and R. Narayanaswamy, *Sens. Actuators, B*, 2005, **107**, 14.
12 M. Altman, A. D. Shukla, T. Zubkov, G. Evmenenko, P. Dutta and M. E. van der Boom, *J. Am. Chem. Soc.*, 2006, **128**, 7374.
13 J. F. Fernández-Sánchez, T. Nezel, R. Steiger and U. E. Spichiger-Keller, *Sens. Actuators, B*, 2006, **113**, 630.
14 T. Gupta, M. Altman, A. D. Shukla, D. Freeman, G. Leitus and M. E. van der Boom, *Chem. Mater.*, 2006, **18**, 1379.
15 B. Lei, B. Li, H. Zhang, L. Zhang and W. Li, *J. Phys. Chem. C*, 2007, **111**, 11291.
16 A. J. Moore, L. M. Goldenberg, M. R. Bryce, M. C. Petty, A. P. Monkman, C. Marenco, J. Yarwood, M. J. Joyce and S. N. Port, *Adv. Mater.*, 1998, **10**, 395.
17 T. Gupta and M. E. van der Boom, *J. Am. Chem. Soc.*, 2006, **128**, 8400.
18 T. Gupta, R. Cohen, G. Evmenenko, P. Dutta and M. E. van der Boom, *J. Phys. Chem. C*, 2007, **111**, 4655.
19 M. Dubey, S. L. Bernasek and J. Schwartz, *J. Am. Chem. Soc.*, 2007, **129**, 6980.
20 A. Gulino, S. Giuffrida, P. Mineo, M. Purrazzo, E. Scamporrino, G. Ventimiglia, M. E. van der Boom and I. Fragalà, *J. Phys. Chem. B*, 2006, **110**, 16781.
21 A. Gulino, S. Bazzano, G. G. Condorelli, S. Giuffrida, P. Mineo, C. Satriano, E. Scamporrino, G. Ventimiglia, D. Vitalini and I. Fragalà, *Chem. Mater.*, 2005, **17**, 1079.
22 T. Xu, M. P. Zach, Z. L. Xiao, D. Rosenmann, U. Welp, W. K. Kwok and G. W. Crabtree, *Appl. Phys. Lett.*, 2005, **86**, 203104/1.
23 G. Ashkenasy, A. Ivanisevic, R. Cohen, C. E. Felder, D. Cahen, A. B. Ellis and A. Shanzer, *J. Am. Chem. Soc.*, 2000, **122**, 1116.
24 A. Generosi, V. R. Albertini, G. Rossi, G. Pennesi and R. Caminiti, *J. Phys. Chem. B*, 2003, **107**, 575.
25 J.-M. Barbe, G. Canard, S. Brandès and R. Guilard, *Chem.–Eur. J.*, 2007, **13**, 2118.
26 B. W.-K. Chu and V. W.-W. Yam, *Langmuir*, 2006, **22**, 7437.
27 G. J. Ashwell, G. A. N. Paxton, A. J. Whittam, W. D. Tyrrel, M. Berry and H. Zhou, *J. Mater. Chem.*, 2002, **12**, 1631.
28 S. Capone, S. Mongelli, R. Rella, P. Siciliano and L. Valli, *Langmuir*, 1999, **15**, 1748.
29 A. Gulino, P. Mineo, E. Scamporrino, D. Vitalini and I. Fragalà, *Chem. Mater.*, 2006, **18**, 2404.
30 A. F. Holleman and E. Wiberg, *Inorganic Chemistry*, Academic Press, San Diego, CA, 2001.