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A reversible resistivity-based nitric oxide sensor†

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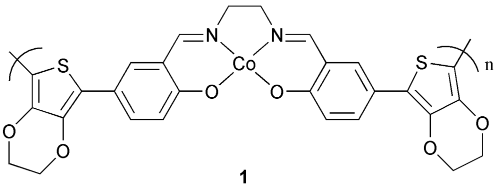
A sensor for nitric oxide is reported that uses a novel redox matching mechanism to induce a resistance change upon binding this important ligand to cobalt.

Nitric oxide (NO) serves as an intercellular signalling agent in a diverse array of living systems.[1] This recognition has stimulated considerable interest in its detection.[2] In particular there has been considerable interest in developing new fluorescence methods which exhibit an irreversible spectroscopic change in response to NO.[3] For many applications it is desirable to detect the concentration of nitric oxide in real time. For example, an increased nitric oxide concentration is associated with up-regulation of the immune system[4] and hence by continuously monitoring nitric oxide in the exhalate of an immune compromised person it may be possible to detect early stage respiratory infections.

As part of our program directed at developing sensors using conducting polymers as a gain medium[5] we have recently turned our attention toward the detection of NO. In this effort we have focused on resistance-based detection schemes. Our choice is based in part on the fact that this type of sensor can be very simple and have low power consumption. For example, using a conducting polymer a sensor can consist simply of two electrodes (preferably microelectrodes), which are interconnected with the sensory polymer. Devices can be inexpensive enough so as to be disposable and have minimal external hardware requirements. In fact all of the necessary electronics for high precision resistance measurements (ppm resolution) can be placed on a single chip. We further considered that the most useful devices would be those that displayed a rapid reversible response that could therefore be used to monitor a NO concentration that varies with time.

To produce a real-time nitric oxide sensor we considered that it must exhibit specificity and an easily detectable signal that responds to changes in its concentration. Coordinatively unsaturated paramagnetic transition metal complexes are ideal candidates for recognizing (binding) nitric oxide, which has one unpaired electron in an antibonding orbital. To produce a resistance change in response to a metal-nitric oxide binding event we utilized a system where the conductivity intimately involves the transition metal center. We previously demonstrated that metal centers contribute optimally to the electronic transport in conducting organic polymers when the redox activity of the metal center is coincident with that of an organic conducting polymer in its low resistance state.[6,7] When this redox-matching condition is met the metal essentially provides additional electroactive pathways for transporting charge throughout the material. Hence, ligand binding events that produce changes in its redox potential can enhance or decrease the conductivity depending upon whether this process produces a better or worse match between the transition metal and the organic conducting polymer. The test this effect for the detection of NO we made use of a redox-matched cobalt salen polymer **1**, which we have previously studied.[7] In this system the $Co^{2+/3+}$ couple is closely, but not perfectly, matched to the redox potential of the organic polymeric backbone.

To perform the experiments we utilized the procedure of Ford and coworkers to purify nitric oxide from a cylinder.[8] Infrared spectroscopy (1 atm NO in a 10 cm pathlength gas cell) was used to determine that the other nitrogen oxides had been completely removed. The purified NO was collected in an acetonitrile solution ([NO] ≈ mM) and its relative concentration was determined using cyclic voltammetry ($E° = 0.867$ V *vs*. Fc/Fc^+, 0.1 M $TBAPF_6$).



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All of the electrochemical experiments were performed in acetonitrile with 0.1 M $TBAPF_6$ electrolyte. As shown in Fig. 1 polymer **1** displays two closely spaced peaks in its cyclic voltammogram. The peak centered at approximately −0.1 V corresponds to the $Co^{2+/3+}$ couple and the peak at 0.05 V is assigned to the organic portion of the polymer. This assignment was previously confirmed by the fact that exposure to pyridine shifts the cobalt centered waves to less positive potentials while leaving the organic centered redox processes untouched.[6] As shown in Fig. 1 exposure to NO shifts the $Co^{2+/3+}$ couple to more positive potentials and effectively creates a better redox match with the organic centered electroactivity. The film rapidly returns to its original state upon placing it in fresh NO-free electrolyte. The observed shift of the $Co^{2+/3+}$ wave to positive potential is consistent with the NO binding to the cobalt center. The highest energy electron of this nominally square planar species is in the dz^2 orbital and bonding of this unpaired electron with the NO radical thereby gives a complex with an overall higher oxidation potential. It appears that upon oxidation the complex remains intact as a reduction wave assigned to NO-free cobalt center is not observed in the presence of NO.

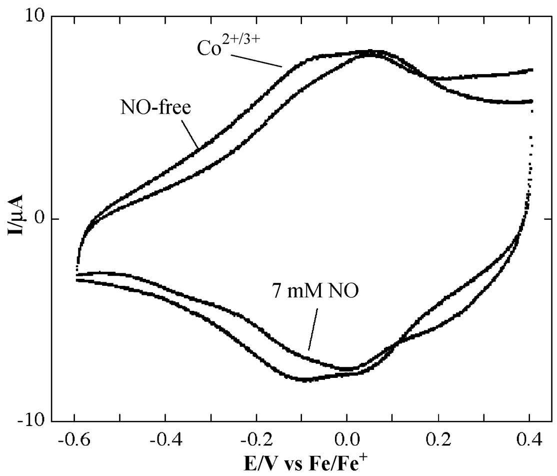

Fig. 1 Cyclic voltammetry of **1** in the absence and presence of nitric oxide. Note that the $Co^{2+/3+}$ wave shifts from its initial position at about −0.1 V to being indistinguishable with the organic centered activity at 0.05 V in the presence of 7 mM NO.

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This indicates that both the Co^{2+} and the oxidized Co^{3+} centers have strong binding affinities to NO.

Consistent with our redox matching model the improved overlap between the cobalt and the organic ligand's electroactivity enhances the materials conductivity. Fig. 2 shows measurements of the relative conductivity of thin films deposited on an array of interdigitated microelectrodes. These devices are effectively electrochemical transistors with the applied electrochemical potential functioning as the gate voltage and the current flowing between the source and drain electrodes is directly proportional to the conductivity.[9] We have previously found polymer **1** to display a peak conductivity of 40 S cm^{-1}. As can be seen in Fig. 2 exposure of a microelectrochemical transistor to a 7 mM NO solution produces approximately a 30% increase in conductivity. The sensor displays a highly reversible response and as shown in Fig. 2b the conductivity returns to normal after 5 electrochemical cycles (100 mV sec^{-1}) in NO-free electrolyte. As a result the NO binding to the cobalt center is highly reversible.

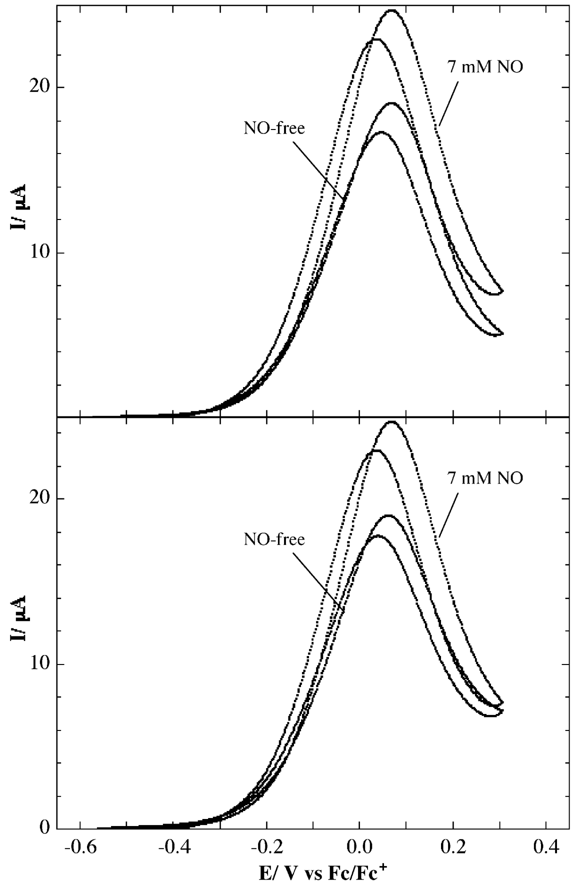

Fig. 2 Drain current profile (conductivity) of a microelectrochemical transistor base upon polymer **1** in the absence and presence of NO. The potential offset between microelectrodes was 40 mV and a sweep rate of 10 mV s^{-1} was used.

Polymer **1** has been found to be very well behaved in aqueous systems and we previously have shown that it also functions as a highly effective catalyst for oxygen reduction at more negative potentials.[10] Interesting in both aqueous and organic media we have found that the conductivity of polymer **1** is insensitive to oxygen concentration. As a result, this material or closely related polymers have excellent prospects to function as selective reversible NO sensors in aerobic aqueous environments. A resistance-based method such as shown here is not only for use in monitoring of bulk NO concentrations, but should also allow for microelectrode sensors to be produced that can be used to map out signals used in intercellular signalling.

Notes and references

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