

RSC Advances

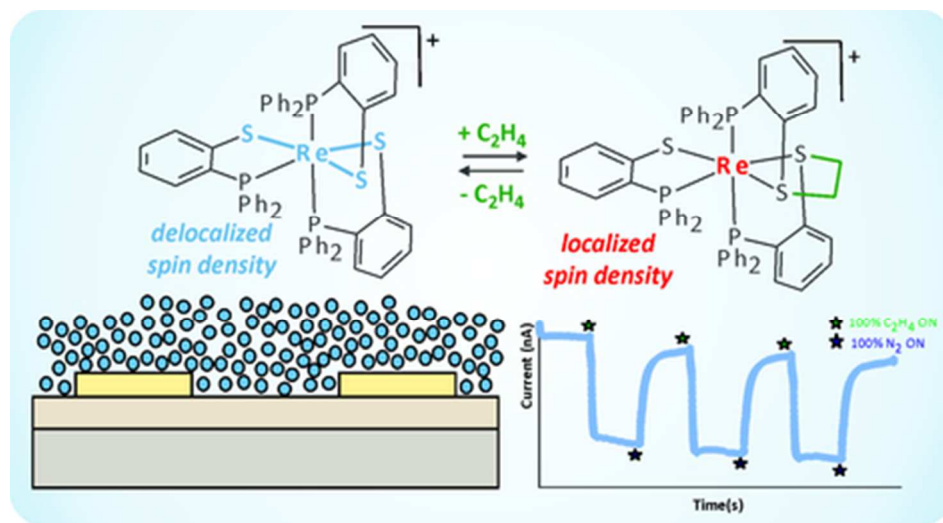


This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



A highly selective chemiresistive ethylene sensor based on reversible and selective ligand-centered substrate binding to a metal-stabilized thiyl radical.
39x21mm (300 x 300 DPI)

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Chemiresistive Metal-Stabilized Thiyl Radical Films as Highly Selective Ethylene Sensors

Rajat Chauhan, Monica Moreno, Douglas M. Banda, Francis P. Zamborini*, and Craig A. Grapperhaus*

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

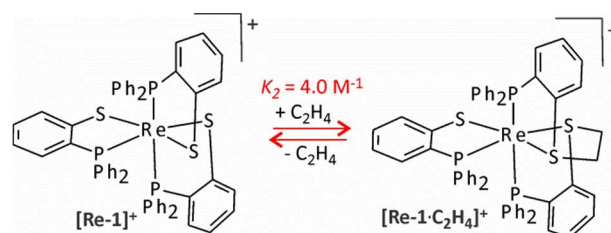
DOI: 10.1039/b000000x

A highly selective chemiresistive ethylene sensor based on reversible and selective ligand-centered substrate binding to a metal-stabilized thiyl radical has been developed. The solid-state device efficiently differentiates between ethylene and other alkene analytes. The sensor is prepared by simple dropcast deposition of the complex as a film across a microgap gold electrode.

Naturally evolved ethylene gas is responsible for the large-scale spoilage of agricultural products due its role as a plant hormone involved in such processes as fruit ripening, germination, and leaf abscission.^{1,2} During transportation/storage, ethylene levels as low as 10 ppb can cause product loss.³ As such, there is a need for simple and portable gas-phase ethylene detectors to complement traditional ethylene detection methods that require laboratory analysis of collected air samples by gas chromatography^{4,6} or photoacoustic spectroscopy.⁷

Recent advances in ethylene detection include a reversible chemiresistor comprised of Pt complexes and Au nanoparticles with ppb detection limits, but with poor selectivity due to the nature of the interaction of the substrate with the Pt metal.⁸ The direct coordination of ethylene and other small molecules including alkenes at the metal-center precludes a differential response for ethylene. Similar selectivity issues were observed for metal-oxide based resistors⁹⁻¹³ and metal-based photoluminescence^{14,15} and colorimetric¹⁶ detectors. To overcome the selectivity problem, herein we report a chemiresistive ethylene sensor based the ligand-centered addition of ethylene to the metal-stabilized thiyl radical complex $[\text{Re-1}]^+$ (Scheme 1) which has been previously reported to display 1) kinetic selectivity for ethylene binding over other alkenes, alkynes, and dienes;^{17,18} 2) inertness towards H_2 , alkanes, and other saturated analytes;¹⁷ and 3) quick and reversible ethylene binding.¹⁹

To translate the solution reactivity of $[\text{Re-1}]^+$ to a solid substrate, a film of the metal complex was deposited by dropcast across a microgap electrode, Figure 1. Two Au electrodes separated by 23 μm were fabricated in a clean room facility by photolithography on a Si/SiO_x substrate, Figure S1, using previously described methods.²⁰⁻²² Wire leads were attached to the Au contact pads with Ag epoxy, which was further insulated with an overlayer of Torr-seal epoxy. The electrodes were cleaned by rinsing in acetone, ethanol, and 2-propanol before drying under N₂. The device was then placed in a UVO ozone cleaner for 10 min prior to film deposition.

Scheme 1 Equilibrium binding of ethylene to $[\text{Re-1}]^+$.

A 3mM $[\text{Re-1}]^+$ complex solution was prepared by oxidation of $[\text{Re-1}]$ with ferrocenium hexafluorophosphate in dichloromethane inside a nitrogen filled glovebox. The deep blue solution of $[\text{Re-1}]^+$ was transferred dropwise to the electrode surface and allowed to evaporate forming a thin film. The radical complex $[\text{Re-1}]^+$ bridges the gap between electrodes E1 and E2 forming an ethylene sensitive resistor. The modified electrode was transferred to a gas mixing chamber with ethylene and nitrogen supplies (Figure S2). A bias of 1 V was applied and the current measured in the presence of variable ethylene : nitrogen ratios under ambient conditions.

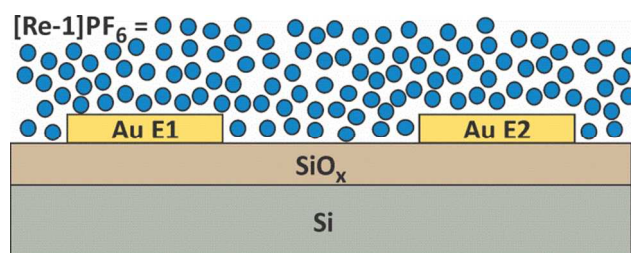


Fig. 1 Schematic of $[\text{Re-1}]^+$ coated Au microgap electrodes showing the metal-stabilized thiyl radical film (blue circles) deposited across a 23 μm gap between the gold electrodes E1 and E2.

Exposure of the $[\text{Re-1}]^+$ modified electrode to 100% ethylene with an applied bias of 1 V results in a significant decrease in current (Figure 2). The mode of detection is attributed to an electron hopping mechanism in the delocalized metal-stabilized thiyl radical $[\text{Re-1}]^+$ that is hindered in the presence of ethylene due localization of the electron spin on the metal-center in the analyte bound complex $[\text{Re-1-C}_2\text{H}_4]^+$.¹⁷ The current is restored when nitrogen is reintroduced. Response time for ethylene detection is less than 10 seconds. Refreshing the electrode with a nitrogen purge requires 100 seconds consistent with the relative values of the rate constants for ethylene addition ($k_f = 0.12(2) \text{ M}^{-1}$

s^{-1}) and ethylene release ($k_r = 0.030(4) s^{-1}$) measured in solution.¹⁹ Repeated cycling of 100% ethylene and 100% nitrogen confirms the reversibility of ethylene binding and reproducibility of the current response.

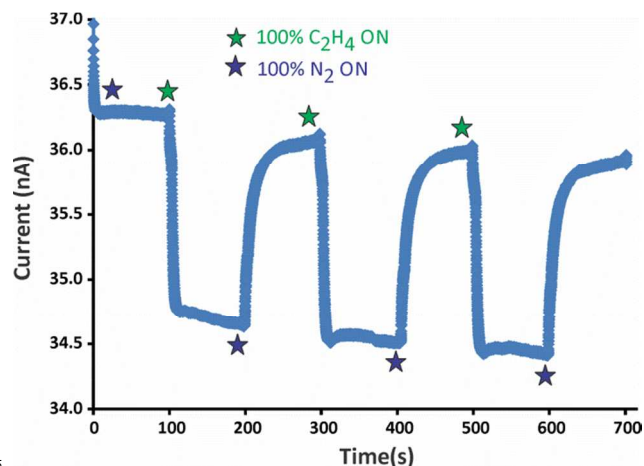


Fig. 2 Plot of current (nA) versus time (s) for the solid-state $[\text{Re-1}]^+$ coated Au microgap electrodes with cycling of gaseous C_2H_4 (green dot) and N_2 (blue dot).

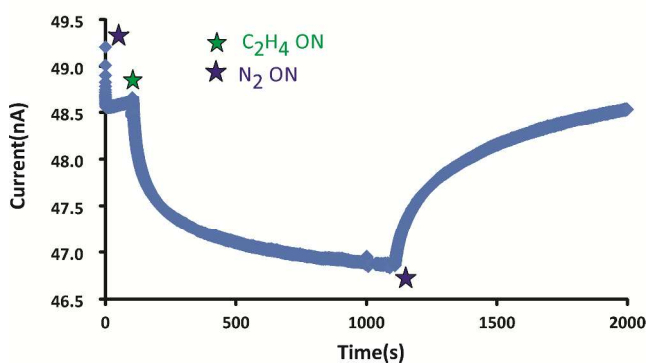


Fig. 3 Plot of current (nA) versus time (s) for the solid-state $[\text{Re-1}]^+$ coated Au microgap electrodes in the presence of gaseous 31.3% C_2H_4 .

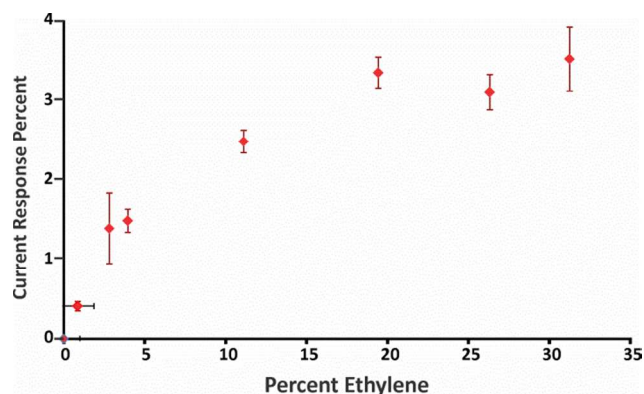


Fig. 4 Plot of current response percent versus gaseous C_2H_4 concentration (0.8% to 31.2%) for solid-state $[\text{Re-1}]^+$ coated microelectrodes.

For ethylene concentrations between 0.9% and 31.3 %, the average percent response of 3 – 5 trials is 0.41 to 3.52 with standard deviations of 0.06 - 0.39, Figures 3 and 4, Table 1, and Figures S3 - S8. Data plotted is for a single sensor, with similar results obtained with other devices. The solid state data shows a

rapid increase in percent response at low ethylene concentrations allowing quantification of gaseous concentrations between 0.4 and 20%. At higher ethylene concentrations, the binding sites within the film become saturated and the response begins to plateau near 30% ethylene with only gradual signal increases with additional analyte. Response times at low ethylene concentrations are significantly longer, up to 1000 seconds, which may be related to the rate constant for ethylene addition and/or film reproducibility. Efforts are underway to lower the limit of detection, which is relatively high compared to other ethylene chemiresistors.

Table 1 Percent current response for solid-state $[\text{Re-1}]^+$ coated Au microgap electrodes in the presence of various gaseous C_2H_4 concentrations.

Percent Ethylene	Percent Response ^a	Standard Deviation
0	0	0
0.9	0.41	0.06
2.8	1.39	0.44
4.0	1.49	0.15
11.1	2.49	0.14
19.4	3.35	0.19
26.3	3.11	0.22
31.2	3.52	0.40

^aPercent response calculated as $100 \times (i_N - i_E)/i_N$ where i_N = current in the presence of N_2 and i_E = current in the presence of C_2H_4 . Reported value are for an average 3 – 5 trials using a single sensor.

A significant advantage of the current system is its high selectivity. The selectivity of the sensor derives from the steric constraint of the ligand-centered ethylene binding site. Prior solution studies revealed kinetically retarded binding of larger alkenes to $[\text{Re-1}]^+$ and no observable binding of H_2 , CO , or other small molecules.^{17,18} To demonstrate the selectivity of the solid state device, the detector was exposed to a gaseous mixture of 19.3% 1-hexene and nitrogen. No detectable change in resistivity was observed, whereas the same concentration of ethylene provided a response of over 3.5%, Figure 5. Additionally, the electrodes are air-stable and can be stored for up to 6 months under ambient conditions with no significant change in response to 100% ethylene despite the air-sensitivity of $[\text{Re-1}]^+$ in solution.

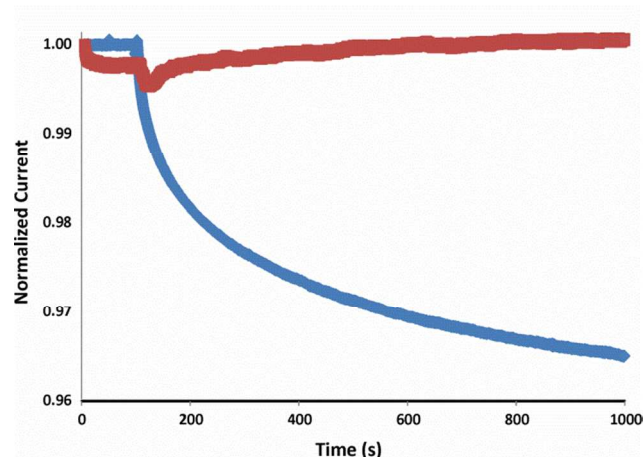


Fig. 5 Plot of normalized current versus time (s) for solid-state $[\text{Re-1}]^+$ coated Au microgap electrodes in the presence of gaseous 19.3% ethylene (blue) and gaseous 19.3% 1-hexene (red) at 19.5 °C.

A comparison of the solid-state and solution sensing data confirms that we have successfully translated the solution reactivity of our metal-stabilized thiyl radical to a heterogeneous system. Solution detection data were collected via square wave voltammetry with an initial potential of +168 mV versus ferrocenium/ferrocene, Figure S10. Under N_2 , a single cathodic event is observed at -345 mV associated with the $[\text{Re-1}]^{+/0}$.¹⁹ When the same conditions were employed under an ethylene atmosphere, an additional cathodic peak at -100 mV corresponding to $[\text{Re-1}\cdot\text{C}_2\text{H}_4]^{2+/+}$ was observed with a relative peak intensity equal to 50% of the remaining $[\text{Re-1}]^{+/0}$ peak. Data collected with a 1:1 ratio of ethylene:nitrogen yielded the same two cathodic peaks with a significant decrease in the relative intensity of the $[\text{Re-1}\cdot\text{C}_2\text{H}_4]^{2+/+}$ couple. Varying the initial hold-time did not significantly alter the ratio of two cathodic events. This potential was held for 120 s during which time **Re-1** is oxidized to $[\text{Re-1}]^+$. The potential was then scanned to a final value of -732 mV. Full experimental details are provided in the Supporting Information.

Multiple squarewave voltammograms were collected at various ethylene:nitrogen ratios and each measurement was repeated at least three times. Average relative peak intensities were plotted versus percent ethylene, Figure 6. The curve shows a sigmoidal pattern with no significant binding detected below 30% ethylene and saturation binding above 70%. The relatively high limit of detection is attributed to the weak ethylene binding affinity, $K_2 = 4 \text{ M}^{-1}$, of the immobilized $[\text{Re-1}]^+$ complex.

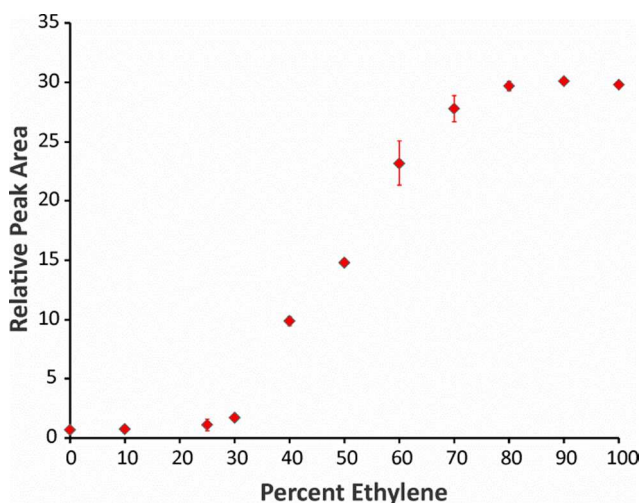


Fig. 6 Plot of relative area of the $[\text{Re-1}\cdot\text{C}_2\text{H}_4]^{2+/+}$ couple in the square wave voltammogram of $[\text{Re-1}]$ in CH_2Cl_2 solution as a function of percent C_2H_4 purged through the solution.

Conclusions

Using simple dropcast methods, a highly selective chemiresistive device has been constructed that allows for the reversible detection of gaseous ethylene. The mode of detection is attributed to an electron hopping mechanism in the delocalized metal-stabilized thiyl radical that is hindered in the presence of ethylene due to localization of the electron spin on the metal-center. The

similar selectivity between the heterogeneous and homogenous phase suggest that mode of binding is similar with a sterically restricted ligand-centered binding site responsible for the high selectivity. The selective and reversible nature of this system is unique. The electrodes are simple to construct, long-lived, and functional under ambient conditions. Improving sensitivity remains a challenge and efforts to construct a device capable of sub-ppm level ethylene sensing based on the stronger binding of $[\text{Re-1}]^{2+}$, which has an equilibrium binding constant of $2.5 \times 10^9 \text{ M}^{-1}$,¹⁹ are underway.

Notes and references

2320 South Brook Street, Department of Chemistry, University of Louisville, Louisville, KY USA 40292 Tel: 502-852-5932; E-mail: grapperhaus@louisville.edu; f.zamborini@louisville.edu

† Electronic Supplementary Information (ESI) available: [Detailed experimental methods including device preparation, detection methodology, and experimental setup]. See DOI:10.1039/b000000x/

‡ Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund (51566-ND3) for support of this work. DMB acknowledges financial support from the Office of the Executive Vice President for Research and Innovation at the University of Louisville through the Summer Research Opportunity Program.

- S. F. Yang and N. E. Hoffman, *Annual Review of Plant Physiology*, 1984, **35**, 155-189.
- R. B. H. Wills, M. A. Warton and V. V. V. Ku, *Aust. J. Exp. Agr.*, 2000, **40**, 465-470.
- G. M. Casciano, J. Moore, M. Rexrode, D. Benmhend and P. Ross, EPA, 2009.
- H. Pham-Tuan, J. Vercammen, C. Devos and P. Sandra, *J. Chromatogr. A*, 2000, **868**, 249-259.
- L. Eklund and C. H. A. Little, *Tree Physiol.*, 1998, **18**, 383-391.
- A. Sklorz, S. Janssen and W. Lang, *Sensor Actuat B-Chem*, 2013, **180**, 43-49.
- H. S. M. deVries, M. A. J. Wasono, F. J. M. Harren, E. J. Woltering, H. C. P. M. vanderValk and J. Reuss, *Postharvest Biol. Technol.*, 1996, **8**, 1-10.
- M. P. Rowe, W. H. Steinecker and E. T. Zeller, *Anal. Chem.*, 2007, **79**, 1164-11172.
- M. Agarwal, M. D. Balachandran, S. Shrestha and K. Varahramyan, *J. Nanonmater.*, 2012, **2012**, 5.
- P. Ivanov, E. Llobet, A. Vergara, M. Stankova, X. Vilanova, J. Hubalek, I. Gracia, C. Cané and X. Correig, *Sens. Actuators, B*, 2005, **111-112**, 63-70.
- S. Pitcher, J. A. Thiele, H. Ren and J. F. Vetelino, *Sens. Actuators, B*, 2003, **93**, 454-462.
- R. Zhang, M. I. Tejedor, M. A. Anderson, M. Paulose and C. A. Grimes, *Sensors*, 2002, **2**, 331-338.
- B. S. Kang, S. Kim, F. Ren, K. Ip, Y. W. Heo, B. Gila, C. R. Abernathy, D. P. Norton and S. J. Pearton, *J. Electrochem. Soc.*, 2004, **151**, G468-G471.
- M. Santiago Cintrón, O. Green and J. N. Burstyn, *Inorg. Chem.*, 2012, **51**, 2737-2746.
- O. Green, N. A. Smith, A. B. Ellis and J. N. Burstyn, *J. Am. Chem. Soc.*, 2004, **126**, 5952-5953.
- P. Cabanillas-Galán, L. Farmer, T. Hagan, M. Nieuwenhuyzen, S. L. James and M. C. Lagunas, *Inorg. Chem.*, 2008, **47**, 9035-9041.

-
17. K. Ouch, M. S. Mashuta and C. A. Grapperhaus, *Inorg. Chem.*, 2011, 9904 - 9914.
 18. K. Ouch, M. S. Mashuta and C. A. Grapperhaus, *Eur. J. Inorg. Chem.*, 2012, **2012**, 475-478.
 - 5 19. C. A. Grapperhaus, K. Ouch and M. S. Mashuta, *J. Am. Chem. Soc.*, 2009, **131**, 64-65.
 20. R. Dasari and F. P. Zamborini, *J. Am. Chem. Soc.*, 2008, **130**, 16138-16139.
 21. F. J. Ibanez and F. P. Zamborini, *Langmuir*, 2006, **22**, 9789-9796.
 - 10 22. F. J. Ibanez and F. P. Zamborini, *ACS Nano*, 2008, **2**, 1543-1552.