Published in final edited form as:

Adv Funct Mater. 2011 November 22; 21(22): 4314–4319. doi:10.1002/adfm.201101324.

Digital Inverter Amine Sensing via Synergistic Responses by n and p Organic Semiconductors

Noah J. Tremblay, Byung Jun Jung, Patrick Breysse, and Howard E. Katz

Departments of Materials Science and Engineering and School of Public Health, Johns Hopkins University, 3400 North Charles Street, Baltimore, MD 21218

Abstract

Chemiresistors and sensitive OFETs have been substantially developed as cheap, scalable, and versatile sensing platforms. While new materials are expanding OFET sensing capabilities, the device architectures have changed little. Here we report higher order logic circuits utilizing OFETs sensitive to amine vapors. The circuits depend on the synergistic responses of paired p- and n-channel organic semiconductors, including an unprecedented analyte-induced current increase by the n-channel semiconductor. This represents the first step towards 'intelligent sensors' that utilize analog signal changes in sensitive OFETs to produce direct digital readouts suitable for further logic operations.

Introduction

Organic conductors and semiconductors have been harnessed for the detection of an enormous variety of molecular vapors,^[1-3] small molecules in solution,^[2,4] biomolecules,^[4,5] electromagnetic radiation,^[6] temperature,^[7] and mechanical force.^[8,9] The transduction mechanism to an electronic signal can be a perturbation of the charge carrier distribution in response to chemical binding, reaction, absorption, or adsorption; a change in carrier energy levels, a change in dipole orientation, and/or a change in the carrier transport pathway between two electrodes.^[11] A rich variety of organic and carbon-based materials have been enlisted for this application, including conjugated organic molecules and polymers,^[10] carbon nanotubes and graphene,^[5,11-14] and polymer composites.^[15] However, the architecture aspect of these devices is still in the first stage, namely, so-called chemiresistors, chemicapacitors, and organic field-effect transistors (OFETs). To take advantage of the true potential of these devices, it is necessary to integrate these sensors into the information medium of electronics, which is binary. Digital or binary language is very powerful in that it allows engineers to interface basic organic sensors with existing electronics components to ultimately produce usable products.

The fundamental idea is to move from changing current levels (in chemiresistors) or changing current levels, mobility, or threshold voltages (in OFETs) to a conversion of those signals into incremental, easily electronically distinguishable steps. Essentially, this is an analog to digital conversion. This principle has already gained some attention for electro-optical sensors.^[16,17] The device that is most fundamental to this conversion is the simple electronic inverter based on the complementary metal-oxide-semiconductor (CMOS)-type structure (shown in Figure 1). The CMOS inverter is the simplest 'NOT' logic gate, converting a high voltage into a low voltage and vice-versa. The CMOS inverter structure takes advantage of the different and opposing behavior of n-channel and p-channel materials in OFETs. N-channel materials turn on when the gate electrode is at a positive voltage relative to the channel, and p-channel materials turn on when the gate electrode is negative. If both p- and n-channel OFETs share the same gate electrode then one OFET can allow current flow (and voltage equilibration) while the other does not. If we connect the n-

channel OFET to the OFF signal (ground), then an applied positive gate voltage induces current flow in the n-channel OSC and the output signal is ground or OFF. When the gate voltage is zero, the n-channel OSC is no longer conductive. The zero gate voltage results in a net negative voltage across the p-channel OSC when it is also connected to a positive voltage; it then allows current flow, making the output a high positive voltage (V_{dd}), the digital equivalent of “one”. The switching voltage of a CMOS inverter is the point at which below this voltage the output approaches an externally set voltage (V_{dd}) and above this voltage the output voltage is low. This switching voltage can be tuned in many different ways to achieve the desired value. This includes simply changing the dimensions of the inverter electrodes. However, the switching phenomenon is not sensitive to the absolute values of the input voltages except near the switching voltage; the outputs are generally either low or V_{dd} , with little variation.

There are several factors that affect inverter behavior. The mobility and threshold voltage matching of the two OSCs used determine at which voltage and how sharply the switching can occur. The externally set voltage (V_{dd}) changes the absolute voltage at which the inverter will switch. This voltage affects inverters made from different OSCs differently. For example, input- output curves for inverters made from two different p-channel semiconductors and the same n- channel semiconductor are shown in Figure 2 (note for figures: x-axes are not identical, and are scaled for maximum distinction of the curves). Clearly, when the materials are better matched in mobility and threshold voltage, the switching occurs closer to the half-way point between zero and V_{dd} . This idea is the basis of our previous work using individual OFET threshold voltage tuning through charged dielectrics to shift the switching voltage.^[18,19] Analytes can affect the switching voltage of inverters made from sensitive semiconductors by changing the threshold voltages and/or mobilities of either or both semiconductors. The use of this effect to generate synergistic and digital responses to amine vapors is the subject of this manuscript. A more application-specific motivation towards development of amine-sensitive devices is the growing demand for cheap ammonia sensors for use in agriculturally intensive areas, specifically to monitor their possible associated health risks to the surrounding communities.^[20,21]

Ammonia and amines on P-channel OFETs

The degenerative effects of ammonia and trimethylamine (a source of “fish odor”) have been known for p- channel conducting polymers for over a decade.^[22-24] The generally accepted mechanism is electron donation from the sp^3 -hybridized nitrogen to the conducting polymer cation. This mechanism would be viable not only for ammonia but for any tertiary, secondary, or primary alkyl amine. Figure 3 shows the detrimental effect of various amines on p- channel metal-oxide-organic semiconductor devices. Upon exposure to amines, all of the p-channel devices display a decrease in current. Through further investigation, we find specifically that exposure both decreases carrier mobility and increases the threshold voltage of p-channel devices. We would expect *any* p-channel material (polymer or small molecule) to display this behavior, though to varying degrees. The resultant changes in current, mobility, and threshold voltage are reversible for very small concentrations over short periods of time. However, for substantial concentrations over longer periods of time, the changes are irreversible, most likely due to the high additional reactivity of the sp^3 -hybridized nitrogen in forming a covalent bond to the cationic site. Some of the materials used in this study are not commercially available;^[25-28] their structures are shown in Figure 4.

Amines on N-channel OFETs

In addition to a p-channel, the CMOS inverter contains an n-channel device. In this work, we employ naphthalene tetracarboxylic diimides (NTCDIs), a class of n-channel semiconductors shown in previous work to be air-operable with highly-fluorinated side chains on the diimide nitrogens.^[29,30] In contrast to p-channel devices, upon exposure of n-channel devices made with NTCDI to ammonia, the current *increases*, the *mobility* increases, and the threshold voltage *decreases*. This new behavior is shown in Figure 5, over a minutes time scale. While the mechanism of this response is not precisely known, the interaction may proceed through an oxygen exclusion mechanism where amines help seal the grain boundaries of the film from the permeation of quenching oxygen. The mechanism may alternatively involve electron doping, or cancellation by ammonia of electron traps. Further investigation is required to determine which mechanism is the most reasonable. However, the increase in mobility tends to be partially reversed upon continued exposure to ammonia or amines for over 10-15 min. This indicates at least two operative interaction pathways may be at work.

While numerous vapors have been shown to decrease currents in OFETs, it is very rare to find a class of chemicals that will increase such currents. In this way, the ‘turn on’ response of amine exposure to n-channel devices is very useful for excluding false positive responses.

CMOS inverter amine sensors

There is a clear benefit to utilizing both the p-channel amine response as well as the n-channel response. Similar to the principle of the proposed ‘electronic nose’, a diversity of responses can give a greater selectivity for a particular analyte. In this case, the difference is substantial given that the responses are opposite in direction, and rather than separate them into distinct output channels, we combine them into a single synergistic one. One might consider this type of detection ‘ratiometric’ given that one can track a changing ratio between two independent responses. The simplest way to combine a p-channel and an n-channel device into a device with one input and one output is the CMOS inverter. Inverter behavior upon exposure to increasing concentrations of isopropylamine is shown in Figure 6A.

The inverter switching voltage shifts to lower voltage due to the additive effect of the p-channel threshold voltage increasing and the n-channel threshold voltage decreasing and mobility increasing. Each concentration shows a gradient of responses toward lower voltage over time. Presumably, the incremental shifting within each concentration is due to an equilibration of the amine between the ambient air and within the OSC film.

To further highlight the cumulative nature of this response, a simple experiment is illustrated in Figure 6. Three identical inverters were made. In one, the n-channel device was isolated from the environment (Figure 6B); in another, the p-channel device was isolated (Figure 6C). The third inverter was left completely exposed (Figure 6A). When the p-channel device is open to the environment, the increasing concentration of isopropylamine (chosen because of its boiling point slightly above room temperature, facilitating injection and complete evaporation) causes a series of incremental shifts in the switching voltage. In comparison, for the completely exposed device, small concentration changes cause larger stepwise jumps. The inverter where the n-channel device is left exposed and the p-channel is isolated is consistent with the behavior of the change in mobility of the n-channel upon exposure to amine. At first the switching voltage shifts dramatically to lower voltage. Upon further increase in concentration, the switching voltage reverses direction and backtracks to slightly a higher voltage. However, this voltage is still lower than the original starting point. At the

smaller concentration values, the potential for a cumulative sensitivity of the CMOS inverter can be seen, as plotted in Figure 7.

Sensitive inverters were also fabricated using different p-channel materials. Figure 8 shows the comparison between CMOS inverter sensor behavior with pentacene, copper(II) phthalocyanine (CuPc), and 6PTTP6 as the p-channel component. In this comparison, the n-channel components were identical. CuPc made low mobility, high threshold voltage transistors. The CuPc OFET sensitivity was also not very high. The inverter made from it had a very low switching voltage, even at high V_{dd} , due to the mismatch with the higher mobility and lower threshold voltage of the n-channel, and therefore displayed small absolute switching voltage shifts with increasing concentrations of isopropylamine (Figure 8A). Pentacene p-channel devices had higher mobilities, better sensitivities, and the inverter made from it showed substantially larger shifts with increasing concentrations (Figure 8B). However, the best CMOS inverter sensors were the ones made with 6PTTP6 (Figure 8C). P-channel devices made from 6PTTP6 were much better matched with the NTCDI n-channel devices in terms of threshold voltage and mobility. A side-by-side comparison shows that the overall current levels of each OFET are within the same magnitude. A secondary indication of the similarity is in the 40V switching voltage, very close to the ideal 50V. These inverters produced very large shifts in switching voltage upon exposure to even small amounts of amine; the data sets within each concentration were completely separate with no overlap.

Future development: higher order logic from inverter sensors

The real benefit to the CMOS inverter sensor is the unambiguous 1 or 0. For example, if one chose to monitor at a constant output voltage just below the switching voltage of the inverter, any small concentration change would drop the signal below the monitoring voltage and the signal would go from a 1 to a 0. A series of these inverters could be arrayed together, each one being monitored at a different output voltage. As the concentration increased, different inverters would be triggered according to the sensitivity. The output would be a digital readout as 0001 for a low concentration or 1111 for a high concentration. This type of setup makes it easy to identify most false readings. For example a readout of 1001 would not make any sense, and one would suspect that at least one of the inverters, the least sensitive one, would be faulty. Also, specificity is increased because the synergistic response would be less likely for an interferent than for an analyte intended for detection.

More sophisticated circuits can be made for the detection of combinations of analytes. If one had an inverter that is sensitive to ammonia and another that is sensitive to water, together one could obtain clear and simple answers to whether or not there is a certain amount of either analyte present. If the readout were 00 there would be no ammonia or water. If the readout were 01 or 10, there would either be a certain amount of ammonia or a certain amount of water. If the readout were 11, then the answer to the question, 'is there a certain amount of ammonia and a certain amount of water?' would be 'yes'. Other technological developments in the organic electronics community would be of additional use for sensors. For example, advances in inkjet printing technology and threshold voltage tuning by the printing of charged dielectrics^[18] should enable high throughput production of organic-based digital sensors and their integration with organic memory transistors^[31] and silicon signal processors.

Methods: Materials, devices, and measurements

All CMOS inverter sensors were fabricated and characterized using standard methods. All materials were purchased from Sigma-Aldrich unless synthesized or otherwise denoted. Highly n-doped <100> silicon wafers with a 300 nm thermally grown oxide were diced into

1 in. by 1 in. substrates. The wafers were cleaned by sonication in acetone and isopropanol, and then dried by forced nitrogen gas. Substrates were dried more thoroughly via 100°C vacuum annealing for 20 min prior to a 2-hour exposure to hexamethyldisilazane (HMDS) vapor at 100°C in a loosely sealed vessel. Individual sensitive transistors were fabricated via spin-coating (PIF-TBT, 7mg/mL in chlorobenzene, 1.5k spin speed) or thermally evaporating (8-3NTDCI, substrate temperature held at 100°C) the OSC directly onto HMDS substrates, followed by thermally evaporated gold electrodes (50nm) through a shadow mask. CMOS inverters were fabricated by thermal evaporation of OSCs onto HMDS substrates, to a thickness of 30 nm, that were first spun-coat with a thin film of poly(*alpha*-methylstyrene) (5mg/mL of toluene, 2k spin speed). High-grade pentacene and CuPc were used as-is from Sigma-Aldrich. 8-3NTDCI^[26] and 6PTTP6^[28] were synthesized according to literature procedure and triply sublimed for purity. 8-3NTDCI was evaporated through a shadow mask at a substrate temperature of 100°C before the p-type material was evaporated onto the same substrate through a different shadow mask. Gold electrodes were evaporated through a shadow mask to the thickness of 60-75 nm. Individual sensitive transistors were measured using an Agilent 4155C semiconductor analyzer in air. CMOS inverter sensors were measured in a four-probe vacuum probe station (Janis Research) with a calculated internal volume of 2.6L attached to a Keithley 4200 semiconductor characterization system. "10-150 μ L/2.6 L volume" = 4-60 ppm liquid V/gaseous V, or 0.05-0.5% as w/w NH₃/air, if the entire amine aliquot were active over the device, making these upper limits of concentration.

Acknowledgments

We are grateful for support from the National Institute of Environmental Health Sciences Training Program [ES 07141] for primary support of NT. We also thank NSF (grant number 0730926), AFOSR (Grant number FA9550-09-1-0259), and the Johns Hopkins Center for a Livable Future for partial support of this work. The authors would like to thank Qingdong Zheng and Jia Huang for the materials PIF-TBT and 6PTTP6 respectively.

References

1. Someya T, Dodabalapur A, Huang J, See KC, Katz HE. Adv Mater. 2010; 22:3799. [PubMed: 20603885]
2. Locklin J, Bao Z. Anal Bioanal Chem. 2006; 384:336. [PubMed: 16328249]
3. Yang W, Ratinac KR, Ringer SP, Thordarson P, Gooding JJ, Braet P. Angew Chem Int Ed. 2010; 49:2114.
4. Roberts ME, Mannsfeld SCB, Queralto N, Reese C, Locklin J, Knoll W, Bao Z. P Natl Acad Sci Usa. 2008; 105:12134.
5. Guo X, Gorodetsky AA, Hone J, Barton Jk, Nuckolls C. Nat Nanotechnol. 2008; 3:163. [PubMed: 18654489]
6. Campbell IH, Crone BK. Appl Phys Lett. 2009; 95:263302.
7. Letizia JA, Rivnay J, Facchetti A, Ratner MA, Marks TJ. Adv Funct Mater. 2010; 20:50.
8. Hsu YJ, Jia Z, Kymissis I. Ieee T Electron Dev. 2011; 58:910.
9. Someya T, Sekitani T, Iba S, Kato Y, Kawaguchi H, Sakurai T. P Natl Acad Sci Usa. 2004; 101:9966.
10. Roberts ME, Mannsfeld SCB, Stoltenberg RM, Bao Z. Org Electron. 2009; 10:377.
11. Huang J, Dawidczyk TJ, Jung BJ, Sun J, Mason AF, Katz HE. J Mater Chem. 2010; 20:2644.
12. Harris KD, Xiao S, Lee CY, Strano MS, Nuckolls C, Blanchet G. J Phys Chem C. 2007; 111:17947.
13. Someya T, Small J, Kim P, Nuckolls C, Yardley J. Nano Lett. 2003; 3:877.
14. Feldman AK, Steigerwald ML, Guo X, Nuckolls C. Accounts Chem Res. 2008; 41:1731.
15. DiBenedetto SA, Facchetti A, Ratner MA, Marks TJ. Adv Mater. 2009; 21:1407.
16. Anthopoulos TD. Appl Phys Lett. 2007; 91:11351.

17. Guo Y, Yu G, Liu Y. *Adv Mater.* 2010; 22:4427–4447. [PubMed: 20853375]
18. Dhar BM, Özgün R, Dawidczyk T, Andreou A, Katz HE. *Mater Sci Eng R.* 2010;10.1016/j.mser.2010.11.001
19. Dhar B, Özgün R, Jung B, Katz HE, Andreou A. *Electron Lett.* 2010; 46:1335.
20. Thorne P. *Environ Health Perspect.* 2007; 115:296–297. [PubMed: 17384781]
21. Heederik D, Sigsgaard T, Thorne PS, Kline JN, Avery R, Bønløkke JH. *Environ Health Perspect.* 2007; 115:298. [PubMed: 17384782]
22. Bao Z, Dodabalapur A, Lovinger AJ. *Appl Phys Lett.* 1996; 69:4108.
23. Assadi A, Gustafsson G, Willander M, Svensson C, Inganäs O. *Synthetic Metals.* 2009; 37:123.
24. Fiorido T, Bendahan M, Aguir K, Bernardini S, Martini C, Brisset H, Fages F, Videlot-Ackermann C. *C Sensor Actuat B-Chem.* 2010; 151:77–82.
25. Zheng Q, Jung BJ, Sun J, Katz HE. *J Amer Chem Soc.* 2010; 132:5394. [PubMed: 20102195]
26. Jung BJ, Lee K, Sun J, Andreou AG, Katz HE. *Adv Funct Mater.* 2010; 20:2930.
27. Jung BJ, Sun J, Lee T, Sarjeant A, Katz HE. *Chem Mater.* 2009; 21:94.
28. Mushrush M, Facchetti A, Lefenfeld M, Katz HE, Marks TJ. *J Am Chem Soc.* 2003; 125:9414. [PubMed: 12889972]
29. Jung BJ, Martinez-Hardigree J, Dhar BM, Dawidczyk TJ, Sun J, See KC, Katz HE. *ACS Nano.* 2011; 5:2723. [PubMed: 21351783]
30. Jung BJ, Tremblay NJ, Yeh ML, Katz HE. *Chem Mater.* 2011; 23:568–582.
31. Sekitani T, Yokota T, Zschieschang U, Klauk H, Bauer S, Takeuchi K, Takamiya M, Sakurai t, Someya T. *Science.* 2009; 326:1516. [PubMed: 20007895]

Figure 1. CMOS inverter structure. a, cross-sectional layout; b, circuit diagram

Figure 2. CMOS inverter behavior, gate voltage vs. output voltage at different values of V_{dd} . a, device made with 8-3-NTCDI and CuPC. b, device made with 8-3-NTCDI and 6PTTP6.

Figure 3. Relative mobility change on exposure to various amines. Relative mobility of PIF-TBT OFETs on exposure to perfluorodecylamine, decylamine, triethylamine, and ammonia. The major difference among the responses is from the vapor pressure of the materials. Perfluorodecylamine is the only solid, and has a lower vapor pressure and a lower response.

Figure 4.
Molecular structures of previously reported OSCs.

Figure 5. N-channel compared to P-channel responses to ammonia exposure. Device made with NTCDI showing a, increase in relative mobility; b, decrease in relative threshold voltage; c, increase in relative current.

Figure 6. CMOS inverter behavior upon exposure to isopropylamine. a, 6PTTP6/NTCDI inverter upon exposure. b, exposing only the p-channel FET to amine. c, exposing only the n-channel FET to amine. d, device structure and exposure scale bar.

Figure 7.
Graph showing the synergistic effect of CMOS inverter sensors.

Figure 8. CMOS inverter sensor behavior with 8-3-NTCDI paired with various p-channel materials. a, CuPc-NTCDI inverter upon exposure. b, pentacene/NTCDI. c, 6PTTP6/NTCDI. d, colorimetric concentration scale bar.