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Highly Sensitive NH_3 Detection Based on Organic Field-Effect Transistors with Tris(pentafluorophenyl)borane as Receptor

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Supporting Information

ABSTRACT: We have increased organic field-effect transistor (OFET) NH_3 response using tris(pentafluorophenyl)borane (TPFB) as a receptor. OFETs with this additive could detect concentrations of 450 ppb v/v, with a limit of detection of 350 ppb, the highest sensitivity reported to date for semiconductor films; in comparison, when triphenylmethane (TPM) or triphenylborane (TFB) was used as an additive, no obvious improvement in the sensitivity was observed. These OFETs also showed considerable selectivity with respect to common organic vapors and stability toward storage. Furthermore, excellent memory of exposure was achieved by keeping the exposed devices in a sealed container stored at −30 °C, the first such capability demonstrated with OFETs.

Ammonia (NH_3) detection has received considerable attention in the fields of agricultural environmental monitoring, chemical and pharmaceutical processing, and disease diagnosis. Existing methods have limitations. For example, mass spectrometry coupled with gas chromatography (GC−MS) and optical sensors is highly sensitive and selective, but it is also expensive and not easily portable and may be unwieldy for environmental monitoring. Organic field-effect transistor (OFET) sensors have been proposed for use in gas sensing because of their potential high sensitivity, low cost, low weight, and potential in making flexible,[1] large-area or mass-produced devices. Many attempts to improve transistor-based NH_3 sensors have been made. Wei and co-workers developed single-crystalline micro/nanostructures of perylenediimide derivatives with a fast response rate, an NH_3 sensitivity of 1%, and long-term stability.[2] Bouvet et al. reported molecular semiconductor-doped insulator heterojunction transducers that can detect "<200 ppm" NH_3 vapor;[3] later, Bouvet and co-workers developed a novel semiconducting molecular material, $Eu_2[Pc(15C5)_4]_2[Pc(OC10H21)_8]$, as a quasi-Langmuir−Shäfer (QLS) film for use as a top layer and vacuum-deposited and cast CuPc and copper tetra-*tert*-butylphthalocyanine (CuTTBPc) QLS films as sublayers, resulting in devices with NH_3 sensitivities of 15−800 ppm.[4] Ju and co-workers used poly-3-hexylthiophene (P3HT) as the semiconductor and a thermally grown SiO_2/Si wafer as the substrate, successfully creating a high-sensitivity NH_3 sensor with a detect limitation of 10 ppm.[5] Zan et al. developed pentacene-based organic thin-film transistors (TFTs) by using UV-treated poly(methyl methacrylate) (PMMA) as the buffer layer to modify a SiO_2 dielectric surface, and these sensors could respond to "0.5 ppm" NH_3;[6] later, a novel hybrid gas sensor based on amorphous indium gallium zinc oxide TFTs that could respond to "0.1 ppm" NH_3 was developed by the same group.[7] These latter detection limits have been placed in quotes because in those experiments, the parts-per-million concentration of NH_3 gas in the chamber was expressed as milligrams per liter of chamber volume,[6] which is *1329 times higher* than a more appropriate definition of parts per million for gas mixtures (μL/L). Therefore, the detection of trace amounts of NH_3 (sub-ppm v/v in the gas phase) by OFETs is still challenging. Herein we report OFET-based NH_3 detectors with sensitivities of 0.35 ppm v/v, which is much higher than previously reported. We also demonstrate the enhancement conferred by tris(pentafluorophenyl)borane (TPFB) as an NH_3 receptor[8] and the ability to store the exposed detector for later electronic assessment.

Boranes have frequently been used as complexation agents for Lewis bases[9−13] because of the strong interaction between boron atoms and lone pairs; furthermore, borane−amine complexes have also been widely used as light-emitting molecules[14] and in fluorescent sensors.[15] TPFB is frequently used as a strongly Lewis acidic cocatalyst in numerous reactions, such as dehydration,[16] Friedel−Crafts reactions,[17] ring-opening reactions,[18] and syndiospecific living polymerization.[19] Here, TPFB was chosen as the NH_3 receptor additive in the OFET semiconductors because of the strong B−N interaction [20] and the known vacuum sublimability of TPFB. Furthermore, the hydrogen bonds formed between H and F atoms also play a role in the complexation process, so the NH_3 molecule is tightly bound to TPFB through all four of its atoms (Scheme 1).

The strong interaction between NH_3 and TPFB was also confirmed by previous reports[20,21] as well as the experiments described in the Supporting Information (SI) and shown in Figure S1. Scheme 1 shows a proposed structure of the

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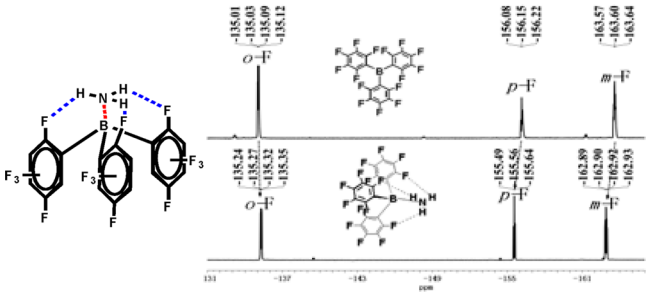
Scheme 1. NH_3–TPFB Interaction (Blue, Hydrogen Bonding; Red, B–N Interaction) and ^{19}F NMR Spectra of TPFB and the TPFB–NH_3 Complex



precipitate, in which one NH_3 molecule forms a complex with one TPFB molecule through the B–N interaction and three hydrogen bonds. The structure was confirmed by ^{19}F NMR and attenuated total reflectance (ATR) spectra, which were in agreement with previous literature data.[20,21]

We used two OFET organic semiconductors (OSCs), copper phthalocyanine (CuPc) and cobalt phthalocyanine (CoPc). As TPFB controls, triphenylmethane (TPM) and triphenylborane (TPB) were used as additives because their molecular shapes are similar to that of TPFB. All of the OFETs were fabricated and characterized using standard methods. Materials were purchased from Sigma-Aldrich. Highly n-doped ⟨100⟩ silicon wafers with 300 nm thermally grown oxide were diced into 1 in. × 1 in. substrates, cleaned with piranha solution (**Caution:** *corrosive!*), sonicated in acetone and isopropanol, and then dried using forced nitrogen gas. The substrates were further dried by vacuum annealing at 100 °C for 20 min prior to a 2 h exposure to hexamethyldisilazane (HMDS) vapor at 110 °C in a loosely sealed vessel. The OSCs (CuPc and CoPc) were thermally evaporated neatly or coevaporated with TPFB, TBP, or TPM directly onto the HMDS-treated substrates with a thickness of 6 nm; the deposition rate was 0.3 Å/s for the OSCs and 0.2 Å/s for the additive. Gold electrodes (50 nm) were thermally vapor-deposited through a mask (channel width/length (W/L) ratio = 32) at 0.3 Å/s. The deposition chamber pressure was $<5 \times 10^{-6}$ Torr, and the substrate temperature was held constant at 25 °C during the deposition. The compositions of the OSC-containing films were examined by X-ray photoelectron spectroscopy (XPS); the results are shown in Figure S2. The fluorine 1s peak (680–700 eV) was seen in the spectra of CuPc+TPFB and CoPc+TPFB but not in the spectra of CuPc and CoPc. All of the OFET properties were measured using an Agilent 4155C semiconductor analyzer. NH_3 gas with a certified dilution (4.5 ppm in nitrogen) was purchased from PRAXAIR; an NH_3 concentration of 0.45 ppm was achieved by mixing the 4.5 ppm NH_3 with pure nitrogen and assayed using a photoionization detector (PID) (Pho Check Tiger, Ion Science, U.K.). A sealed exposure chamber with a volume of 4 L and a rotating fan inside to create a uniform vapor concentration was used; the flow rate of gas through the chamber was 0.2 L/min.

Typical OFET transfer and output curves for CuPc and CoPc with and without additives are shown in Figure S3 [drain voltage (V_{ds}) = −60 V] and Figure S4, respectively. The mobilities, threshold voltages, and on/off current ratios of these transistors are summarized in Table S2. OFETs with TPFB as the additive showed lower mobilities and required higher gate voltages (V_g) for turn-on than the other OFETs. One possible reason may be that TPFB contains many more locally dipolar bonds than TPM and TPB, which makes TPFB more likely to trap holes in the channel, thus giving a lower mobility and more negative threshold voltage.

The responses of these devices to NH_3 vapor were investigated by plotting the percent change in drain current, $100\% \times (I_{d,0} - I_d)/I_{d,0}$ (measured at $V_g = -60$ V, $V_{ds} = -60$ V) versus time of exposure to NH_3 vapor. For some p-type semiconductors, such as CuPc, CoPc, 6PTTP6, and pentacene,[22−25] the OFET current is known to be higher in dry air than in nitrogen (the carrier gas used for NH_3) because of oxygen doping. To obtain accurate and reproducible responses to NH_3, all of the devices were subjected to ambient aging for 3 days before the NH_3 exposure experiments. The responses shown in the following figures have been corrected for the current decrease caused by replacing oxygen with nitrogen.

As shown in Figure 1a,b, after exposure to 4.5 ppm NH_3 vapor for 30 min, the drain currents of CuPc, CuPc+TPM, and

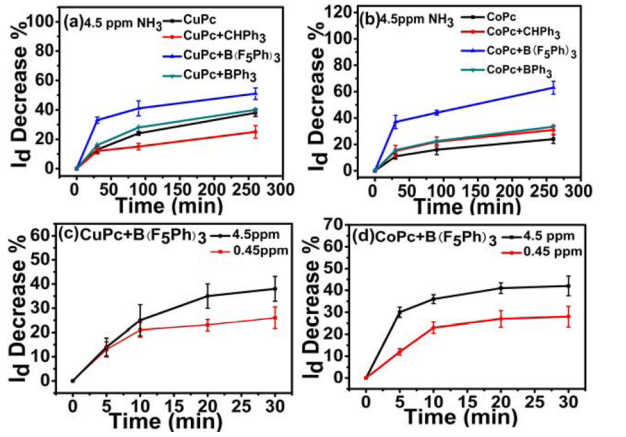


Figure 1. (a, b) Drain current decreases for (a) CuPc, CuPc+TPM, CuPc+TPFB, and CuPc+TPB devices and (b) CoPc, CoPc+TPM, CoPc+TPFB, and CoPc+TPB devices vs time of exposure to 4.5 ppm NH_3. (c, d) Drain current decreases for the (c) CuPc+TPFB and (d) CoPc+TPFB devices vs time of exposure to 4.5 ppm or 0.45 ppm NH_3 vapor.

CuPc+TPB decreased 13, 12, and 16%, respectively. For CuPc +TPFB, the decrease in I_d was 33%, which is much higher than the responses of CuPc, CuPc+TPM, and CuPc+TPB. For CoPc, CoPc+TPM, and CoPc+TPB, the decreases were 11, 15, and 16%, respectively, while for CoPc+TPFB, the decrease was 37%, which is also much higher than those for CoPc, CoPc +TPM, and CoPc+TPB. This larger decrease is consistent with the strong interaction between TPFB and NH_3 vapor increasing the binding of NH_3 to the semiconductor surface, thus giving a much higher relative response. While TPM has a similar molecular structure as TPFB, it has no host–guest interaction with NH_3, and an enhancement in relative response was not obtained. Although TPB has a B atom in the molecular center, it is a much weaker Lewis acid than TPFB,[26] and moreover, there is no hydrogen bonding between TPB and NH_3. Therefore, the response of TPB was also much lower than the response of TPFB. After 90 min of exposure, the decreases in I_d for CuPc, CuPc+TPM, CuPc+TPB, and CuPc +TPFB were 24, 15, 28, and 41%, respectively. For CoPc, CoPc +TPM, CoPc+TPB, and CoPc+TPFB, the decreases were 16, 22, 23, and 44%, respectively. After 260 min of exposure, the drain current of CuPc, CuPc+TPM, CuPc+TPB, and CuPc

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+TPFB decreased by 38, 25, 40, and 51%, respectively. For CoPc, CoPc+TPM, CoPc+TPB, and CoPc+TPFB, the drain current decreased by 24, 31, 33, and 63%, respectively. Over time, the rate of I_d decrease became lower. A list of the numbers of different evaporations, wafers, and devices used in this study is provided in Table S1.

Sensing cycle experiments were also done (Figure S5). In this set of experiments, the NH_3 exposure time was 90 s; the devices gave instant responses and recovered immediately after airflow over the device surface. The recovery took a relatively long time only when the response was high (>30%). Within the range of concentrations measured (0.45−20 ppm), we observed a relatively linear change in response. Therefore, the devices gave instantaneous responses and reflected the real concentration of the analyte in the air. At later stages, the system worked according to an accumulative model.

In a third set of experiments, CuPc+TPFB and CoPc+TPFB were exposed to a much lower NH_3 concentration (0.45 ppm in nitrogen), and the results are shown in Figure 1c,d. After exposure for 5 min, the drain currents of CuPc+TPFB and CoPc+TPFB decreased by 13 and 12%, respectively, while after 10 min, the drain currents decreased by 21 and 23%, respectively; after 20 and 30 min exposure, the I_d of CuPc +TPFB decreased 23 and 26%, respectively, and the I_d of CoPc +TPFB decreased by 27 and 28%, respectively. For comparison, the responses of CuPc+TPFB and CoPc+TPFB to 4.5 ppm NH_3 after 5, 10, 20, and 30 min are also shown in Figure 1c,d. While the higher concentration gave greater responses, the time for equilibration may be increased because of barriers preventing NH_3 from reaching some of the sites complexed at higher concentrations. Additionally, we also exposed the device to 0.35 and 0.25 ppm NH_3 (Table S3). According to the definition of limit of detection[25,27] (LOD = R_{blank} + 3S, where R_{blank} is the blank response and S is the standard deviation of the response), we obtained a conservative estimate of 0.35 ppm for the LOD.

The selectivity of these devices was also investigated. Figure 2 displays the change in I_d for CuPc+TPFB and CoPc+TPFB

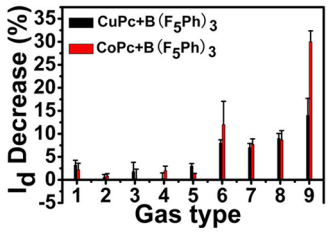

Figure 2. Drain current changes for CuPc+TPFB and CoPc+TPFB devices upon exposure to different gas vapors for 5 min: 1, methanol (2000 ppm); 2, acetone (1800 ppm); 3, dichloromethane (3900 ppm); 4, ethyl acetate (1500 ppm); 5, 5% H_2 (50000 ppm); 6, isopropylamine (10 ppm); 7, isobutylamine (10 ppm); 8, H_2S (5 ppm); 9, NH_3 (4.5 ppm).

after exposure to different gas vapors. Methanol, acetone, and ethyl acetate were chosen because of the possibility of oxygen interactions with TPFB involving the O and B atoms.[28] Dichloromethane is a highly volatile solvent that may exist under some circumstances at high concentration, so it was also desirable to check this vapor. As shown in Figure 2, all these solvents gave only small responses even at very high concentrations (several thousand ppm). The devices were also stable toward high hydrogen concentrations. It is not surprising that these devices were sensitive to volatile amines; however, the responses were smaller than the response to NH_3 (4.5 ppm NH_3 vs 10 ppm isopropylamine or 10 ppm isobutylamine).[8] The possible reason may be that the alkyl chain of the amine causes steric hindrance while binding with TPFB, resulting in a relatively longer B−N bond than for NH_3,[20] thus giving a lower response than NH_3. Another reason may be that one TPFB molecule can bind with two NH_3 molecules,[20] while there is no prior report that one TPFB can bind with two amine molecules. Thus, TPFB is more sensitive and efficient in detecting NH_3 vapors than organic amine vapors. For H_2S, these devices also showed relatively high responses, although the responses were lower than those for NH_3. Furthermore, H_2S is an acidic gas, while NH_3 is a basic gas. Because of their significantly different properties, it would be easy to filter H_2S selectively with basic powder, the same method used in some previous literature.[29,30] These devices also showed good stability to moisture, with I_d remaining above 50% of its original value even after 7 days of exposure to <30% relative humidity (RH) at 25 °C; only when the RH was higher than 50% did the devices show relatively fast linear decay (Figure S6). Water is also filterable from NH_3 using a highly basic desiccant.

Retention of the exposure effect is important if reading the device right after exposure is impractical. Diffusion of the analyte out of the device or even within the device must be prevented. Maintaining the NH_3-exposed device in open air or in a sealed, air-filled container (1″ diameter Fluoroware) at room temperature was insufficient to keep the postexposure current constant. However, when the exposed device was placed in the container and stored at low temperature (−30 °C), the signal change after 1 day was small. As shown in Figure 3, for CuPc+TPFB, an exposed device with a response of 70%

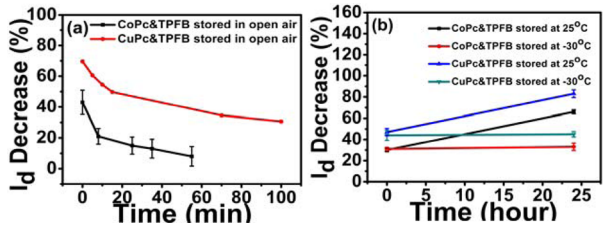

Figure 3. Current changes for differently stored devices.

I_d decrease gradually lost its response signal when stored in open air; the device stored in the container at 25 °C showed a signal change from 47 to 83% after 24 h, perhaps because of NH_3 diffusion within the device to more electronically active sites. However, for the device stored in the container at −30 °C, the signal showed only an insignificant change from 44 to 45% after 24 h,. For CoPc+TPFB, the device stored in open air also lost its signal and recovered eventually; the device stored in the container at 25 °C showed a signal change from 30 to 66% after 24 h, while for the device stored in the container at −30 °C, the signal showed a negligible change from 31 to 33%. The change after 1 day of storage in the container at −30 °C was usually less than 3% and invariably less than 6% of the original current, even for responsive current changes of >50%. The changes in I_d after 24 h at other storage temperatures are shown in Figure S7.

In conclusion, we have successfully developed a highly responsive NH_3 detector using TPFB as a receptor. OFETs

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using this additive could detect concentrations at least as low as 450 ppb v/v with an LOD of 0.35 ppm. In comparison, when TPM or TPB was used as the additive, no obvious improvement in sensitivity was observed. The specific host–guest interaction between NH_3 and TPFB appears to be critical for the enhancement observed relative to neat semiconductors. Additionally, these OFETs also showed good selectivity and storage stability. Device current changes were preserved by keeping the devices in a sealed container stored at −30 °C. To the best of our knowledge, this is the first report of the use of a borane as a receptor in a sensitive OFET, the first use of OFETs to record responses to vapors, and the most sensitive semiconductor-based NH_3 detection demonstrated to date.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details about the NH_3–TPFB interaction, XPS data, typical transfer and output curves for CuPc and CoPc with and without additives, ATR and ^{19}F NMR spectra of the TPFB–NH_3 complex, humidity experiment, sensing cycle data, LOD determination, memory behavior at different storage temperatures, and a table of samples investigated. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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