

# Volatile Organic Compound Detection Using Insect Odorant-Receptor Functionalised Field-Effect Transistors

by

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# 1. Verifying Non-Covalent Functionalisation of Carbon Nanotubes and Graphene

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In previous chapters, we have discussed methods of fabricating carbon nanotube and graphene devices and then shown that they can be operated effectively as chemical sensors. However, to detect specific chemical traces while ignoring others ('specific sensing'), the devices require chemical modification, often called 'functionalisation'. Instead of responding to stimuli themselves, the sensing signal is picked up by attached receptors. The devices then act as passive transducers for the received signal. Receptors previously used with carbon nanotube and graphene devices include aptamers and a range of proteins, including odorant receptors. A common approach to attaching receptors to the transducer involves the use of a linker molecule to tether the receptor to the transducer. Verifying that this linker molecule is bridging between the transducer and the receptor element is important for a complete understanding of the behaviour of these sensors. This verification involves providing evidence for effective attachment of linker molecule to the transducing device channel, then showing successful tethering of odorant receptors and other biomolecules to the attached linker molecule.

This chapter therefore takes some time to explore the attachment of linker molecules to carbon nanotube and graphene device channels, using methods such as Raman spectroscopy, fluorescence microscopy and electrical characterisation. Linker molecules used are discussed in detail, and numerous hurdles to successful functionalisation via linker molecules are identified and addressed.

## 1.1. Non-Covalent Functionalisation & Linker Molecules

Linker molecules may be attached via covalent or non-covalent bonding to carbon nanomaterials, such as carbon nanotubes and graphene. Non-covalent binding is weaker than covalent binding. However, the advantage of non-covalent binding is that it disrupts the structure of the nanomaterial less than covalent bonding does, and therefore has less of a negative impact on the electrical properties of the transducer [1]. For example, one

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group found covalent bonding of diazonium linker caused a  $\sim 50$  drop in channel mobility [2]. In particular, this thesis discusses  $\pi - \pi$  bonding, a particular strong type of non-covalent bonding.

### 1.1.1. 1-Pyrenebutanoic acid N-hydroxysuccinimide ester (PBASE)

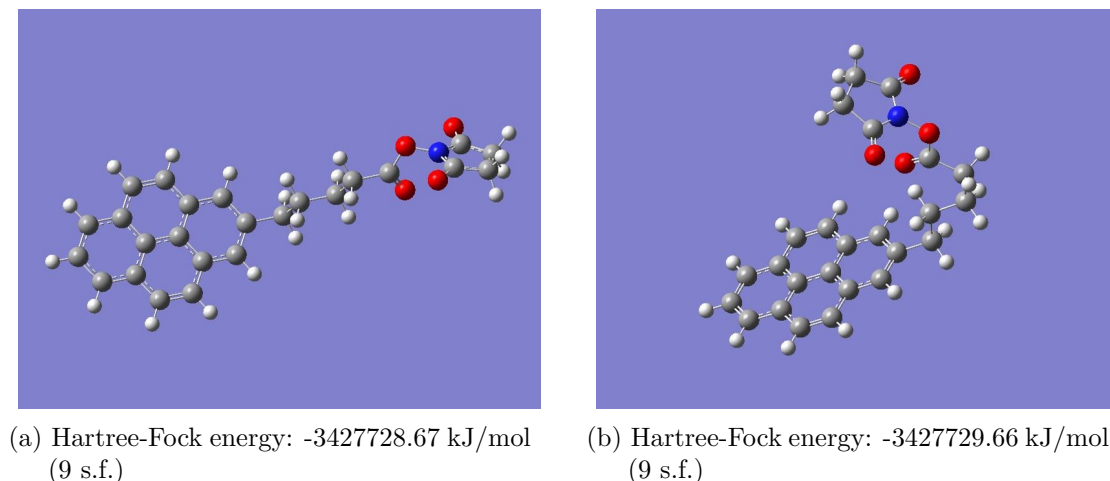


Figure 1.1.: Two conformations of PBASE molecule with geometry optimised via *ab initio* calculations (computed using Gaussian 16 [3]). The difference between computed Hartree-Fock energies is 1.0 kJ/mol, small enough that the existence of both molecular conformations is physically possible.

1-Pyrenebutanoic acid N-hydroxysuccinimide ester (variously known commercially and in the literature as 1-Pyrenebutyric acid N-hydroxysuccinimide ester, PBASE, PBSE, PASE, PyT-NHS, PyBASE, PANHS) is a aromatic, bifunctional molecule commonly used for tethering biomolecules to the carbon rings of graphene and carbon nanotubes. The optimised molecular structure of PBASE is shown in Figure 1.1.

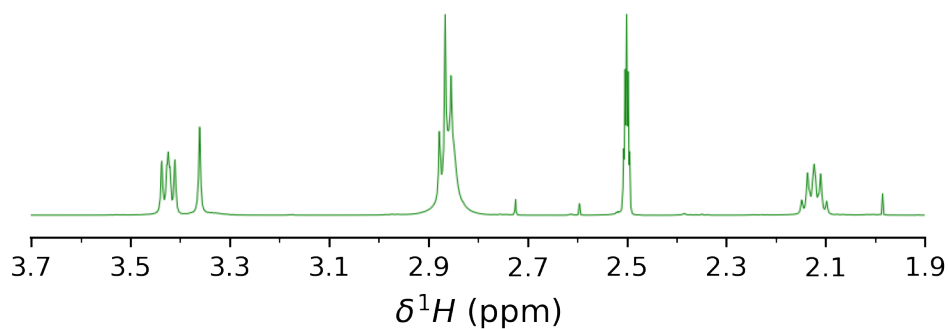
The non-covalent functionalisation of proteins onto a single-walled carbon nanotube using PBASE was first reported by Chen *et al.* in 2001 [4]. Two methods for protein functionalisation and immobilisation were successfully used, with the only differences being the solvent used to dissolve the PBASE powder (DMF, methanol) and the final concentration of the resulting solutions (6 mM, 1 mM respectively). The lower concentration may have been used for PBASE in methanol as PBASE powder appears to dissolve poorly in methanol at higher concentrations. Cella *et al.*, Campos *et al.*, Zheng *et al.* and Ohno *et al.* all directly cite Chen *et al.* when discussing functionalisation with PBASE [5]–[8]. Other groups using PBASE for graphene or carbon nanotube functionalisation do not explicitly reference Chen *et al.* in their methodology, but it is apparent they often draw on one of these two original methods. This common ancestry becomes

apparent from the high frequency of methods detailing the use of 6 mM PBASE in DMF and 1 mM PBASE in methanol, as seen in Table 1.1.

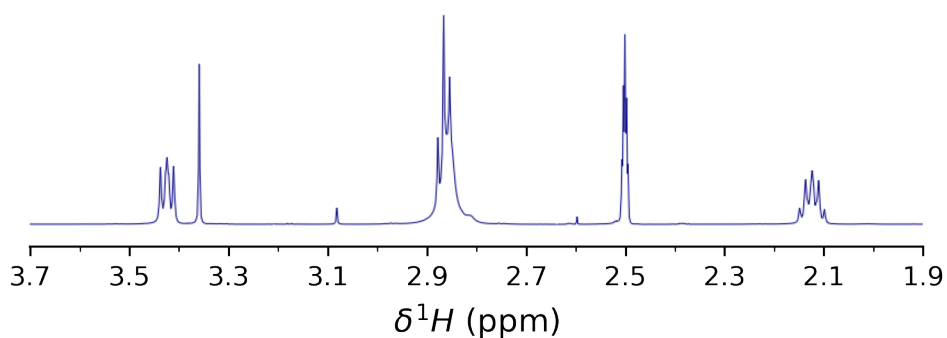
However, it is also apparent from Table 1.1 that there is a large degree of variation in the methods used for PBASE functionalisation. Various electrical characterisation, microscopy and spectroscopy techniques have been used to demonstrate successful functionalisation. However, there has historically been little justification provided for the exact parameters used in the procedure. As noted by Zhen *et al.* and Hinnemo *et al.*, there is more generally a lack of systematic research into formation of pyrene-derivative monolayers on graphene and other carbon nanomaterials, despite the wide use of this chemistry in the literature [9], [10].

We purchased PBASE from two suppliers, Sigma-Aldrich and Setareh Biotech. Sigma recommended DMF and methanol as suitable solvents for dissolving PBASE alongside chloroform and DMSO. Setareh Biotech indicated methanol can be used for dissolving PBASE. The two suppliers had conflicting information for suitable storage of PBASE, with Sigma recommending room temperature storage while Setareh Biotech recommends storage of  $-5$  to  $-30^{\circ}\text{C}$  and protection from light and moisture. Figure 1.2 compares the shapes of NMR spectra of PBASE from each supplier dissolved in DMSO, alongside a blank DMSO spectrum.

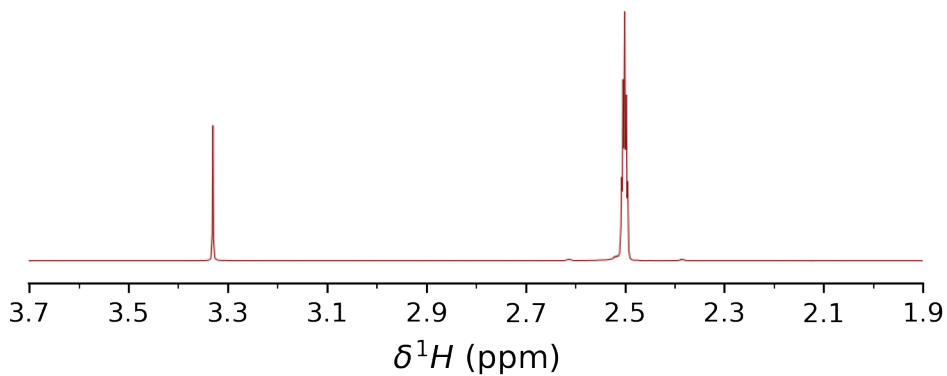
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(a)



(b)



(c)

Figure 1.2.:  $^1\text{H}$  Nuclear Magnetic Resonance (NMR) spectra, performed with DMSO- $\text{d}_6$  used as the NMR solvent. (a) and (b) show NMR spectrum for commercially purchased PBASE, from Sigma-Aldrich and Setareh Biotech respectively, while (c) shows the blank spectrum taken with only DMSO- $\text{d}_6$  present (spectra taken by Jennie Ramirez-Garcia).



### 1.1. Non-Covalent Functionalisation & Linker Molecules

Table 1.1.: Comparison of PBASE functionalisation processes used for immobilisation of proteins and aptamers onto liquid-gated CNTFET and graphene FET sensors

Solvent	Channel	Conc. (mM)	Incubation type	Time (hr)	Rinse steps	References
DMF	CNTs	5	Immersed	1	PBS	Maehashi <i>et al.</i> [11]
		6	Immersed	1	DMF, PBS	García-Aljaro <i>et al.</i> [12]
		6	Immersed	1	DMF	Chen <i>et al.</i> [4]
		6	Immersed	1	DMF	Cella <i>et al.</i> [5]
		6	Immersed	1	DMF	Das <i>et al.</i> [13]
	Graphene	-	-	2	DMF	Kwong Hong Tsang <i>et al.</i> [14]
		-	-	20	-	Wiedman <i>et al.</i> [15]
		0.2	Immersed	20	DMF, IPA, DI water	Gao <i>et al.</i> [16]
		1	100 $\mu$ L droplet	6	DMF, IPA, DI water	Nekrasov <i>et al.</i> [17]
		5	Immersed	1	DMF, DI water	Hwang <i>et al.</i> [18]
		5	Immersed	3	DMF	Hao <i>et al.</i> [19]
		6	6 $\mu$ L droplet	2	DMF, DI water	Nur Nasufiya <i>et al.</i> [20]
		10	10 $\mu$ L droplet	2	DMF, DI water	Campos <i>et al.</i> [6]
		10	Immersed	2	DMF, PBS	Kuscu <i>et al.</i> [21]
		10	Immersed	1	DMF	Xu <i>et al.</i> [22]
		10	Immersed	12	DMF, ethanol, DI water	Khan <i>et al.</i> [23]
2-Methoxyethanol	Graphene	1	Immersed	1	DI water	Ono <i>et al.</i> [24]
Methanol	CNTs	1	Immersed	1	Methanol, DI water	Zheng <i>et al.</i> [7]
		1	Immersed	2	Methanol	Kim <i>et al.</i> [25]
	Graphene	5	Immersed	2	-	Sethi <i>et al.</i> [26]
		5	Immersed	1	Methanol, PBS	Ohno <i>et al.</i> [8]
DMSO	CNTs	10	-	1	DI water	Lopez <i>et al.</i> [27]
		10	Immersed	1	PBS	Strack <i>et al.</i> [28]

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**1.2. Verifying Pyrene Attachment to CNT network and graphene**

**1.2.1. Photoresist contamination**

**1.2.2. Raman Spectroscopy**

**1.2.3. Pyrene-PEG-FITC fluorescence microscopy**

Plasma clean comparison

Surfactant comparison

**1.2.4. Pyrene-PEG electrical characterisation**

# A. Python Code for Data Analysis

## A.1. Code Repository

The code used for general analysis of field-effect transistor devices in this thesis was written with Python 3.8.8. Contributors to the code used include Erica Cassie, Erica Happe, Marissa Dierkes and Leo Browning. The code is located on GitHub and the research group OneDrive, and is available on request.

## A.2. Atomic Force Microscope Histogram Analysis

The purpose of this code is to analyse atomic force microscope (AFM) images of carbon nanotube networks in .xyz format taken using an atomic force microscope and processed in Gwyddion (see [?@sec-afm-characterisation](#)). It was originally designed by Erica Happe in Matlab, and adapted by Marissa Dierkes and myself for use in Python.

$$f(x) = k_1 \exp\left(-\frac{(x - m_1)^2}{2s_1^2}\right) + k_2 \exp\left(-\frac{(x - m_2)^2}{2s_2^2}\right) + \dots \quad (\text{A.1})$$

The .xyz data is initially sorted into bins with 0.15 nm size. The bin with the maximum number of counts is set at 0 nm, as this peak represents the mean of the surface roughness of the bare silicon. The parameters  $m_i$ ,  $s_i$ ,  $k_i$  ( $i = 1, 2, 3$ ) are used with objective function Equation A.1 to overlay the data with normal distributions. These fitting parameters represent the mean (m), standard deviation (s) and amplitude (k) of each normal distribution. We can make approximations of some of these fitting parameters using the histogram data.

$k_1$  is taken to be the maximum y-value of the data being fitted,  $m_1$  is set to zero (used as a point of reference) and  $s_1$  is taken as one-third of the difference between  $m_1$  and the x-value of the first datapoint where the y-value is greater than 1% of  $k_1$  (approximating one standard deviation). We find the distribution given by these values using Equation A.1, and subtract it from the existing dataset.

Then, using the analysis technique outlined by Vobornik *et al.* [29] in Gwyddion, we manually find estimates for the mean  $m_2$  and standard deviation  $s_2$  of the carbon nanotube bundle distribution. We then take  $k_2$  to be the maximum y-value of this modified

### A. Python Code for Data Analysis

dataset, and  $m_1$  to be the x-value of the maximum y-value. We then set  $k_2$  so that the height of the resulting distribution at one standard deviation matches the height of the .xyz data histogram. We take this distribution, and subtract it from the existing dataset.

The code also allows for discretely binning continuous data from fitted normal distributions and examining the proportion of counts above or below a particular height. 2.9 nm is roughly where 2 bundles with average size 1.45 nm can start to be present, and is used as an estimate of the boundary value between single-tube bundle diameters and multi-tube bundle diameters.

### A.3. Field-Effect Transistor Analysis

The purpose of this code is to analyse electrical measurements taken of field-effect transistor (FET) devices. Electrical measurements were either taken from the Keysight 4156C Semiconductor Parameter Analyser, National Instruments NI-PXIe or Keysight B1500A Semiconductor Device Analyser as discussed in **?@sec-electrical-characterisation**; the code is able to analyse data taken from all three measurement setups. The main Python file in the code base consists of three related but independent modules: the first analyses and plots sensing data from the FET devices, the second analyses and plots transfer characteristics from channels across a device, and the third compares individual channel characteristics before and after a modification or after each of several modifications. The code base also features a separate config file and style sheet which govern the behaviour of the main code. The code base was designed collaboratively by myself and Erica Cassie over GitHub using the Sourcetree Git GUI.

The first of the three modules is for processing sensing datasets. This module imports sensing measurements in .csv format and analyses them, then outputs a plot of the raw data, alongside multiple plots which have been modified in various ways. It can also fit exponential and linear trendlines to regions of the sensing data, as well as find the signal change per analyte addition, and returns spreadsheets containing the results of these analyses. These spreadsheets include the standard deviation for all included parameters. Modified plots include normalised plots (type of normalisation can be set in config file), plots with fitted curves, plots with the linear baseline drift removed, plots of signal with analyte addition, “despiked” plots and “filtered” plots. It is possible to add annotations to any of these plots using the config file, and it is possible to produce a plot with a combination of these modifications.

The `scipy.optimize.curve_fit` module is used to fit linear and exponential curves to regions of interest of the sensing data. Initial parameters for the `scipy.optimize.curve_fit` module are chosen by approximating fitting parameters in a similar manner to the approach in Section A.2. For a linear fit  $mt + b$ , the parameters are simply set as  $m = 1$  and  $b = 0$ . For an exponential fit  $a \exp(-t/\tau) + c$ ,  $c$  is set as the final current measurement of the

region of interest and  $a$  is set as the initial current measurement minus  $c$ . Then,  $\tau$  is set as the time where current has dropped to  $e^{-1}a + c$ .

“Despiked” plots have had spurious datapoints removed through the use of an interquartile range rolling filter. The window size of the rolling filter used was 40 datapoints, and datapoints in each window with a z-score above  $\pm 3$  were removed from the plotted/processed data. “Filtered” plots had noise reduced using a moving median filter. The moving median filter is more effective at removing noise than a simple moving average, and has advantages over other filters (such as the Savitzky-Golay filter) when removing noise from data with sharp edges, as is the case for sensing data. Median filtering can also be used for baseline drift compensation, though this approach was not used in this thesis [30]. The moving median filter used had a window of 40 datapoints.

Plots of signal with analyte addition were constructed from current data after first removing baseline drift and applying a moving median filter. A simple difference calculation between the mean of the filtered current before an addition and the mean of the filtered current after the addition was performed at each addition. These differences were then normalised relative to the initial current. The signal with analyte addition give reasonably consistent results regardless of whether baseline drift was removed from the data, as shown in Figure A.1. We can therefore be confident that robust signal with analyte addition plots are robust even in the presence of significant drift.

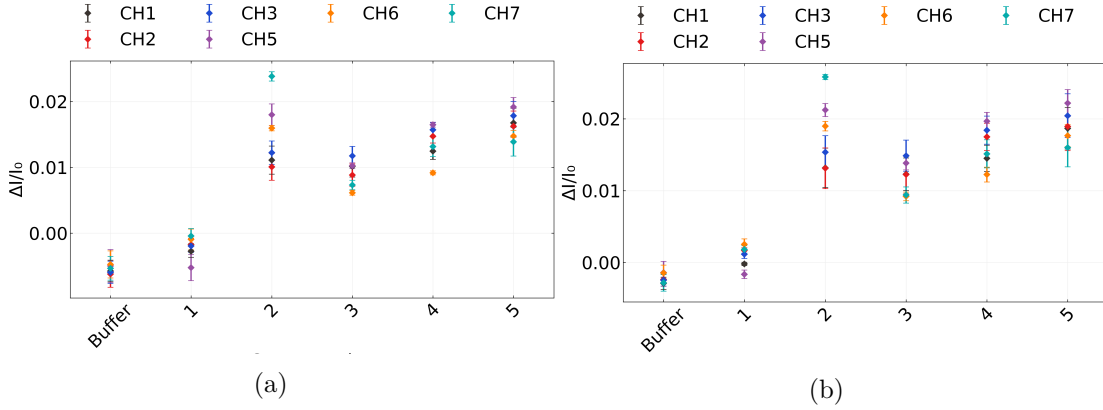


Figure A.1.: A comparison of signal with analyte addition plots taken from the same salt concentration sensing dataset (the same dataset as used in `?@fig-salt-conc-sensing`). In (a), a simple difference calculation performed on filtered data was used, while in (b) the same calculation was performed on filtered data with the baseline drift removed, the method used in the body of the thesis.

The second module imports transfer measurements in .csv format and creates combined and individual plots of the eight channels on a single device. In combined plots, channels which are non-working, due to being shorted or non-conducting, are removed via setting a maximum and minimum possible on-current in the config file. Various parameters from

### *A. Python Code for Data Analysis*

the transfer characteristics are saved as a spreadsheet along with standard error. These parameters include on current, off current, subthreshold slope and threshold voltage for the carbon nanotube devices, and on current, off current and major Dirac point voltage for graphene devices. The device type being analysed can be set in the config file.

The third module imports several transfer measurements in .csv format and allows for comparison of the same channel before and after some modification. It also calculates the shift in either threshold voltage or major Dirac voltage of the device.

## B. Vapour Delivery System

### B.1. Technical Notes

Two LabView Virtual Instruments (VIs) were adapted from pre-existing VIs for operating the mass flow controllers and monitoring vapour flow into the device chamber, as well as monitoring temperature and humidity in the vapour delivery system's manifold. These VIs were named " " A third VI was developed in parallel which combined the first two Virtual Instruments, alongside allowing the sequence of values to control the mass flow controllers.

From Honours report: " " Figure 12 gives the right side of the front panel of the LabView VI sample with vapour.VI, which lets us preset an autonomously-performed vapour sensing sequence. Each row in each array module corresponds to a different step in this sequence. The 'howManySteps' module lets us set how many of these steps are performed. The 'Durations Array' module determines the length of time in seconds each step is performed over. The 'Carrier Flows Array' and 'Dilution Flows Array' modules let us set the carrier flow and dilution flow, respectively, in standard cubic centimetres per minute (sccm) through the gas rig at each step. The carrier flow pushes analyte vapour into the vapour-sensing device chamber, while dilution flow is used to modify the flow behaviour of the analyte vapour entering the chamber. The vapour sensing sequence as depicted in Figure 12 was used for all vapour sensing runs in this investigation. At the end of the sequence, the data collected about the vapour sensing process was saved as an .lvm file. " " "

### B.2. Future Improvements





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