

# 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 bonding is weaker and therefore less stable than covalent bonding. However, non-covalent bonding has the advantage of having less of an impact on the structure of a nanomaterial than covalent bonding, and therefore is less likely to negatively affect the electrical properties of the transducer [1]–[4]. For example, one group found covalent bonding of diazonium linker

caused a  $\sim 50\%$  drop in graphene channel mobility [5]. In comparison, only a  $\sim 5\%$  drop in mobility was seen for attachment of a mixture of linkers containing pyrene to a graphene channel via non-covalent  $\pi$  stacking [6].

$\pi$  stacking or  $\pi - \pi$  interaction is often used to describe a type of non-covalent bonding which occurs due to dispersion forces between unsaturated polycyclic molecules [7]. It has been argued that this label is unhelpfully specific and a misrepresentation of what can be simply classed as a type of Van Der Waals bonding [7], [8]. However, as the use of the term is widespread in the literature, it is also used here for ease of reference. Carbon nanotubes and graphene consist of a network of carbon atoms attached to each other by  $sp^2$  hybrid orbitals in a polycyclic structure. They are therefore able to strongly interact with linker molecules with aromatic moieties, such as pyrene [4], [7], [9]. Figure 1.1 is a visual demonstration of the relationship between the pyrene-based linker molecule with the transducer and receptor elements.  $\pi - \pi$  stacking with pyrene is the bonding mechanism underlying all the functionalisation processes in this thesis.

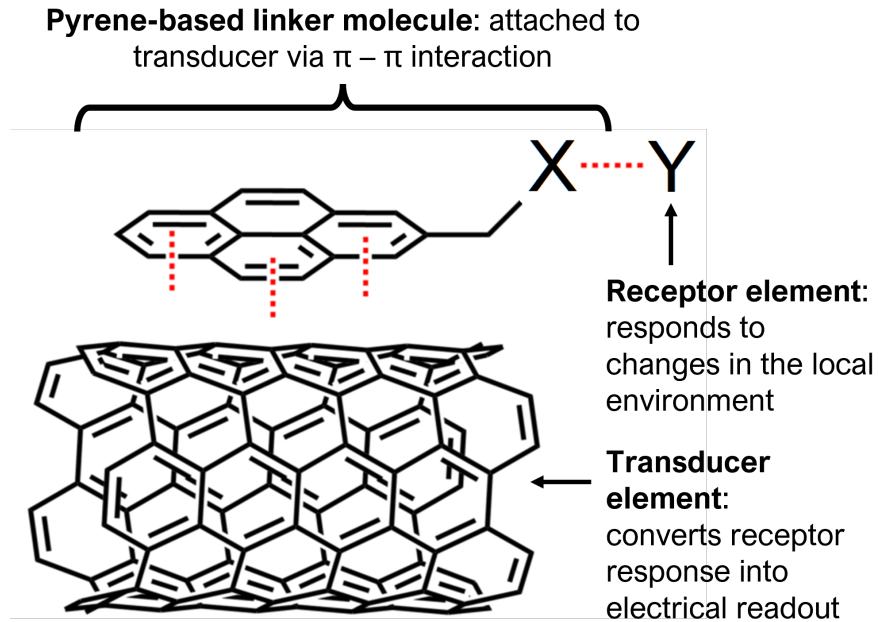


Figure 1.1.: Attachment of pyrene-based linker molecule pyrene-X and receptor Y to a carbon nanotube, representing the transducer element of a field-effect transistor. Source: Adapted from [10].

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

Table 1.1.: Comparison of PBASE functionalisation processes used for immobilisation of proteins and aptamers onto carbon nanotubes and graphene. Experimentally optimised variables are marked with a star (\*). Blank entries indicate there was no mention of the parameter in a particular paper.

Solvent	Channel	Conc. (mM)	Incubation type	Time (hr)	Rinse steps	References
DMF	CNT	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> [13]
		6	Immersed	1	DMF	Cella <i>et al.</i> [14]
		6	Immersed	1	DMF	Das <i>et al.</i> [15]
		6	-	2	DMF	Besteman <i>et al.</i> [16]
	Graphene	-	-	2	DMF	Kwong Hong Tsang <i>et al.</i> [17]
		-	-	20	-	Wiedman <i>et al.</i> [18]
		0.2	Immersed	20	DMF, IPA, DI water	Gao <i>et al.</i> [19]
		1	100 $\mu$ L droplet	6	DMF, IPA, DI water	Nekrasov <i>et al.</i> [20]
		5	Immersed	1	DMF, DI water	Hwang <i>et al.</i> [21]
		5*	Immersed	3*	DMF	Hao <i>et al.</i> [22]
		5	Immersed, with agitation	4*	DMF, DI water	Mishyn <i>et al.</i> [4]
		6	6 $\mu$ L droplet	2	DMF, DI water	Nur Nasufiya <i>et al.</i> [23]
		10	10 $\mu$ L droplet	2	DMF, DI water	Campos <i>et al.</i> [24]
		10	Immersed	2	DMF, PBS	Kuscu <i>et al.</i> [25]
		10	Immersed	1	DMF	Xu <i>et al.</i> [26]
		10	Immersed	12	DMF, ethanol, DI water	Khan <i>et al.</i> [27]
		50	Immersed	4*	Methanol	Wang <i>et al.</i> [3]
2-Methoxyethanol	Graphene	1	Immersed	1	DI water	Ono <i>et al.</i> [28]
Methanol	CNT	1	Immersed	1	Methanol, DI water	Zheng <i>et al.</i> [29]
		1	Immersed	2	Methanol	Kim <i>et al.</i> [30]
		100	2 $\mu$ L droplet	1	DI water	Yoo <i>et al.</i> [31]
	Graphene	5	Immersed	2	-	Sethi <i>et al.</i> [32]
		5	Immersed	1	Methanol, PBS	Ohno <i>et al.</i> [33]
DMSO	CNT	10	-	1	DI water	Lopez <i>et al.</i> [34]
		10	Immersed	1	PBS	Strack <i>et al.</i> [35]

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

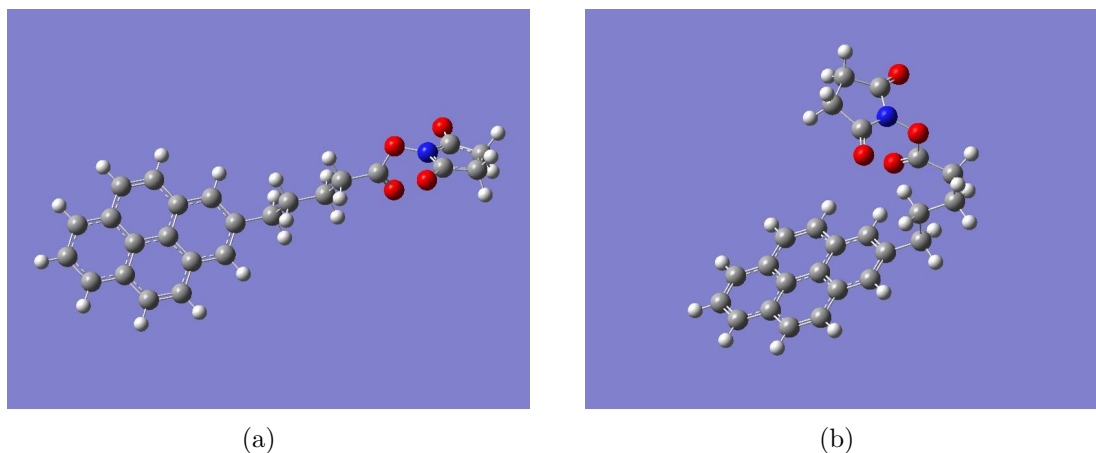


Figure 1.2.: Two conformations of PBASE molecule with geometry optimised via *ab initio* calculations (computed using Gaussian 16 [36]). White balls correspond to hydrogen, grey to carbon, red to oxygen and blue to nitrogen. The conformation in (a) has a Hartree-Fock energy of -3427728.67 kJ/mol, while the conformation in (b) has a Hartree-Fock energy of -3427729.66 kJ/mol. The difference between computed Hartree-Fock energies is 1.0 kJ/mol, small enough that the existence of both molecular conformations is physically feasible.

1-Pyrenebutanoic acid N-hydroxysuccinimide ester (variously known commercially and in the literature as 1-Pyrenebutyric acid N-hydroxysuccinimide ester, PBASE, PBSE, PASE, Pyr-NHS, PyBASE, PANHS) is a aromatic, bifunctional molecule commonly used for tethering biomolecules to the carbon rings of graphene and carbon nanotubes. The molecular structure of PBASE is shown in Figure 1.2. Two locally stable molecular conformations were found to exist, a straight (Figure 1.2a) and bent (Figure 1.2b) structure. Similar locally stable structures have previously been computed for PBASE attached to graphene [37]. The pyrene moiety, seen at the bottom of the molecular structure, non-covalently bonds to the carbon rings of the carbon nanotube and graphene surface. An N-hydroxysuccinimide (NHS) ester group is found at the top of the molecular structure, attached to the rest of the molecule via a O-C bond. The NHS ester group is highly reactive with amine groups; it can undergo a nucleophilic substitution reaction with amines attached to proteins or aptamers, tethering these biomolecules via an amide or imide bond [4], [9], [13], [38].

The non-covalent functionalisation of proteins onto a single-walled carbon nanotube using PBASE was first reported by Chen *et al.* in 2001 [13]. 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 con-



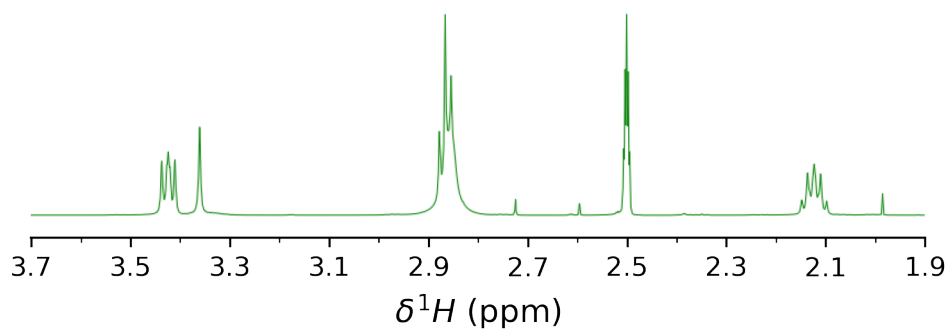
centration may have been used for PBASE in methanol as PBASE powder appears to dissolve poorly in methanol at higher concentrations. Several groups directly cite Chen *et al.* when discussing functionalisation with PBASE [14], [16], [24], [29], [33]. Other groups using PBASE for graphene or carbon nanotube 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 dimethylformamide (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. Until recently, there has been little justification provided for the selection of variables used in the functionalisation procedure (e.g. length of time submerged in solvent containing PBASE), despite the wide-ranging use of this process in the literature [3], [39], [40]. This is surprising, given that the sensitivity of functionalised devices is considered to be closely related to the density of surface functionalisation [38], [41], [42]. Furthermore, a detailed investigation of PBASE functionalisation process variables has only been undertaken for graphene-based devices [3], [4], [22], [40].

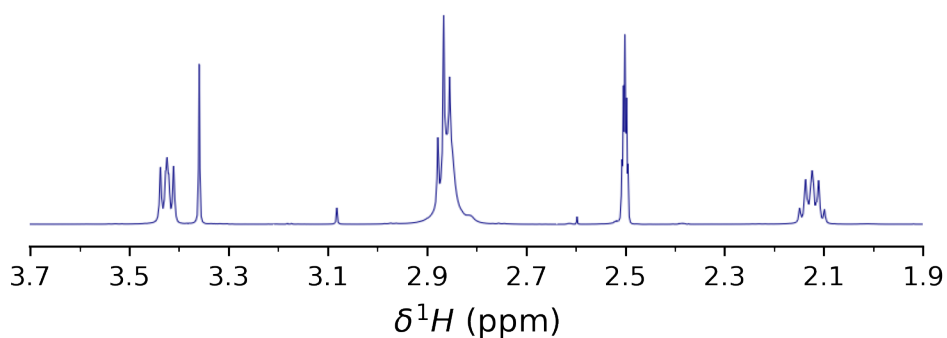
Zhen *et al.*, Wang *et al.* and Mishyn *et al.* claim that carefully tuning the surface concentration of PBASE is required to avoid multilayer coverage of the graphene surface, as this negatively impacts sensing. Mishyn *et al.* use cyclic voltammetry to demonstrate that less receptor attachment to the graphene surface occurs when multiple layers of PBASE are present. However, neither group lends further support to their claim by performing analyte sensing using their functionalised graphene devices [4], [40]. In contrast, Hao *et al.* find that maximising surface coverage of PBASE results in more sensitive aptameric sensing, thus drawing the opposite conclusion [22]. The inconsistency in these recent findings mean more work is needed to understand the PBASE functionalisation process to achieve optimal biosensor sensitivity. It may also be the case that a specific functionalisation process is required for optimal sensitivity with the use of a specific type of receptor.

Once fastened to a bioreceptor via an amide or imide bond, the attachment to the linker molecule is not easily broken. However, prior to use in functionalisation processes, the NHS ester may react with any water present (hydrolysis). This reaction converts PBASE to 1-pyrenebutyric acid (PBA), leaving it unavailable to react further with amine groups [4], [38], [43]. If the amine group functionalisation is performed within a  $\sim 1$  hour period, with a high concentration of bioreceptor used at close to neutral pH, competing hydrolysis should not have an overly adverse impact on the functionalisation process [38]. However, if PBASE is exposed to water during storage over a significant length of time, the presence of 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and N-Hydroxysuccinimide (NHS) can be used to restore the NHS ester and enable the substitution reaction to take place (see discussion of EDC in Section 1.1.2).

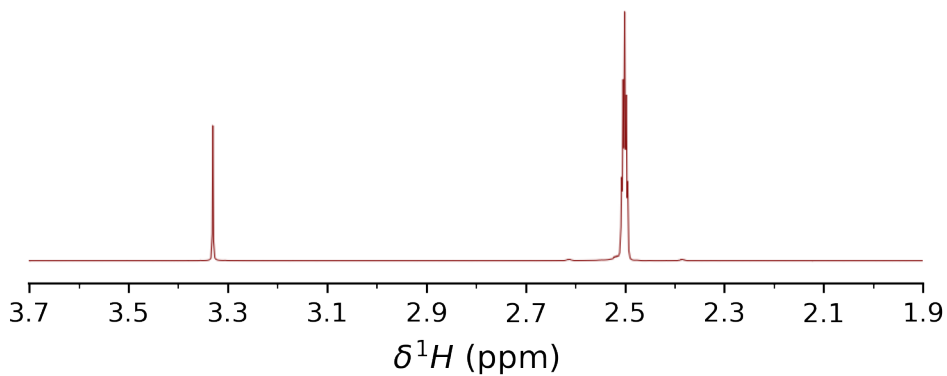
1. Verifying Non-Covalent Functionalisation of Carbon Nanotubes and Graphene



(a)



(b)



(c)

Figure 1.3.:  $^1\text{H}$  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).

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 dimethyl sulfoxide (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. Given the long travel time of the PBASE samples under uncertain storage conditions, we used nuclear magnetic resonance (NMR) spectroscopy to verify the purity of the PBASE as recieved from each supplier. In light of the negative effect of water on PBASE, in particular we wanted to find out if any water was present in the samples.

Figure 1.3 compares the shapes of hydrogen (NMR) spectra of PBASE from each supplier when dissolved in deuterated DMSO, alongside a blank deuterated DMSO spectrum. We see both PBASE samples possess characteristic chemical shift features between  $2.1 - 2.2$  ppm,  $2.8 - 2.9$  ppm, and  $3.4 - 3.5$  ppm. These chemical shifts roughly correspond to those seen in previous NMR spectra for PBASE [44]. The feature at  $2.50$  ppm represents the deuterated DMSO solvent, while the single peak between  $3.3 - 3.4$  ppm represents the water present in the sample. By comparing the area of these peaks, we can estimate the amount of water originally present in the PBASE sample. The  $\text{H}_2\text{O}:\text{DMSO}$  ratio is  $1:7$  in the blank spectrum, but  $\sim 1:3$  in the provided samples, possibly indicating the introduction of water to the PBASE during production or storage. However, DMSO is strongly hygroscopic and slight differences in DMSO storage time, as well as differences in humidity during sample preparation, may have had a significant impact on this result [45]. Other impurities are also seen on both PBASE spectra, though their small size indicates they make up only a small percentage of each sample. Note that Strack *et al.* recommend leaving frozen PBASE at room temperature for 15 minutes before opening to prevent the introduction of condensation [35].

The electrical characteristics of the carbon nanotube or graphene transistor are often used to verify successful functionalisation and make a statement about the effect of chemical modification on the channel. However, this verification usually does not account for the effect of the solvent on the transistor channel. Figure 1.4a and Figure 1.4b show that by exposing a carbon nanotube network channel to solvents commonly used in PBASE functionalisation processes (Table 1.1), such as methanol (MeOH) or dimethyl sulfoxide (DMSO), a significant negative shift in channel threshold voltage occurs even after thorough rinsing with deionised water. Besteman *et al.* reported observing a similar effect from prolonged exposure of a single carbon nanotube to dimethylformamide (DMF) [16]. It appears that the carbon nanotubes have adsorped solvent which persists even after device cleaning. From the shape of the change in the transfer curve, it seems the residual polar solvent molecules capacitively gate the channel [46], [47].

In contrast, previous work has shown that  $\pi$ -stacking carbon nanotube network to PBASE does not significantly affect the channel gating and therefore the channel threshold voltage [16], [48]. Murugathas *et al.* observed a slight increase in channel conductance after PBASE functionalisation. In Figure 1.4, we also observe a slight increase in

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

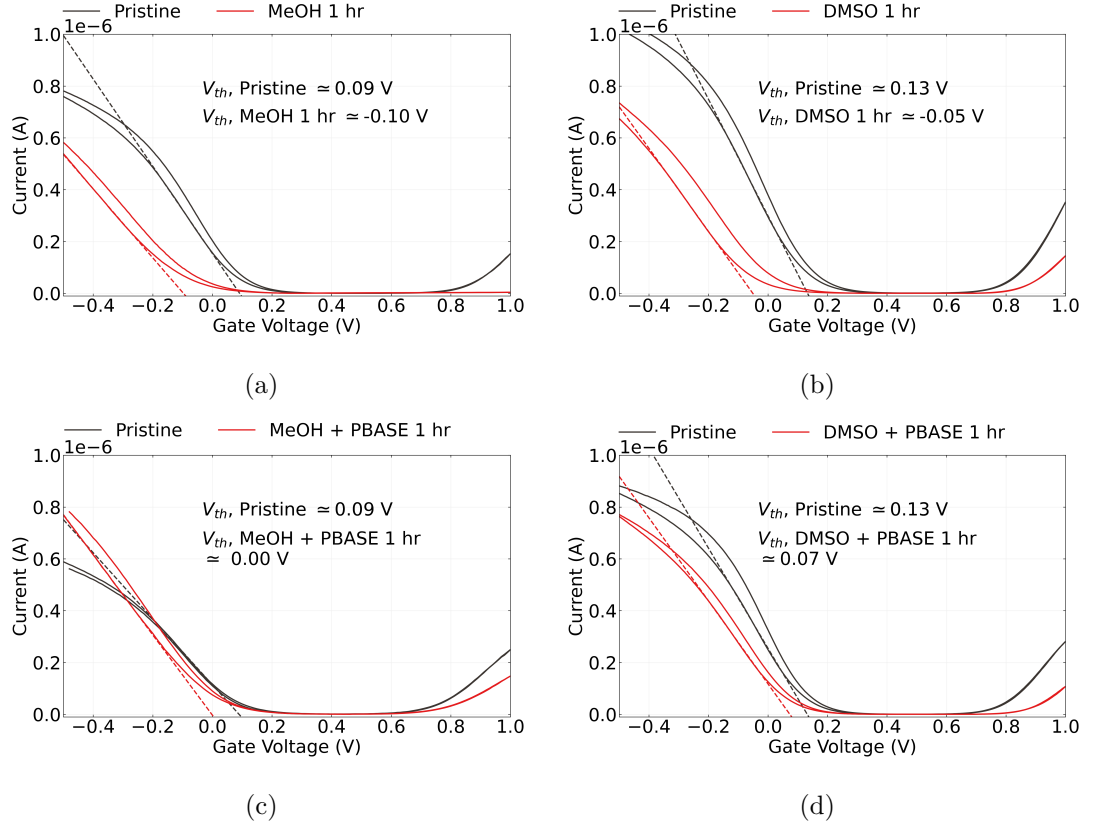


Figure 1.4.: The change in the electrical transfer characteristics of carbon nanotube transistors after being submerged in solvent for one hour and then rinsed thoroughly is demonstrated in (a) and (b), where the solvents used are methanol (MeOH) and dimethyl sulfoxide (DMSO) respectively. The change in characteristics of similar transistor channels after being submerged in these same solvents for one hour along with 1 mM PBASE then rinsed are shown in (c) and (d) respectively. Threshold voltages for each transfer characteristic are also shown.

channel conductance post-functionalisation for both Figure 1.4c and Figure 1.4d relative to the solvent only case in Figure 1.4a and Figure 1.4b. This result indicates that the presence of PBASE molecules increases channel conductance due to additional pathways provided by the presence of PBASE [47], [48].

Capacitive gating results from dense coverage of adsorbed molecules on the carbon nanotube surface which have a low permittivity relative to the surrounding electrolyte [47]. The relative permittivity of MeOH and DMSO are  $\sim 33$  [49] and  $\sim 47$  [50] respectively, which are both much lower than  $\sim 80$ , the relative permittivity of phosphate buffer saline [51]. From Figure 1.4a and Figure 1.4b, we find the average threshold shift values resulting from exposure to each solvent were  $\Delta V = -0.18 \pm 0.03$  V and  $\Delta V = -0.17 \pm 0.02$  for MeOH and DMSO respectively. The threshold voltage shift in Figure 1.4c and Figure 1.4d are comparatively small - this is likely due to the effect of increased conductance from the PBASE competing with the gating effect from the residual solvent.

This example illustrates why the use of electrical characteristics when making conclusions around a successful functionalisation process should individually take into account each substance used in the process. The qualitative presence of a change in characteristics (or lack of one) over the full process is not sufficient to make conclusive remarks about the electrical changes due to functionalisation. A full set of electrical control measurements are required for an understanding of electronic changes occurring during the functionalisation process, in the manner of Besteman *et al.* [16].

### 1.1.2. Other Pyrene-Based Linkers

#### 1-Pyrenebutyric Acid (PBA) with EDC/NHS

Another linker molecule that can be used to attach receptor molecules to a carbon nanotube or graphene channel is 1-pyrenebutyric acid (PBA). As with PBASE, the pyrene group of PBA has a  $\pi$  interaction with the carbon rings of the channel surface. It is possible to react PBA with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC or EDAC) to form an *O*-acylisourea intermediate, which can then react with an amine group on a biomolecule and form an amide bond [52], [53]. The water solubility of EDC means that, unlike PBASE, it is possible to functionalise with EDC dissolved in water rather than in an organic solvent. However, like PBASE, EDC and the *O*-acylisourea intermediate are prone to hydrolysis, especially in acidic conditions. Therefore, like PBASE, it should be stored at  $-20^\circ\text{C}$ , and warmed to room temperature to prevent condensation build-up, since exposure to condensation will hydrolyse the reagent [52]. Furthermore, N-Hydroxysuccinimide (NHS) or N-hydroxysulfosuccinimide (sulfo-NHS) can

As mentioned in Section 1.1.1, it is possible to convert the carboxylic acid group of PBA into a reactive NHS group using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide

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

hydrochloride (EDC or EDAC), forming molecules of PBASE. As described earlier, the attached PBASE can then form amide or imide bonds with proteins or aptamers.

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

Table 1.2.: Comparison of 1-pyrenebutyric acid (PBA) functionalisation processes used for immobilisation of proteins and aptamers onto carbon nanotubes and graphene. 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and NHS were co-mingled in buffer/electrolyte solution or DI water in each process - some papers used N-hydroxysulfosuccinimide instead of N-hydroxysuccinimide, and both compounds are abbreviated to NHS in this table. <sup>†</sup>PEG or PEG pyrene were used to reduce non-specific binding. <sup>††</sup>Several pyrene-based linkers were compared and PBA was found to give an optimal result.

Solvent	Channel	PBA (mM)	PBA Time (hr)	EDC (mM)	NHS (mM)	EDC/NHS Time (hr)	References
DMF	Graphene	0.6	1	-	-	120	Gao <i>et al.</i> <sup>†</sup> [54]
		5	2	2	5	30	Mishyn <i>et al.</i> [4]
	CNT	100	3	200	-	30	Min <i>et al.</i> [55]
DI water	CNT	-	-	32	12	Overnight	Pacios <i>et al.</i> <sup>†</sup> [56]
Ethanol	CNT	1	1	100	100	20	Filipiak <i>et al.</i> <sup>†</sup> [57]
Acetonitrile	Graphene	1	1	400	100	60	Tong <i>et al.</i> <sup>††</sup> [58]
Borax solution	CNT	2	24	2.5	-	1080	Liu <i>et al.</i> <sup>†</sup> [59]
DMSO	Graphene	5	1	50	50	90	Fenzl <i>et al.</i> [60]

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

More reliable re hydrolysis but problem is it introduces more variables (see table)

**Pyrene-PEG-NTA and Pyrene-PEG-Biotin**

### **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.* [61] 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 [62]. 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.

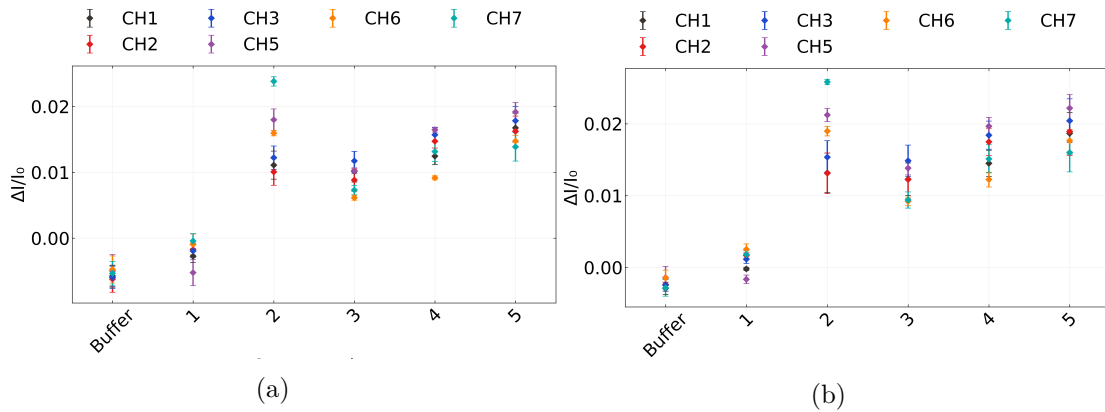


Figure A.1.: A comparison of signal with analyte addition plots taken from the same salt concentration sensing dataset (the same dataset as used in `?@fig-salt-conc-sensing`). In (a), a simple difference calculation performed on filtered data was used, while in (b) the same calculation was performed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