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

by

Eddyn Oswald Perkins Treacher

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School of Physical and Chemical Sciences
Te Herenga Waka - Victoria University of Wellington

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Acknowledgements

Thanks for all the fish.

Abstract

This is a thesis skeleton written with quarto. Make a copy of this thesis repo and start to write!

Make a new paragraph by leaving a blank line.

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1. Introduction

This is a book created from markdown and executable code.

See for additional discussion of literate programming.

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2. Carbon Nanotube and Graphene Field-Effect Transistors

2.1. Device Functionalisation

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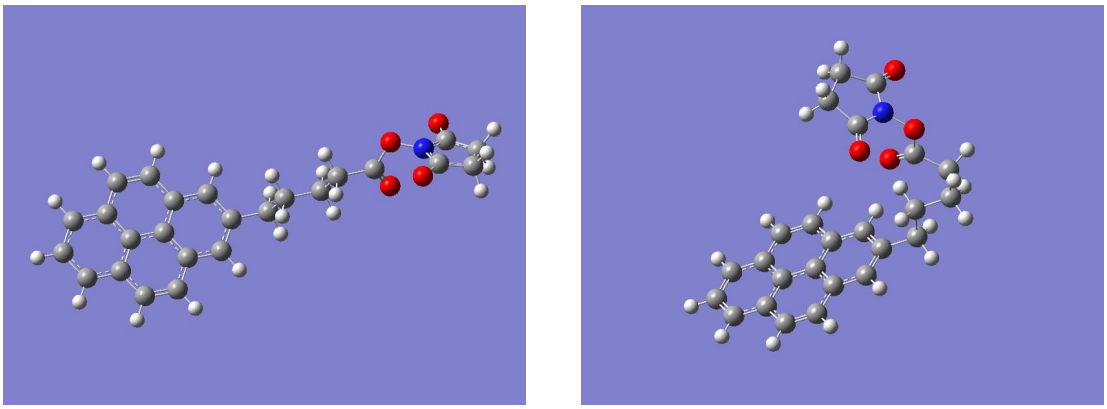
4. Fabrication

Stuff I did to get the results.

5. Functionalisation of Carbon Nanotubes and Graphene with Odorant Receptors

5.1. Linker molecules

5.1.1. 1-Pyrenebutanoic acid N-hydroxysuccinimide ester (PBASE)



(a) Hartree-Fock energy: -3427728.67 kJ/mol (9 s.f.)

(b) Hartree-Fock energy: -3427729.66 kJ/mol (9 s.f.)

Figure 5.1.: Two conformations of PBASE molecule with geometry optimised via *ab initio* calculation (computed using Gaussian 16 [1]). The difference between computed Hartree-Fock energies is 1.0 kJ/mol, small enough that the existence of both molecular conformations is physically possible.

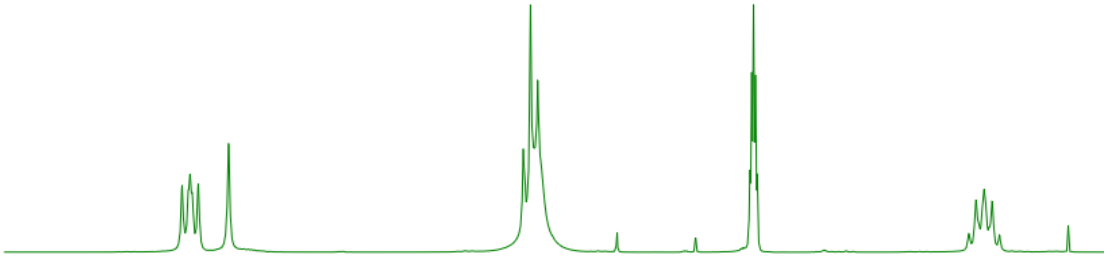
1-Pyrenebutanoic acid N-hydroxysuccinimide ester (variously known commercially and in the literature as 1-Pyrenebutyric acid N-hydroxysuccinimide ester, PBASE, PBSE, PASE, Pyr-NHS, PyBASE, PANHS) is a aromatic, bifunctional molecule commonly used for tethering biomolecules to the carbon rings of graphene and carbon nanotubes. The optimised molecular structure of PBASE is shown in Figure 5.1.

The non-covalent functionalisation of proteins onto a single-walled carbon nanotube using PBASE was first reported by Chen *et al.* in 2001 [2]. 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

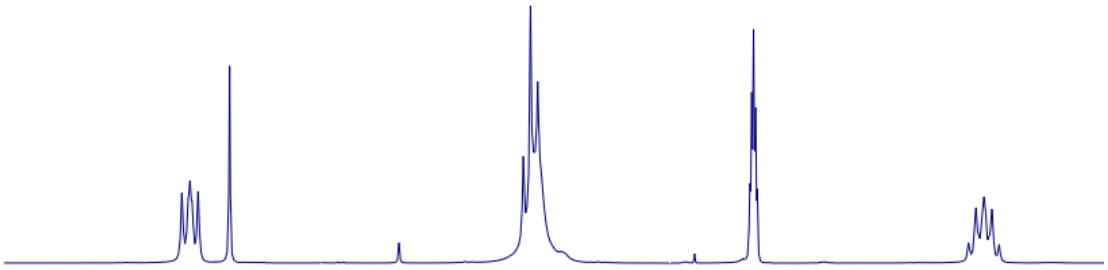
concentration of the resulting solutions (6 mM, 1 mM respectively). The lower concentration may have been used for PBASE in methanol as PBASE powder appears to dissolve poorly in methanol at higher concentrations. Cella *et al.*, Campos *et al.*, Zheng *et al.* and Ohno *et al.* all directly cite Chen *et al.* when discussing functionalisation with PBASE [3]–[6]. 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 5.1.

However, despite this shared heritage, it is also apparent from Table 5.1 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 [7], [8].

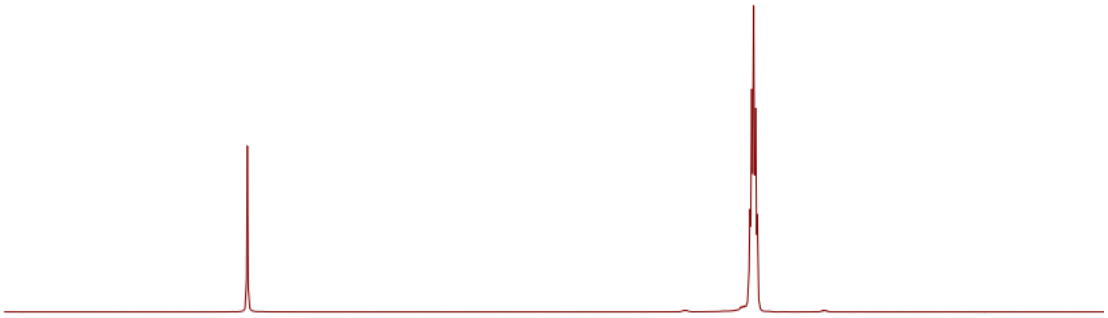
We purchased PBASE from two suppliers, Sigma-Aldrich and Setareh Biotech. Sigma recommends DMF and methanol as suitable solvents for dissolving PBASE alongside chloroform and DMSO. Setareh Biotech indicates methanol can be used for dissolving PBASE. The two suppliers have conflicting information for suitable storage of PBASE, with Sigma recommending room temperature storage while Setareh Biotech recommends storage of -5 to -30°C and protection from light and moisture. Figure 5.2 compares the shapes of NMR spectra of PBASE from each supplier dissolved in DMSO, alongside a blank DMSO spectrum.



(a) Sigma PBASE in DMSO



(b) Setareh PBASE in DMSO



(c) Blank (DMSO only)

Figure 5.2.: Comparison of NMR spectrum profiles (arbitrary units)

Table 5.1.: 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 *et al.* [9]
		6	Immersed	1	DMF, PBS	García-Aljaro *et al.* [10]
		6	Immersed	1	DMF	Chen *et al.* [2]
		6	Immersed	1	DMF	Cella *et al.* [3]
		6	Immersed	1	DMF	Das *et al.* [11]
	Graphene	-	-	2	DMF	Kwong Hong Tsang *et al.* [12]
		-	-	20	-	Wiedman *et al.* [13]
		0.2	Immersed	20	DMF, IPA, DI water	Gao *et al.* [14]
		1	100 μL droplet	6	DMF, IPA, DI water	Nekrasov *et al.* [15]
		5	Immersed	1	DMF, DI water	Hwang *et al.* [16]
		6	6 μL droplet	2	DMF, DI water	Nur Nasufiya *et al.* [17]
		10	10 μL droplet	2	DMF, DI water	Campos *et al.* [4]
		10	Immersed	2	DMF, PBS	Kuscu *et al.* [18]
		10	Immersed	1	DMF	Xu *et al.* [19]
		10	Immersed	12	DMF, ethanol, DI water	Khan *et al.* [20]
2-Methoxyethanol	Graphene	1	Immersed	1	DI water	Ono *et al.* [21]
Methanol	CNTs	1	Immersed	1	Methanol, DI water	Zheng *et al.* [5]
		1	Immersed	2	Methanol	Kim *et al.* [22]
	Graphene	5	Immersed	2	-	Sethi *et al.* [23]
		5	Immersed	1	Methanol, PBS	Ohno *et al.* [6]
DMSO	CNTs	10	-	1	DI water	Lopez *et al.* [24]
		10	Immersed	1	PBS	Strack *et al.* [25]

6. Results

What I found out.

See for more detailed results

7. Vapour Phase Sensing with Transistor Biosensors

7.1. Testing Vapour Delivery System

7.1.1. System Description

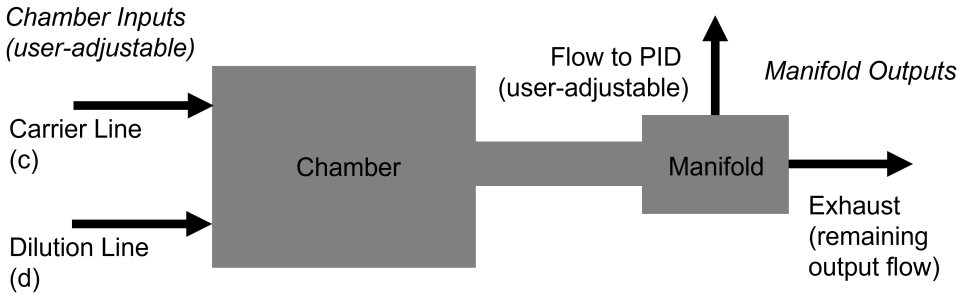


Figure 7.1.: Vapour Delivery System - Schematic of device chamber and manifold

7.1.2. Temperature and Humidity Indicator

7.1.3. Photoionisation Detector

Bubbling Vapour

First year report: “ ““First, a 200 sccm flow of N2 gas was sent through the dilution line to the device chamber until 1000 s. Then, the flow controller three-way valves were manually adjusted so that the same 200 sccm flow was directed through 50 mL of EtOH analyte in the carrier line. This continued until 2200 s, where the valves were again manually adjusted so that 200 sccm clean N2 again flowed through the device chamber. The resulting current across the device channel was monitored over this time, and is shown in Figure 19. A response to EtOH exposure and removal is visible.”“ ”

8. Summary

In summary, this book has no content whatsoever.

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A. More results

Some results that wouldn't fit into the main thesis

B. Another appendix

Something else

C. Vapour Delivery System

C.1. Technical Notes

Two LabView Virtual Instruments are used for the operation of the mass flow controllers and for monitoring vapour flow into the device chamber, as well as the temperature and humidity of the vapour delivery system's manifold.

From Honours report: " " Figure 12 gives the right side of the front panel of the LabView VI sample with vapour.VI, which letsus 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. " "

C.2. Future Improvements

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