

# Towards Explosives Detection Using Functional Polyaromatic Hydrocarbon Materials

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## Abstract

During this research several phosphorus based compounds were synthesised from polyaromatic hydrocarbon (PAH). In turn these have been complexed to a platinum(II) metal centre. The syntheses are centred around compounds containing a naphthalene backbone, which have potential to act as a fluorophore.

## Introduction

Explosives have been used for many applications within the military and are employed by industry. They are however, increasingly involved in acts of terrorism. With the growing global concerns over the actions of terrorists, enhancements in national security and defence are required to rapidly monitor and detect the presence of high explosives. This must take place in a fast, efficient and economically viable fashion.<sup>1</sup> Nitrated compounds are a popular choice of explosives and come in many forms, these include: nitroaromatics, nitramines, nitrate esters and nitroaliphatics. The detection of explosives is a key area of interest within research and development. Current research has focused around larger molecules, figure 1, synthesised using several steps.<sup>1,2</sup> As a working model, we have employed the strategy outlined in figure 2 for the potential detection of nitroaromatics. The key motif here is the presence of a PAH thereby acting as a fluorophore. In this study the smallest PAH based on naphthalene has been used.

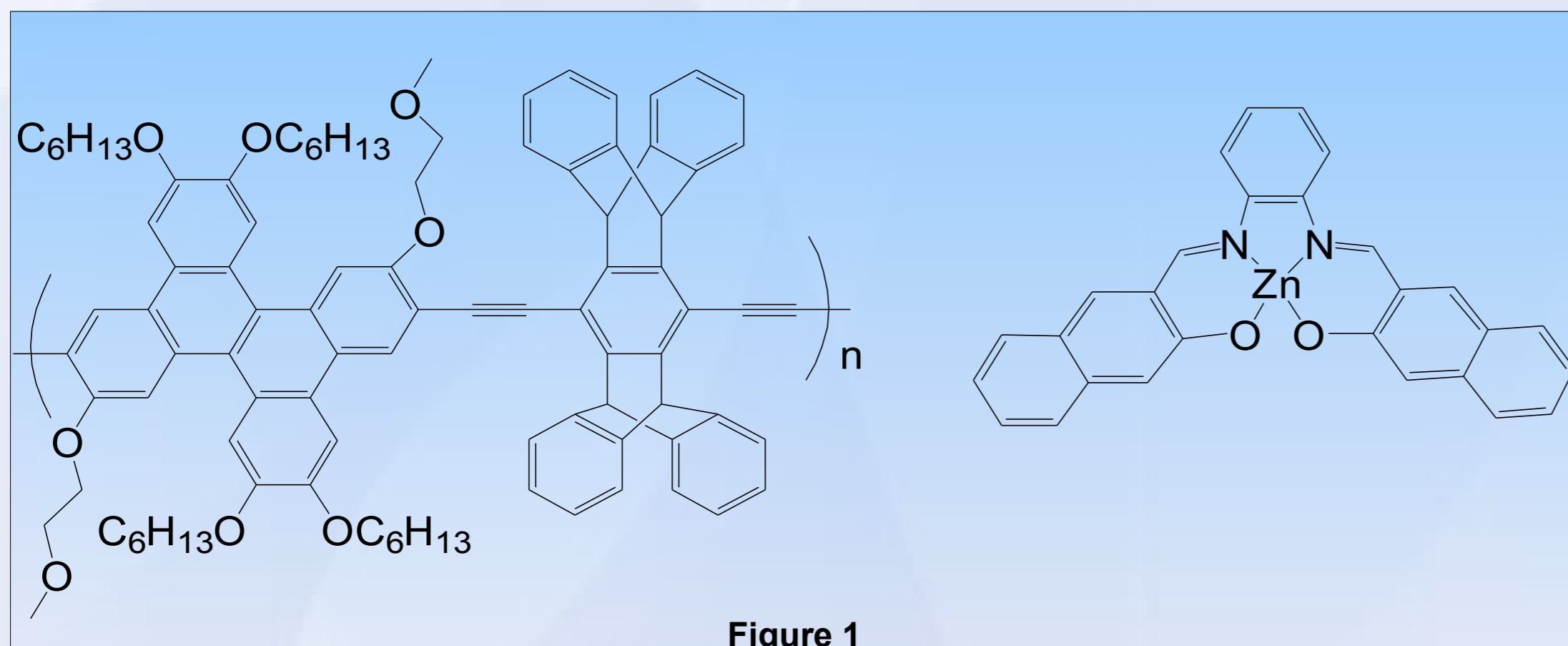


Figure 1

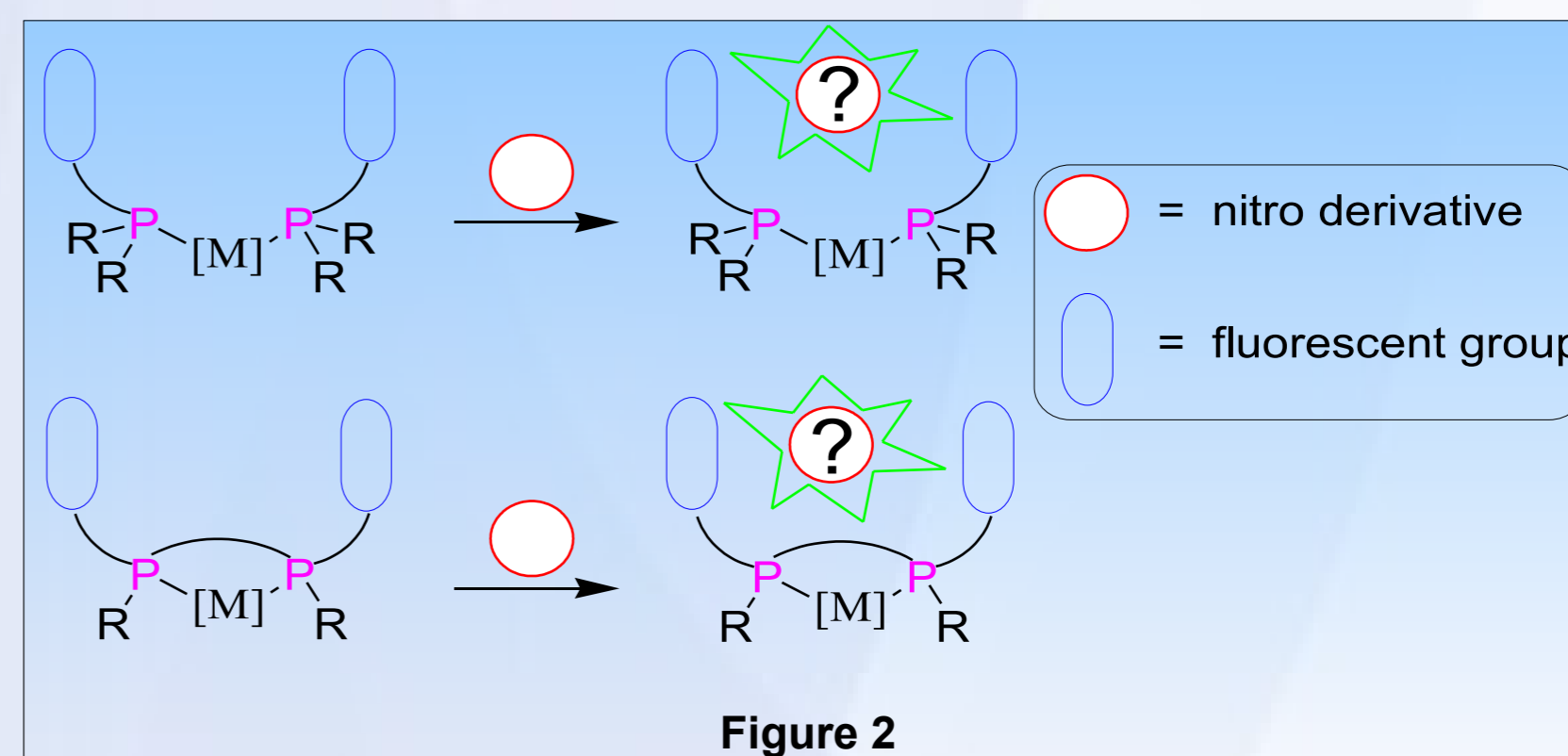


Figure 2

## Results and Discussion

### Step 1

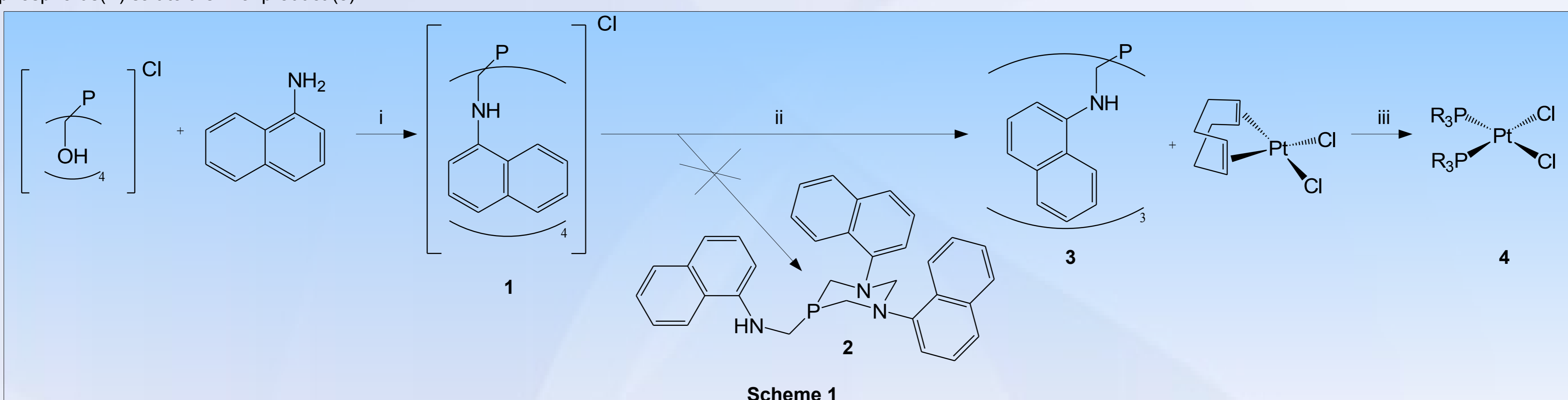
Using a modified literature method<sup>3</sup>, 1-aminonaphthalene was reacted in a 4:1 ratio with tetrakis(hydroxymethyl)phosphonium chloride (THPC). When isolated, the product was found to be a phosphonium salt, as supported via NMR and elemental analysis. This showed the substrate was of lower base strength than stated in the literature, in which the reaction proceeded to yield a tertiary phosphine product. Due to the lower base strength, an intermediate step was employed to reduce the phosphorus(V) salt to the final product (3).

### Step 2

To facilitate the reduction of 1, triethylamine was first employed. This was found initially to give a poor yield. This led to a series of optimisation reactions for this substrate, in which changes including solvent levels and molar equivalents of triethylamine were trialled. All of these reactions showed little change in yield. In the final reaction, a stronger base - potassium *tert*-butoxide was used. This afforded a greater yield, along with a sample of high phosphorus purity. When analysed, the reaction yielded an unexpected product, 3. This led to a revision of the previously expected structure 2.

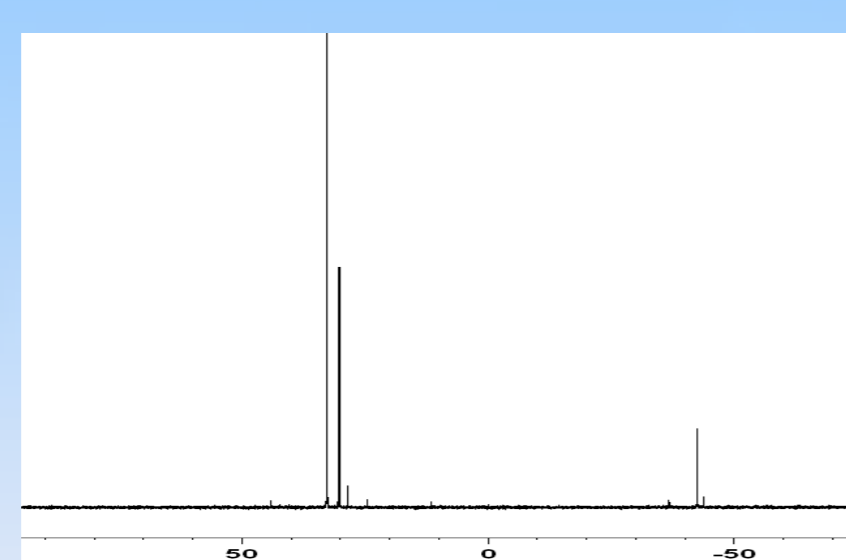
### Step 3

The final step in this reaction scheme was the formation of a complex with a platinum(II) metal centre. This reaction utilises a simple ligand substitution, in which the labile cyclooctadiene ligand is displaced by 3 whilst retaining a square planar geometry about the metal centre. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 4 showed a <sup>1</sup>J<sub>PtP</sub> coupling of 3482 Hz.

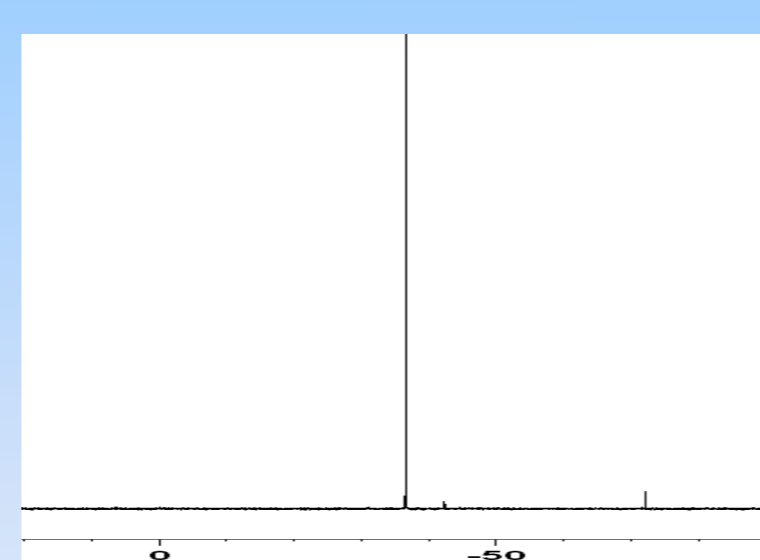


Scheme 1

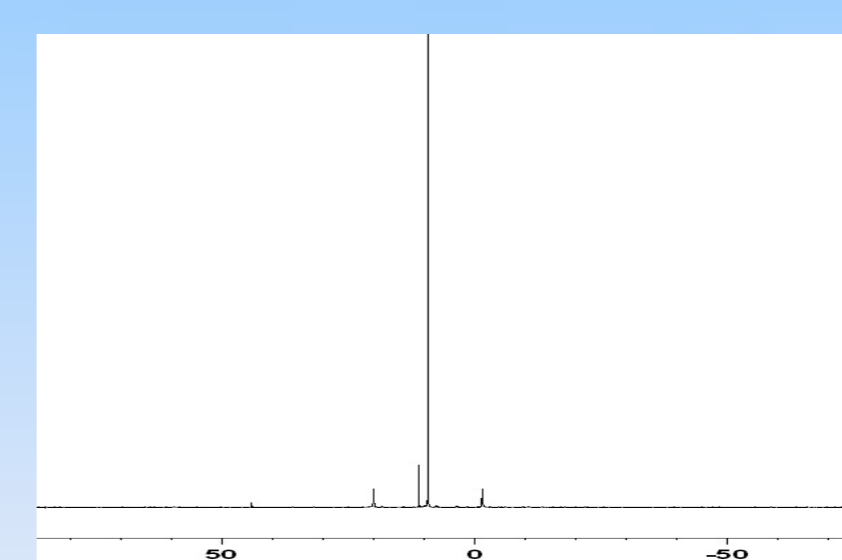
### <sup>31</sup>P{<sup>1</sup>H} NMR spectra for compounds 1, 3 and 4.



NMR spectrum of 1



NMR spectrum of 3



NMR spectrum of 4

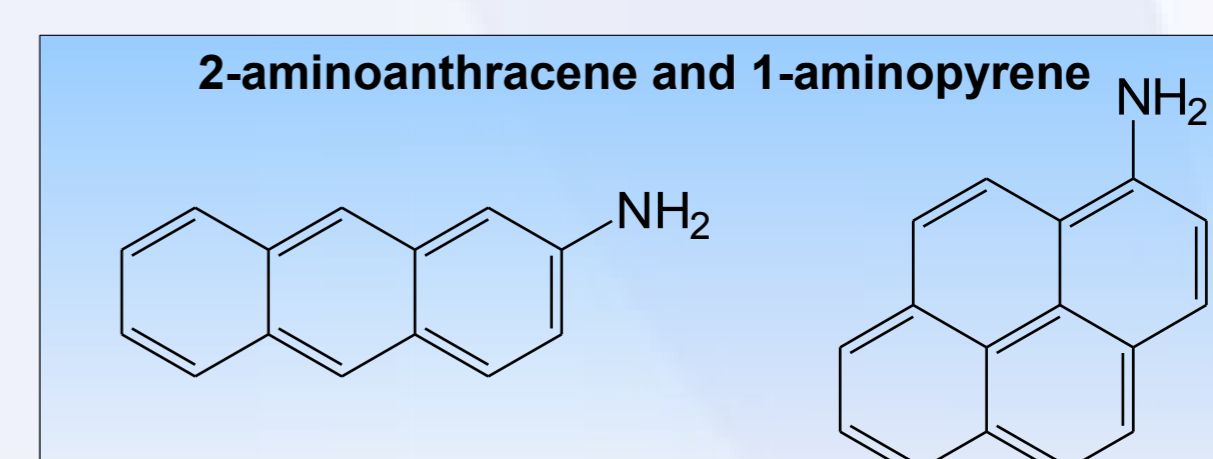
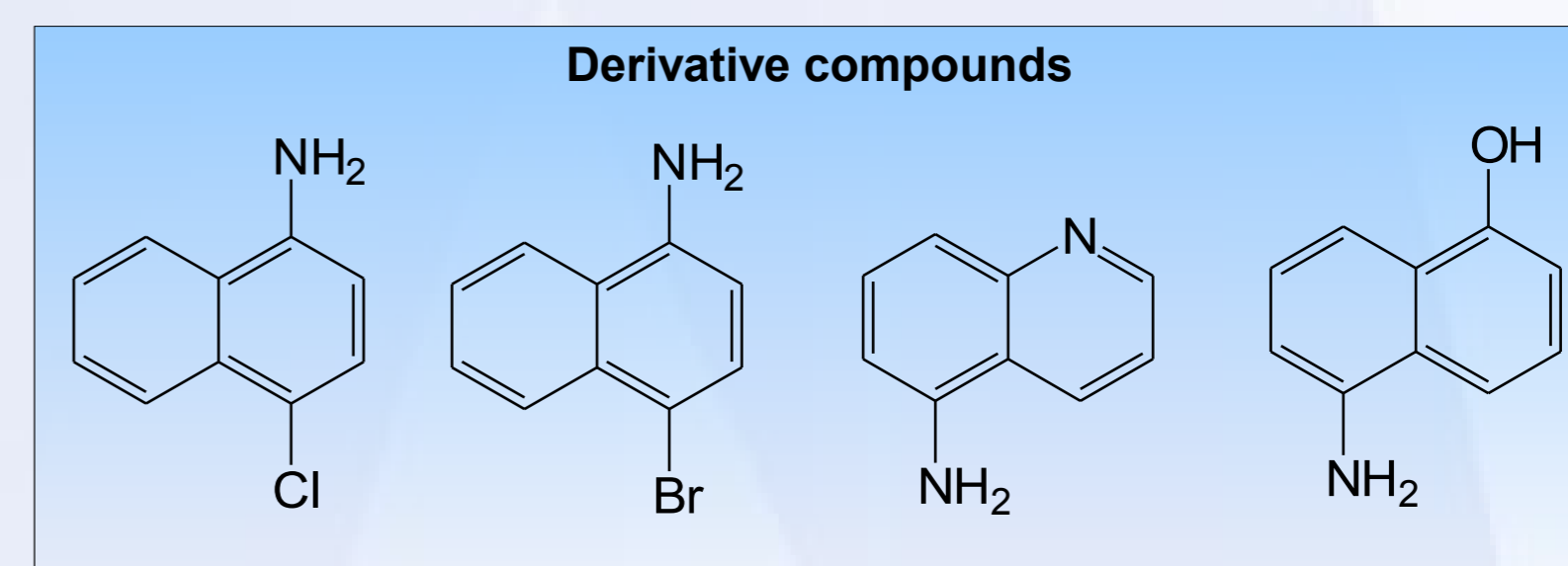
### Further Developments

With the new compound (4), synthesis, and the results reproducible, further work around the naphthalene backbone was expanded. Using four simple derivative compounds, and the same synthetic procedures, analogues of 1, 3, and 4 have been synthesised. This shows an ability to further enhance these compounds with ease, unlike the current larger, more complex chemical explosive sensors.

The aminoquinoline and aminonaphthol derivatives are of particular interest due to their extra donor atoms. Assuming the final tertiary phosphine is arranged in a similar conformation as the aminonaphthalene ligand, a further site for binding is produced between the 3 nitrogen or oxygen atoms.

### Conclusions and Further Work

Several compounds have been synthesised during this research and there are still areas for further work within this class of substrates alone. Future work with the current compounds would include assessing their fluorescent properties using spectroscopic techniques, and given time investigating their chemical sensing capabilities. However, further stages of study would be centred around the use of larger conjugate ring systems such as anthracene and pyrene and their respective properties with regards to ease of synthesis, fluorescence and, chemical sensing.



### Acknowledgements:

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### References:

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2. M. E. Germain and M. J. Knapp, *J. Am. Chem. Soc.*, 2008, **130**, 542.
3. A. T. Ekubo, M. R. J. Elsegood, A. J. Lake and M. B. Smith, *Inorg. Chem.* 2009, **48**, 2633.