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SCHOOL OF CHEMISTRY
THE UNIVERSITY OF EDINBURGH



**Amine and Amide containing Novel Polymers of Intrinsic
Microporosity**

Thesis submitted for the degree of Doctor of Philosophy by:

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2024

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Lay Summary

Polymers of Intrinsic Microporosity (PIMs) represent a fascinating class of materials with a distinct molecular structure characterized by very small pores. Unlike conventional polymers, which typically have dense, compact structures, PIMs possess a high degree of internal free volume due to their highly branched and rigid molecular chains. This unique architecture results in the formation of tiny, nanometer-scale pores within the polymer matrix. The inherent microporosity of PIMs gives rise to exceptional properties, including high surface area, gas permeability, and selective adsorption capabilities. These attributes make PIMs highly desirable for various applications, such as gas separation, membrane technology, and molecular filtration.

In gas separation processes, PIM membranes can selectively separate different gases based on their molecular size and affinity, enabling efficient purification and separation of gas mixtures. Furthermore, PIMs have garnered interest in energy storage and catalysis applications due to their porous structure, which facilitates enhanced adsorption of molecules and ions. This property opens possibilities for the development of advanced materials for battery electrodes, gas storage, and heterogeneous catalysis. Overall, polymers of intrinsic microporosity represent a versatile class of materials with significant potential across various industrial sectors, including environmental protection, energy, and healthcare. Continued research and development in this field are likely to unlock further opportunities for harnessing the unique properties of PIMs to address pressing societal and technological challenges.

Abstract

Polymers of Intrinsic Microporosity (PIMs) are a class of material that possess rigid and contorted structures so that their lack of flexibility and rotational freedom reduces the packing efficiency in the solid-state giving rise to microporosity and a large internal surface area. A great many combinations of functional groups can be introduced to the macromolecular structure of PIMs which helps to tune these polymers for application in heterogeneous catalysis, gas storage electrochemistry, as well as gas separation. Importantly, owing to their solution processability, PIMs are suitable for membrane fabrication or electrospinning of fibres.

Research reported in this thesis was focused on the incorporation of basic and nucleophilic sites within PIMs by introducing amide and amine functional groups into novel spirocyclic and propellane-based monomers that were suitable for polymerisation. In addition, these novel PIMs were further functionalised by converting nitrile groups into amidoximes. By increasing the basicity of the polymeric backbones of PIMs and introducing amidoxime groups, we aim to explore new applications, such as the catalytic destruction of organophosphate-based chemical warfare agents (CWAs) by amalgamating them into personal protective equipment (PPE). The effect of increasing the overall basicity of PIMs on gas separation, particularly on acidic gases such as carbon dioxide was investigated by analysing the gas permeability of the novel PIMs. Although these objectives were unfulfilled, as the combination of high porosity, super nucleophilic functionality and basis cut proved difficult to achieve, novel PIMs did have potential as gas separation membranes due to a combination of high permeability and moderate selectivity for a number of gas pairs.

Abbreviation

∞	Infinity
^1H NMR	Proton nuclear magnetic resonance
^{13}C NMR	Carbon-13 nuclear magnetic resonance
2D	Two-dimensional
3D	Three-dimensional
Å	Angstrom
A	Free nitrogen molecules
AS	Volume of adsorbed species
Ac	Activated carbon
AC	Hydrogen cyanide
Ach	Acetylcholine
AChE	Acetylcholinesterase
AlPO ₄	Aluminium phosphate
atm	Atmosphere
b.p.	Boiling point
BET	Brunauer-Emmett-Teller
C (equation)	BET constant
CG	Phosgene
CK	Cyanogen chloride
COFs	Covalent organic frameworks
CS	2-chlorobenzalmalonitrile
CWAs	Chemical warfare agents
CX	Phosgene oxime
DCB	1,4-Dichlorobenzene
DCE	1,2-Dichloroethane
DCM	Dichloromethane
DMAc	Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide

DP	Diphosgene
E_1	Heat of adsorption of initial layer
EI	Electron Ionisation
E_L	Heat of adsorption beyond the first layer
FT-IR	Fourier Transform Infrared
f	Multi functionalisation
GA	Tabun
GB	Sarin
GD	Soman
GF	Cyclosarin
HCPs	Hyper Crossed-linked Polymers
HD	Sulphur mustard
HRMS	High Resonance Mass Spectroscopy
HN	Nitrogen mustard
Hz	Hertz
i	Interception of BET plot
IMFV	Internal Molecular Free Volume
ITM	Institution on Membrane Technology
IUPAC	International Union of Pure and Applied Chemistry
J	Coupling Constant
K	Kelvin
K_a	Rate of adsorption
K_d	Rate of desorption
L	Lewisite
Lit	Literature
LRMS	Low Resonance Mass Spectroscopy
m	Gradient of BET plot
M	Mass of sample
MAS	Magic angle spinning
MIP	Mercury Intrusion Porosimetry
MOFs	Metal Organic Frameworks

MOR	Mordenite
Mp	Melting point
MS	Mass Spectroscopy
Mw	Molecular weight
N _A	Avogadro's Constant
nm	Nanometre
NMP	N-methyl-2pyrrolidone
NMR	Nuclear Magnetic Resonance
OC	Oleoresin capsicum
OMIM	Organic Molecule of Intrinsic Microporosity
<i>P</i>	Partial volume pressure
<i>P_o</i>	Saturation pressure
<i>p</i>	Deformation parameter
Pa	Pascal
PAN	Polyacrylonitrile
PANox	Polyacrylamidoxime
PHS	Chloropicrin
PIM-ET-TB	Ethanoanthracene
PIMS	Polymers of Intrinsic Microporosity
PNPA	<i>p</i> -Nitrophenyl acetate
POPs	Porous Organic Polymers
PPE	Personal Protective Equipment
PS	Polystyrene
PSD	Pore Size Distribution
RCP	Random Close Packing
rt	Room Temperature
S	Porous material
SA	Surface Area
S _{BET}	BET Surface Area
SBI	Spirobisindane
SDL	Spirodilactam

SPS	Solvent Purification System
SSA	Specific Surface Area
T2	NMR relaxation
TB	Tröger's Base
TEA	Triethylamine
TFTPN	2,3,5,6-tetrafluoroterephthalonitrile
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
THSBI	5,5',6,6',-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
TTSBI	5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane
UNDRR	United Nation Office for Disaster Risk Reduction
UV-Vis	Ultraviolet-visible
V _a	BET Volume of gas adsorbed
VE	(s-(dimethylamino)ethyl o-ethylphosphonothioate)
VG	Amiton
V _m	BET volume of gas adsorbed in monolayer
VM	Edemo
VR	R-33
V _{STP}	Molar volume (22414 mL) occupied by a gas at ambient temperature
VT	Variable Temperature
VX	Ethyl N-2-diisopropylaminoethyl methylphosphonothioate
WWI	World War One
σ	Effective cross-sectional area of one diatomic nitrogen molecule
θ	Functional surface coverage of a system
Φ	Random packing efficiency

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Chapter 1 : Introduction

1. Introduction to Porous Materials

Porous materials are naturally occurring or synthetic materials, which by definition contain voids, cavities and interstices that can be filled with a fluid (liquid or gas),¹ where the free space occupied should have greater depth than width. As shown in **(Figure 1)** pores are categorised based on their availability to an external probe. Closed pores **(a)** are isolated and do not communicate with other pores or the external environment. Open end pores contain continuous network channels to the external body as depicted in **Figure 1** by pores labelled **(b)**, **(c)**, **(d)** and **(f)**. These open pores are further categorised into blind pores **(b)** and **(f)** possessing one open end, through pores **(e)** where the pores are open at either end. Pores can also be categorised by their shapes: inkbottle shaped **(b)**, open cylindrical **(c)**, closed cylindrical **(f)** and funnel shaped **(d)**.² This group of materials have numerous applications within research and industry, because of their large surface area as well as the possibility to significantly modify their physical and chemical properties by altering the surface area to volume ratio.¹

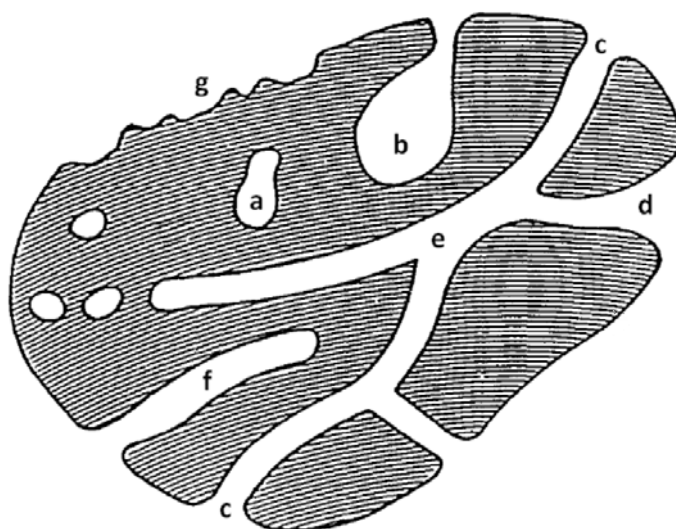


Figure 1: Cross-section of a porous material displaying different pore types.

The International Union of Pure and Applied Chemistry (IUPAC) has classified porous materials based on pore size distribution (PSD),³ the pore size ranges shown in **Table 1** are determined by nitrogen adsorption/desorption mechanism.⁴

Table 1: IUPAC classification of pore size distribution

	Pore width (nm)
Micropore	< 2
Mesopore	2 – 50
Macropore	> 50

1.1 Microporous materials

Microporous materials are a family of porous materials defined by IUPAC as solid materials consisting of interconnected pore networks less than 2 nm (20 Å) in diameter, exhibiting very large surface areas (SA) normally around 300 – 2000 m² g⁻¹ (Figure 1.1a).^{5,6}

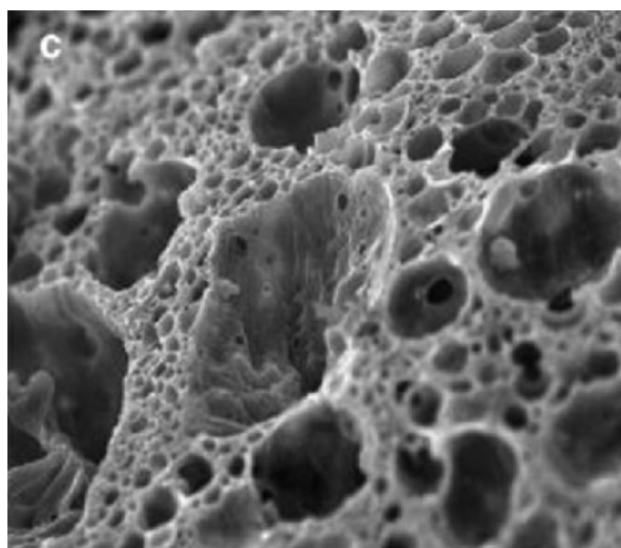


Figure 1.1a: SEM image of porous material with interconnecting pores.⁷

Microporous structures can range from pure inorganic framework to organic – inorganic hybrid or in some cases pure organic (Figure 1.1b) allowing for introductions of various functional groups.^{8,9} The large surface area and highly functionalised structure of porous materials gives these materials their application in:⁸

- Heterogeneous catalysis:
For example, PIM-1 functionalised with metal complexes (e.g. palladium) acts as an excellent catalytical support for cross-coupling reactions such as the Suzuki reaction.
- Energy conversion:
PIMs are used in fuel cell and battery industries for energy conversion and storage.
- Gas storage/separation:
PIM-1 and PIM-7 are famously studied for their high permeability and selectivity for CO₂, which can be further enhanced by incorporation of hydroxyl, amino, or carboxyl groups.
- Adsorption of environmental impurities:
PIMs can effectively remove pollutants from air or water. Functionalising PIMs with chelating groups (e.g. thiol, amine) can promote the removal of mercury, lead, or organic dyes from water.
- Gas purification
Amine functionalised PIMs are used for gas purification processes, such as removal of H₂S and CO₂ from natural gases due to their enhanced selectivity towards said acidic gases.

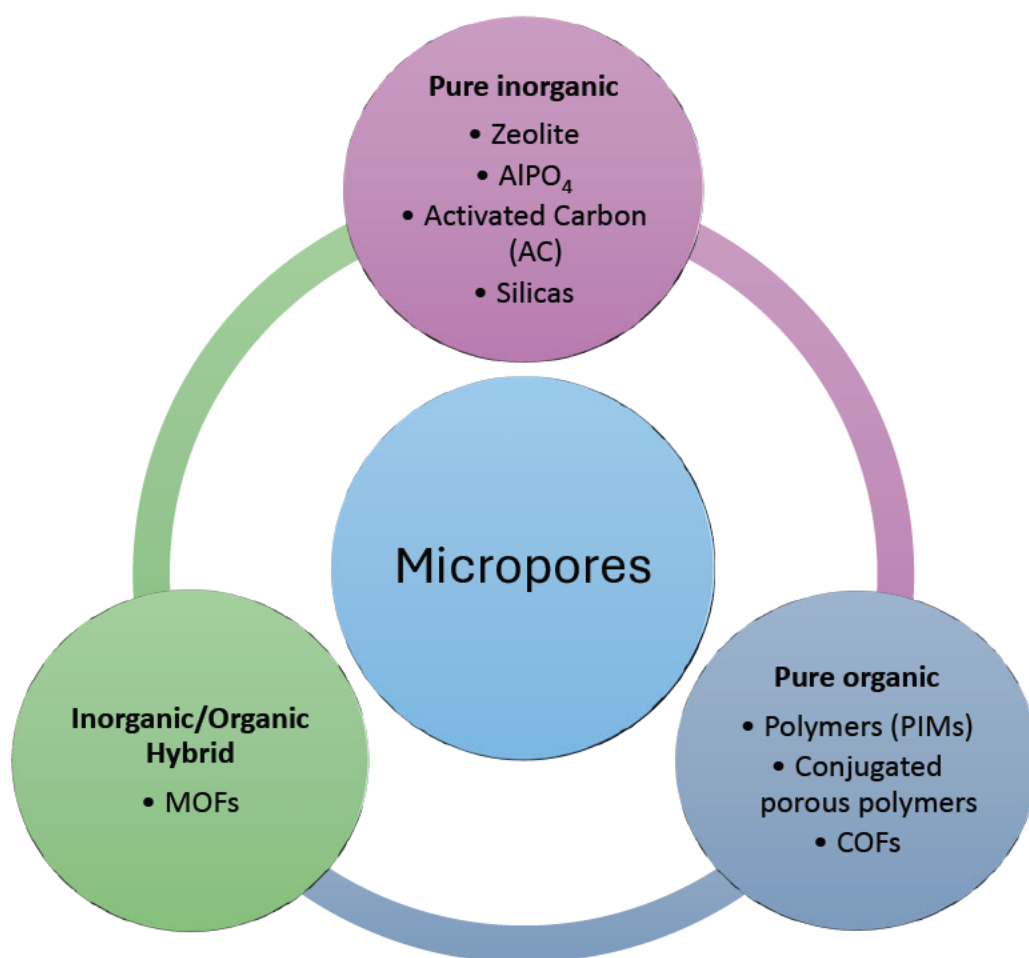
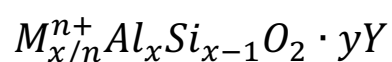


Figure 1.1b: Chart displaying microporous material classification.

1.1.1 Zeolites

The first zeolite, stilbite $\text{NaCa}_2\text{Al}_5\text{Si}_{13}\text{O}_{36} \cdot 14\text{H}_2\text{O}$, was discovered in 1756 by Axel Fredrik Crönstedt.¹⁰ He named this class of material zeolite from the Greek words *zein* “to boil” and *lithos* “rock” after noticing that naturally occurring zeolite appear to “boil” when heated as water molecules evaporated from the cavities.¹¹ Zeolites are a class of ‘tectosilicate’ minerals containing tetrahedral-linked, three-dimensional frameworks made up of corner-sharing TO_4 tetrahedra building blocks (with T = Si, Al, P, Zr, etc). Pure silica frameworks are neutral in terms of electrical charge. However, when trivalent aluminium or other charged elements are introduced into the framework to substitute for some of the tetravalent silica, a negative charge is introduced to the framework, therefore charge balancing ions such as Na^+ , Mg^+ and K^+ are used to compensate the negative charge (**Figure 1.1.1a**).¹² Therefore, zeolites have the general formula:



Where **M** is the charge balancing cation and **Y** represents molecules such as H_2O that may be adsorbed within the framework.

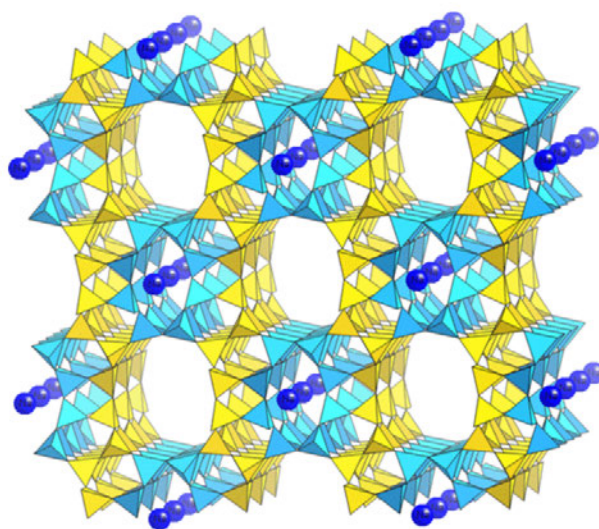


Figure 1.1.1a: Structure of mordenite (MOR), SiO_4 (yellow) tetrahedra, AlO_4 (aqua blue) tetrahedra, charge balancing ions are represented by sphere (dark blue).

Some zeolites are naturally occurring, while others can only be synthesised in laboratories using complex template molecules. Zeolites are made up of various types and arrangement of building units, giving them all different shapes and pore sizes (**Figure 1.1.1b**).¹³ The types of pores present within zeolites can be one of the two: **(a)** intracrystalline channels, which are well-defined pores and pathways present within the crystalline frameworks formed by specific bonding of silica (SiO_4) and alumina (AlO_4) tetrahedra forming zeolite frameworks or **(b)** interconnecting voids which are cavities within the zeolite frameworks that are interconnected by the intracrystalline channels. These voids play a critical part in roles such as ion exchange and applications such as molecular sieves or catalysis.¹⁴ Large open cavities within aluminosilicates give rise to properties such as ion exchange, molecular absorption, molecular sieves, and catalytic cracking.¹⁵

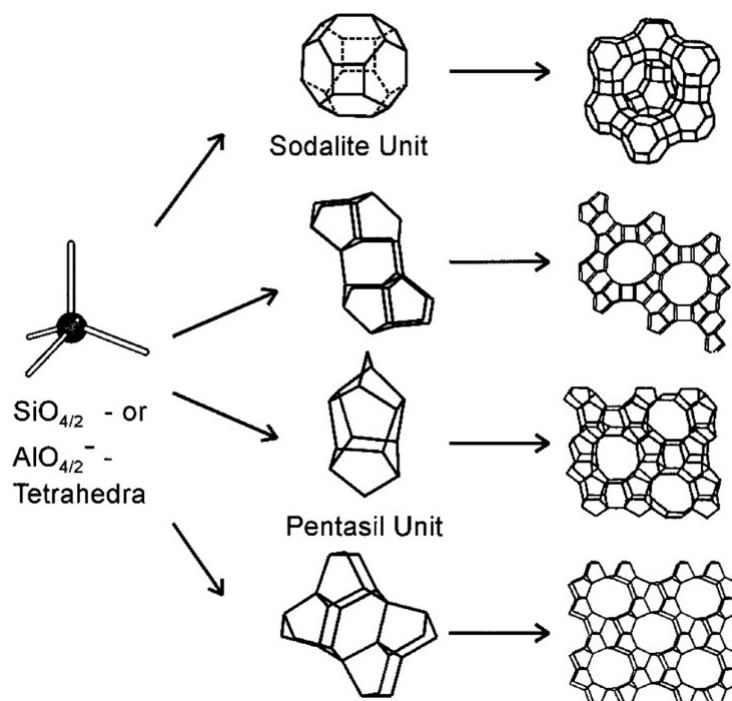


Figure 1.1.1b: Structure of four different zeolites and their micropore system.

1.1.2 Metal Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) are porous frameworks composed of organic linkers connecting metal clusters known as secondary building units. The most common organic linker to form robust structures are dicarboxylates (**Figure 1.1.2a**).^{16,17} MOFs are crystalline materials with high porosity (up to 90% free volume) and large surface area ($>6000 \text{ m}^2 \text{ g}^{-1}$).¹⁸ Due to these properties, they have applications such as gas separation, gas purification, gas storage and heterogenous catalysis and are highly sought after both in the research field and industry.^{19–21} By alteration of these organic linkers, chemical and physical properties of MOFs can be modified *i.e.* functionalisation of organic linkers can increase affinity of MOFs towards specific chemicals/molecules and different pore sizes can be obtained by alternation of the organic linkers chain length.²²

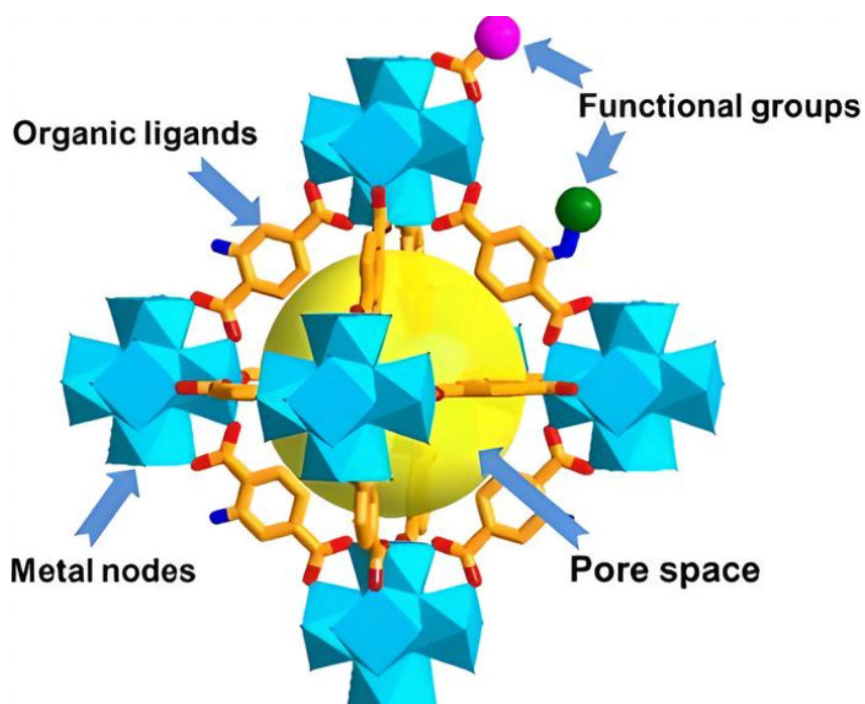


Figure 1.1.2a: Illustration of MOFs organic ligands and metal oxide building blocks.

1.1.3 Covalent Organic Frameworks (COFs)

Covalent-organic frameworks are a class of crystalline materials made entirely from organic linkers, without the presence of metal centres, in a reversible condensation reaction and are held together by strong covalent bonds. COF structures consist of two types of ordered structures. The monomers and linkers groups form the first polymeric growth units called the primary order structures, which in turn forms the high order structure through non-covalent bonding (usually within 2D layer stacking) through **(1)** electrostatic interaction such as ionic bonds (salt bridges), dipole-dipole interactions, ion-dipole interactions. **(2)** hydrogen bonding, **(3)** Van der Waals and **(4)** π - π interactions to produce the porous structure of COFs (**Figure 1.1.3a**).²³ The absence of the metal oxide centres within the COF structure makes the frameworks lighter increasing the specific surface of COFs.^{24–26} COFs with large surface area and high chemical stability have a wide range of applications²⁷ in energy conversion and storage,^{28,29} optoelectronic devices,³⁰ adsorption and desorption,^{31,32} sensing,^{33,34} organic catalysis,^{35,36} and biomedicine.³⁷

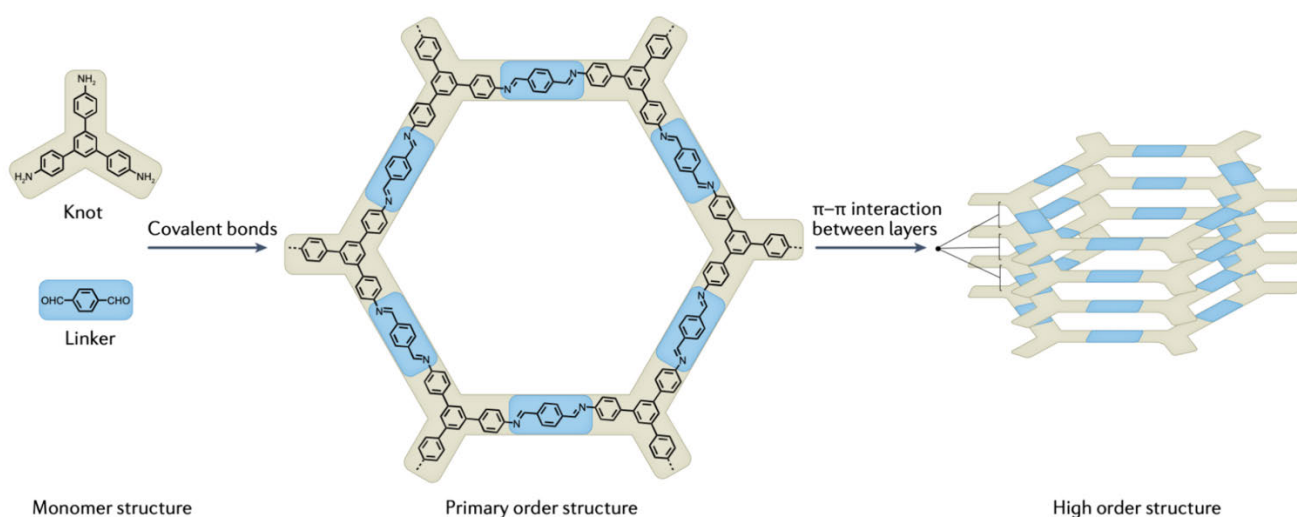


Figure 1.1.3a: Illustration of primary and high order structure of COFs.

1.1.4 Activated carbon

Activated carbon (Ac) is the name given to a family of carbonised material with high degree of porosity and large surface area.³⁸ Graphite tends to have low porosity ranging between 1-5% for naturally occurring and synthetic graphite and low surface area of approximately 1-10 m²/g.³⁹ To achieve the high degree of porosity and high surface area displayed by Ac (**Figure 1.1.4a**),⁴⁰ starting materials, normally renewable sources, such as wood, coal, coconut shells⁴¹ and other organic materials undergo physical or chemical activation. Physical activation on carbonaceous material involves pyrolysis followed by an activation step by steam or carbon dioxide at elevated temperatures (700 – 1000 °C). Alternatively, chemical activation of carbonaceous compound can be employed: in this method the raw materials are impregnated by activating agents (*i.e.* zinc, potassium hydroxide, potassium carbonate or sodium hydroxide) followed by pyrolysis at temperatures around 400 – 800 °C.^{42,43}

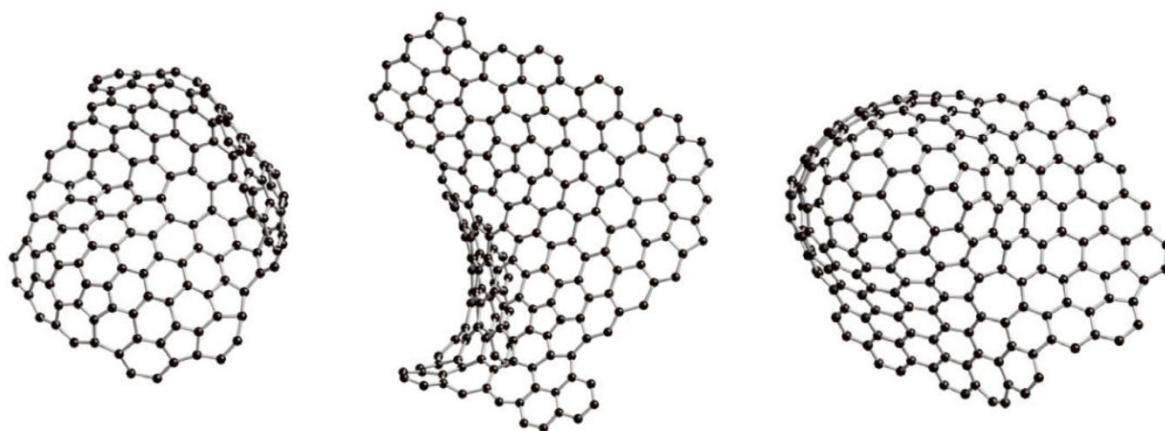


Figure 1.1.4a: Proposed structure of Activated carbon.

Since Activated carbons are manufactured from renewable resources (e.g. wood, bamboo, agricultural waste, etc.) and their sponge-like structure gives them high porosity and large surface areas, they have many applications in different fields such as gas storage namely methane and hydrogen,^{44,45} waste-water treatment,⁴⁶ water

purification,⁴⁷ gas purification,⁴⁸ and medical applications such as oral administration for poisoning or overdose treatments.⁴⁹

1.2 Porous Organic Polymers (POPs)

Porous organic polymers (POPs) have fast become a popular research subject as they are able to offer properties of both polymeric and porous materials.^{50–52} Moulded microporous polymers can be fabricated to give a monolithic interconnective porous network^{53–55} (**Figure 1.2a**).^{53–55} Some porous polymers are solution processible making it possible to dissolve them in organic solvents^{56–58} to form thin films for use in wider applications such as; gas separation and storage, catalysis, adsorption and filtration, sensors, Energy storage, and functional coating (e.g. anti-reflective coatings)^{59,60} without alternation to its chemical or physical structure, which is a property not shared by other porous materials including zeolites, COFs and MOFs. Porous polymers are used within industries for gas separation,^{54,61–63} catalysis⁶⁴ and sensors.^{65,66} Microporous materials face limitations in monomer selection as monomers selected for polymerisation of microporous polymers should exhibit rigid or contorted sites to provide rigid structure to assist with the inefficient packing of the polymeric chains. Polymers synthesised with non-rigid or contorted sites have efficient packing, therefore, display low to no porosity known as linear polymers.⁶⁷ Linear polymers can be commonly defined as an extended carbon-carbon chain with both terminal ends as small hydrocarbon moiety. However, these polymers are not limited to carbon-carbon chains and may consist of heteroatoms, examples of which are Nylon-6 (-CONH-), polyesters (-COO-) and polysiloxanes (-Si-O-Si-).⁶⁸ They tend to have very little surface area as semi-crystallinity and efficient chain packing results in lack of porosity. Porous polymers, unlike other porous materials such as zeolites, can be synthesised through various bond-forming synthetic routes.^{69,70} Their very high BET (Brunauer-Emmett-Teller) surface area up to 6000 m² g⁻¹,⁷¹ and the wide range of monomers available for synthesis of porous polymers make them a versatile group of porous material that can be modified and functionalised to fit a wide range of applications. They have historically been used as ion-exchange resins in water

treatment,^{72–74} pharmaceutical industry,^{75–77} food industry,^{78,79} synthetic chemistry^{80,81} and so on dating back to the 1930s.⁸²

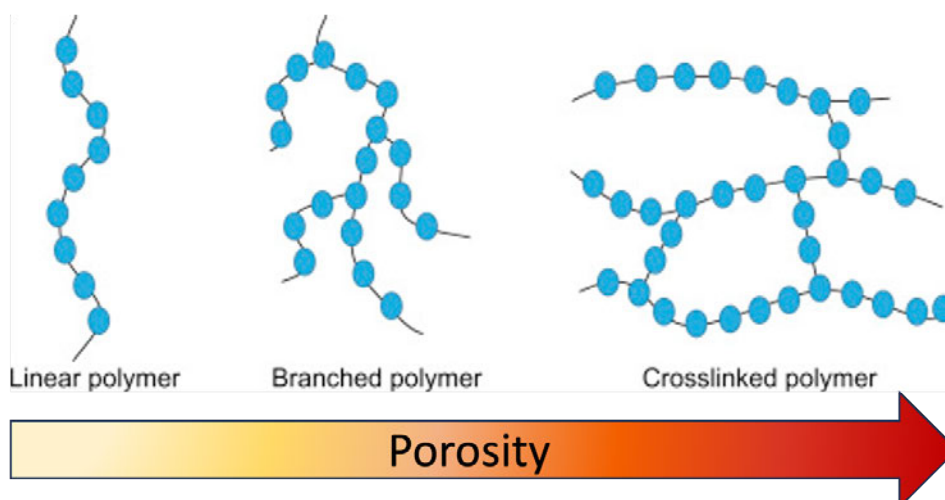


Figure 1.2a: Illustration of linear, branched, and crosslinked polymers.⁸³

Porous polymers can be classified into soluble and non-soluble categories depending on the material's solubility in common organic solvents. Conventional porous polymers with higher degrees of cross-linkage (hyper cross-linked polymers) tend to show lower solubility and hence very low to no processability. Polymers of intrinsic microporosity are a class of porous polymers with high solubility and processability as their porosity rises from the site of contortion and rigidity of the polymeric backbone and not a result of hyper cross-linkage.^{84,85}

1.2.1 Hyper Cross-linked Polymers (HCPs)

Hyper-Cross-linked Polymers (HCPs) were first reported by Davankov in 1969⁸⁶ and those made from polystyrene are known as “*Davankov resins*”.⁸⁷ Hyper cross-linkage is a method of introducing pores into polymeric structures through extensive chemical or physical cross-linking.⁸⁸ Extensive cross-linking of polymer chains will result in an unsystematic three dimensional (3D) interconnected porous network (**Figure 1.2.1a**) and is the result of covalent (permanent), non-covalent (reversible) or physical interactions.⁸⁹ These interactions can take place between repeating units of the same polymer stand (intramolecular cross-linking) or repeating units of multiple polymers (intermolecular

cross-linking).^{90–93} Traditional methods of HCP synthesis reported by Davankov, where polystyrene (PS) was swollen in organic solvents such as dichloroethane (DCE) to then undergo Friedel-Crafts Alkylation reaction initiated by Lewis-acid catalyst (e.g. AlCl_3 , FeCl_3 or SnCl_4) to enable electrophilic substitution of the chloromethyl group onto the aromatic rings of polystyrene chains, followed by crosslinking agents, causing cross-linkage between linear repeating units via methylene ($-\text{CH}_2-$) bridges.^{94,95} Cross-linkages of polymers through chemical crosslinking gives better defined pores by providing higher rigidity in the final structure.^{90,96} Polymers with higher degrees of cross-linkage will have a more rigid structure and higher glass transition temperatures compared to their linear counterpart,⁹⁷ hence crosslinked polymers are insoluble and therefore not processible.⁹⁸

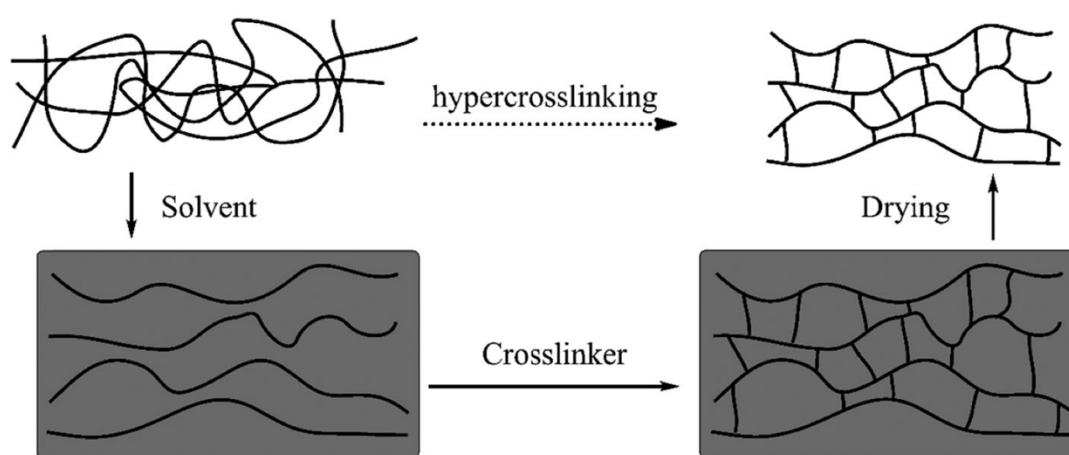


Figure 1.2.1a: Schematic representation of HCPs.⁸⁴

Due to their porous structure and high surface area, HCPs have wide range of applications across different industries.⁹⁹ Novel HCPs have been synthesised displaying a high humidity sensing ability,¹⁰⁰ as well as applications in photocatalysis,¹⁰¹ drug delivery,¹⁰² membrane gas separation¹⁰³ and removal of pollutants.¹⁰⁴

1.2.1 Organic Molecules of Intrinsic Microporosity (OMIMs)

As noted in the next section (1.2.2), Polymers of Intrinsic Microporosity (PIMs) are a class of solvent processable porous polymer which differ from classical linear polymers in that they have properties similar to porous network polymers but without possessing a

covalent network.¹⁰⁵ The microporosity of PIMs arises from rigid and contorted centres present within the monomers causing the polymeric skeleton to fold and bend resulting in inefficient packing creating pore like cavities.^{106,107} Classical polymers and organic molecules have a non-porous structure due to conformational and rotational freedom in their skeleton, increasing the packing efficiency maximising interchain or intermolecular interactions. The concept of intrinsic microporosity from inefficient packing has mathematically been described by S. Torquato et al. for 2D shapes (**Figure 1.2.1a**)¹⁰⁸ and 3D shapes (**Figure 1.2.1b**),¹⁰⁹ the former called “superdisks” and the latter “superballs”. They have described the random packing efficiency (Φ) of the concave and convex “superballs” as the function of its deformation parameter (p) (**Figure 1.2.1c**)

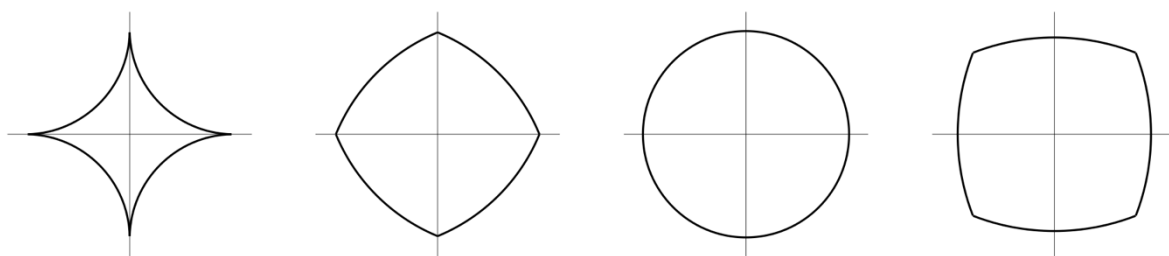


Figure 1.2.1a: 2D Illustration of superdisks with different values of deformation parameter p .

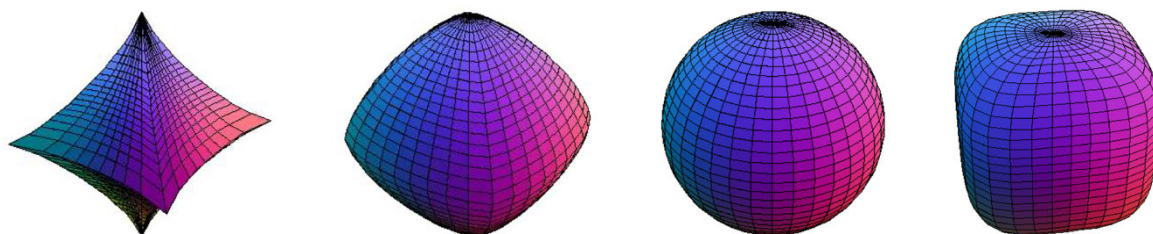


Figure 1.2.1b: 3D Illustration of superballs with different values of deformation parameter p .

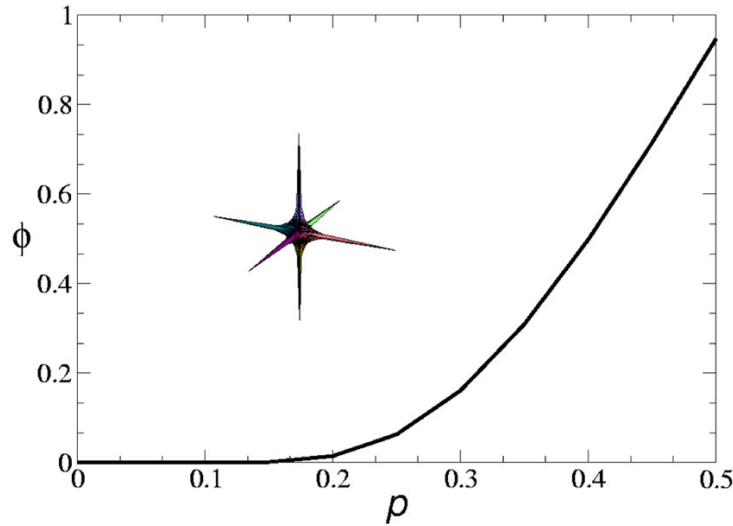


Figure 1.2.1c: Packing efficiency versus deformation parameter. insert illustrates concave superball $p = 0.1$, the shape will become a 3D cross at $p = 0$.¹¹⁰

This study was carried out on octahedra structure with diverse incurvation and convexness measure by their deformation parameter. The authors describe a superball with $p = 1$ as a perfect sphere, where it can take an octahedra or a cubic configuration with change in deformation parameter. As the deformation parameter increases from $p = 1$ to $p = \infty$ the sphere will take on a more noticeable cubic like shape, in contrast when the deformation parameter decreases from $p = 1$ to $p = 0.5$ the sphere will take on a more prominent octahedron shape (**Figure 1.2.1d**). Higher degree of contortion equals to less packing efficiency, as has been mathematically modelled. This phenomenon is also applied to porous polymers, where the backbone of the polymers is made up of rigid and contorted monomers the rigidity will cause inefficient folding of the polymeric skeleton creating cavities with free volumes and surface area.

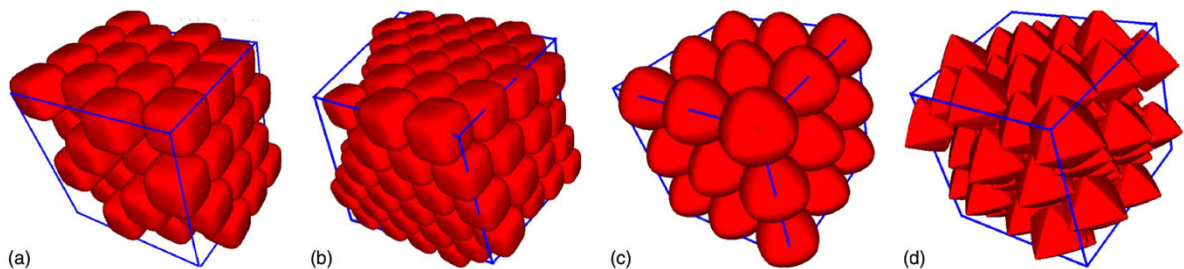


Figure 1.2.1d: Illustration of superballs packing, a) superballs with $p=1.8$, b) superballs with $p=2.0$, c) superballs with $p=0.8$ and d) superballs with $p=0.55$.

One classic example of molecule with clear concavities is triptycene (**Figure 1.2.1e**), which has a shape-persistent bridge-bicyclic structure. The concaved nature of triptycene will decrease packing efficiency, inherently when molecules of triptycene come together in a solid form they will pack very inefficiently creating voids of free volume. This is an effect that was called “internal molecular free volume (IMFV)” by Swager.^{111,112}

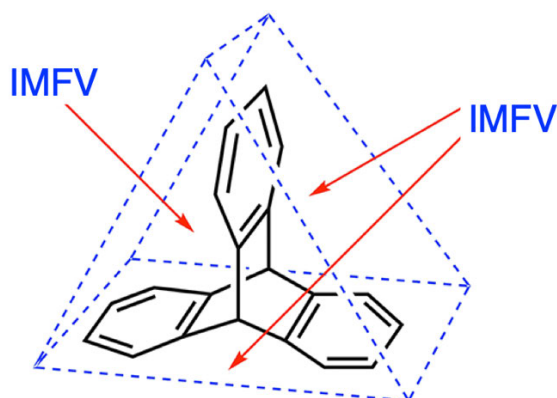


Figure 1.2.1e: Triptycene molecule in perspective view. Internal molecular free volumes of triptycene are indicated by red arrows.¹¹³

Organic molecules with rigid structures containing a large amount of IMFV are defined as “organic molecules of intrinsic microporosity (OMIMs)”.¹¹⁴ When designing porous macromolecules or polymers it is important to take the above theory into account to ensure maximum IMFV. Some highly concave precursors were designed and prepared by Taylor *et al.* (**Figure 1.2.1f**), where each precursor possesses obstinate molecular geometry or imposed orthogonality in such a way that when these cores and terminus are combined an organic molecule of intrinsic microporosity is formed.¹¹⁵

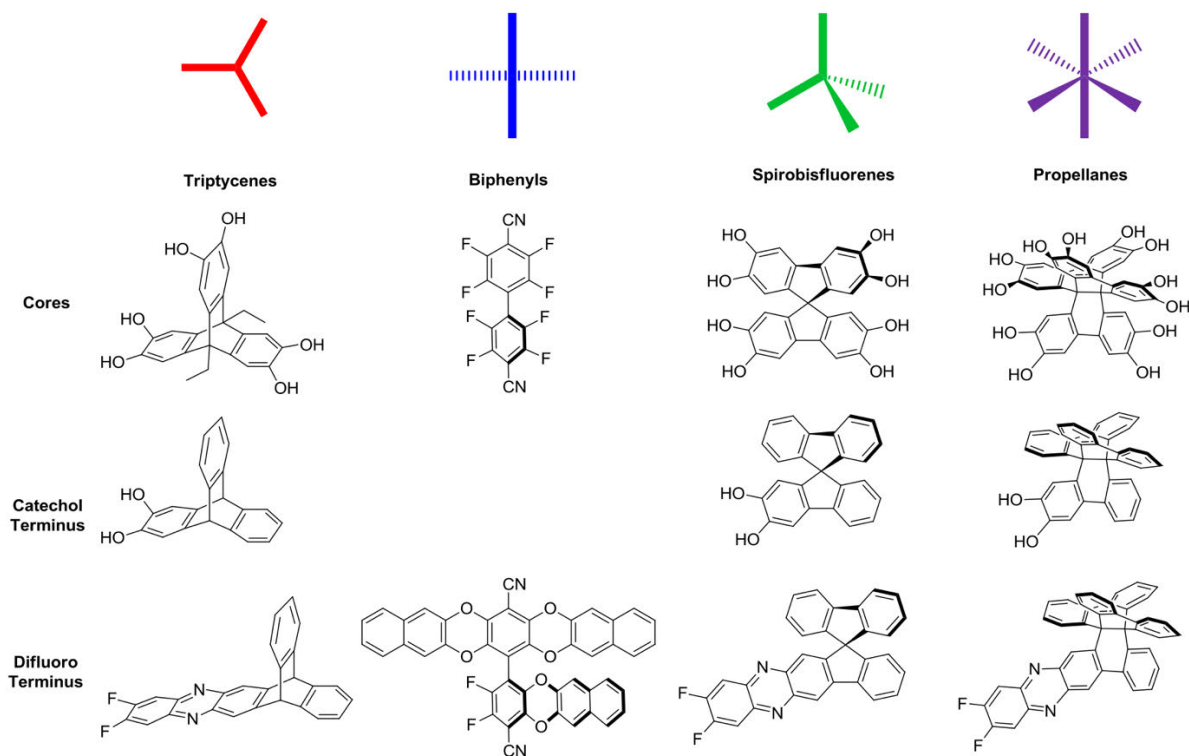


Figure 1.2.1f: Potential OMIM precursors proposed by R. Taylor.¹¹⁵

The concept of OMIMs can be further stretched into the synthesis of porous polymers namely PIMs. By choosing similar monomers to the cores and terminus of OMIMs as shown in **Figure 1.2.1f** longer chains of porous polymers known as Polymers of Intrinsic Microporosity can be assembled.¹¹⁶

1.2.2 Polymers of Intrinsic Microporosity (PIMs)

Polymers of Intrinsic Microporosity were first introduced by N. McKeown and P. Budd in 2004.⁵⁶ PIMs are solution processable polymers whose microporosity, like OMIMs, arises from the introduction of a site of contortion inherited from the monomer structure, which yields a nonlinear and nonplanar rigid backbone with reduced efficient space packing creating IMVF and interconnected pore-like voids.¹¹⁷ PIM building blocks consist of two components: concaved structural units that will introduce rigidity and contortion to the polymeric skeleton and linking groups used to join the concaved units together during polymerisation (**Figure 1.2.2a**). These linking units will ideally have a restricted rotational axis to maintain the rigid structural integrity of PIMs.¹¹⁸

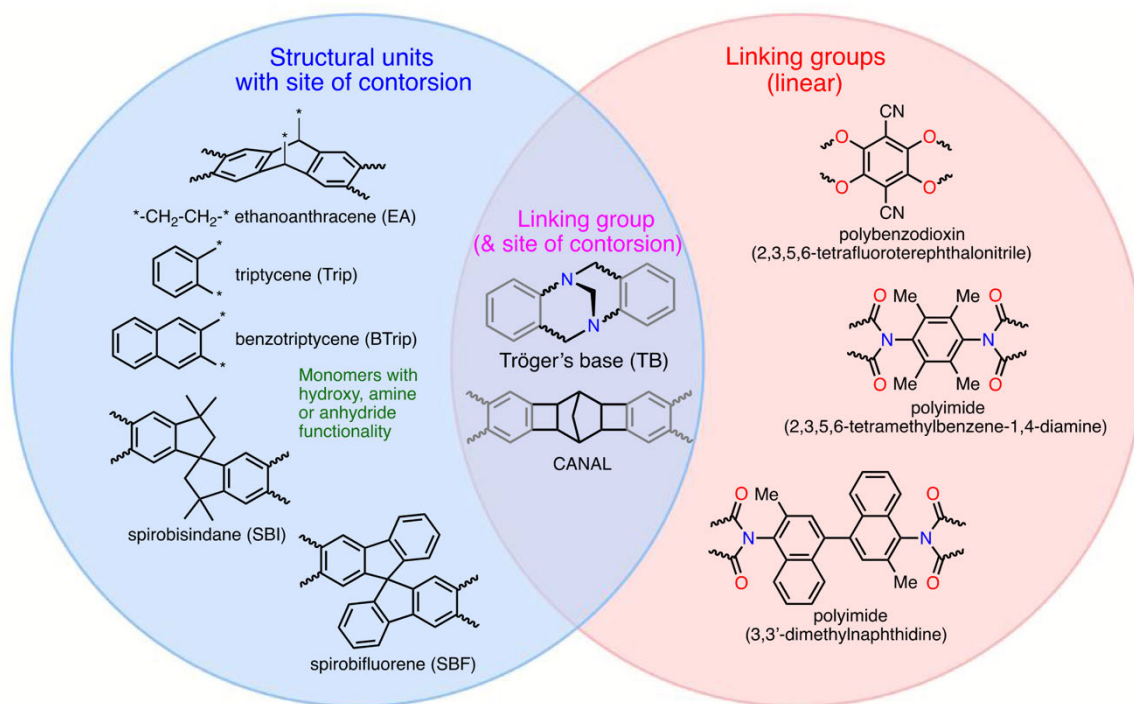


Figure 1.2.2a: Depiction of several structural units and linkers used in PIMs synthesis.¹¹⁹

To conclude, structural units with awkward molecular geometry (e.g. triptycene)¹²⁰ or a contorted centre (e.g. Spirobisindanes (SBI))⁵⁶ can be linked together to form rigid and contorted backbones, causing the polymer to possess low packing efficiency and thereby create a porous network.^{56,120}

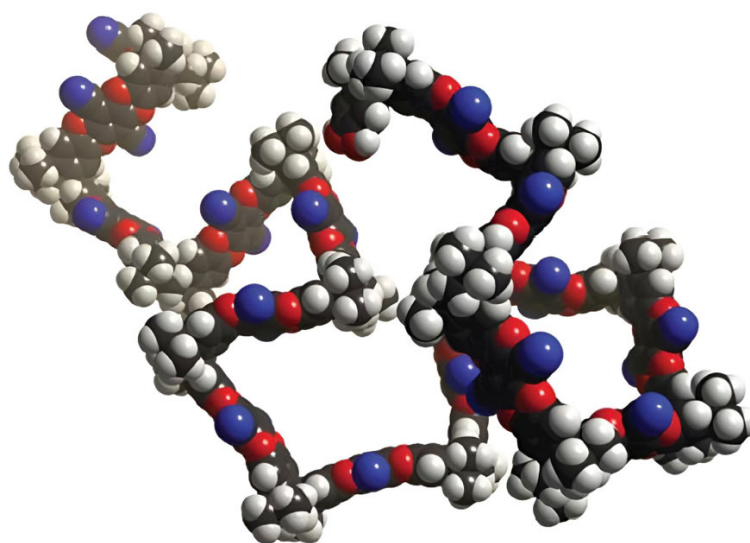


Figure 1.2.2b: modelled structure of PIM-1 showing the voids created due to inefficient packing.¹²¹

To achieve rigid formation of the backbone the monomers used typically consist of ortho-di-hydroxy / tetrahydroxy compounds namely catechol/bis-catechol and ortho-di/tetra-halo units, generally tetrafluoroterephthalonitrile (**Figure 1.2.2c**) via aromatic nucleophilic substitution reaction in a step-growth polymer synthesis.⁵⁶ Although synthesis of PIMs using diamino groups could lead to difficulties or potential failure of reaction due to the electron-donating nature of amino groups. This can impact the reactivity of the diamine groups in condensation reactions. Due to the highly nucleophilic nature of amino groups, they can partake in side-reaction to give by-products such as polymer crosslinkers or oligomers. It is also important to note that some diamino-containing monomers may not be able to withstand the acidic or basic conditions required for the synthesis of PIMs.

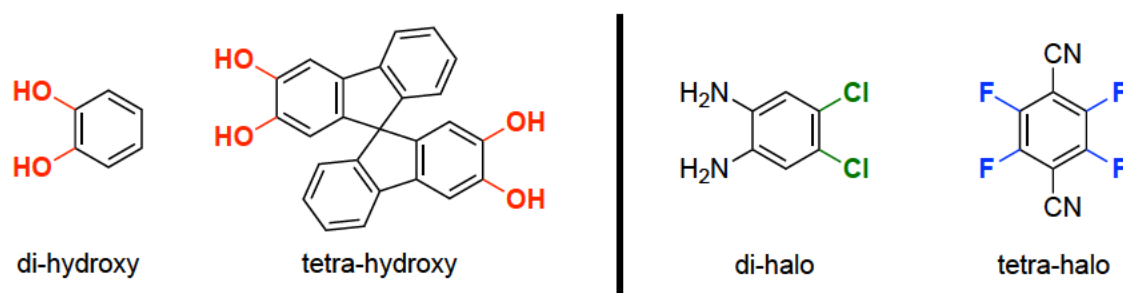
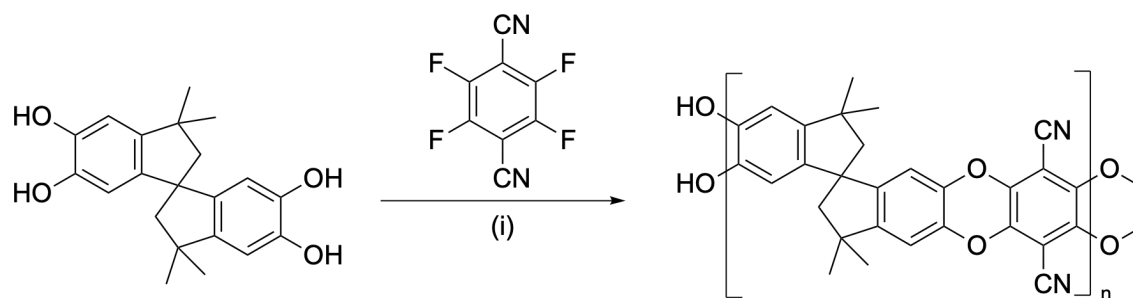


Figure 1.2.2c: examples of typical monomers used in PIMs synthesis.

PIM-1 was the first polymer of intrinsic microporosity introduced by P. Budd and N. McKeown and is synthesised by the nucleophilic aromatic substitution reaction between two commercially available monomers, namely 5,5',6,6',-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (THSBI) and 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN) (**Scheme 1.2.2d**), resulting a fluorescent yellow product with high molecular weight ($M_w > 200,000 \text{ g mol}^{-1}$). Using nitrogen adsorption at 77K, which provided a type-1 isotherm (see below), a BET surface area of $760 \text{ g}^{-1} \text{ m}^2$ could be calculated.⁵⁶



Scheme 1.2.2d: Synthesis of PIM-1 (i) K_2CO_3 , DMAc/DCB, 160°C, 40 min.¹²²

PIMs form amorphous glasses which thermodynamically is in a non-equilibrium state, therefore, their IM is lost over time in process called “*physical aging*” and this loss can be observed from the reduction over time in gas permeability of thin films.^{123–125} However, this process is reversible and the IM can be recovered by swelling the PIMs as a solid or film in an organic solvent such as methanol.¹²⁴ Freshly synthesised PIMs will also be treated with methanol to both reverse the aging process and to remove trapped solvents from the pores before performing analysis such as gas adsorption and gas permeability.¹²⁶

1.2.3 Properties and Applications of PIMs

Conventional ladder-polymers would display a rigid rod-like structure with poor solubility due to strong inter-chain interaction and high packing efficiency.¹²⁷ However, for the development of ladder polymers the use of long alkyl chains increases the solubility of these polymers.¹²⁸ Unlike conventional ladder polymers, PIMs are not faced with the solubility issues as they tend to be freely soluble in common organic solvents. This is one of the most important properties that gives PIMs the advantage over other classes of porous material to produce self-standing films for gas permeability measurements via solution processing,¹²⁹ hollow fibre membranes,¹³⁰ and thin film for sensor application.¹³¹ Commercially, PIMs have been utilised as end-of-life detector for 3M’s respirator cartridges.¹³²

The solubility of PIMs permits the use of solution based analytical techniques such as NMR spectroscopy and GPC for their characterisation . Although NMR spectroscopy can be used to aid with the characterisation of PIMs, it is important to note that high rigidity causes significant peak broadening in ^1H NMR spectra.¹³³ The peak broadening observed is a consequence of shorter relaxation time (T_2) caused by greater spin-spin interaction between ^1H nuclei in polymers with fixed conformations. Peak broadening is related to rigidity so that the NMR peaks of PIMs originated from bridged bicyclic structural units (e.g. PIM-EA-TB)¹³⁴ will tend to have broader NMR peaks compared to that of the more flexible spirobisindane (e.g. PIM-1) (Figure 1.2.3a).^{119,135}

Molecular mass of PIMs can be estimated by GPC, also known as Size Exclusion Chromatography (SEC), which uses a cross-linked polymer gel column calibrated using a standard with well-defined molecular masses such as poly(methyl)methacrylates or polystyrenes (most commonly used) to measures the retention time of a polymer sample.¹³⁶

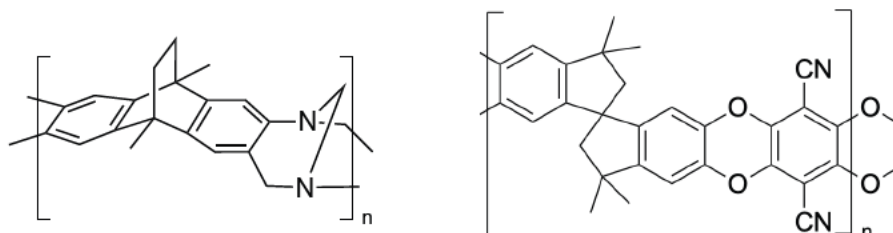


Figure 1.2.3a: Chemical structure of (left) **PIM-EA-TB**, and (right) **PIM-1**.

PIM membrane technology provides energy efficient and cost-effective separations for an extensive range of potential applications.^{137–142} When considering membrane separation there is a balance between the achievable separation (*i.e.* selectivity) and the productivity (*i.e.* permeance). It is essential to boost permeability of the membranes as this will decrease the amount of membrane area needed to separate a given gas mixture, thus decreasing the capital cost.¹⁴³ Scientists are faced with the challenge of developing highly permeable membranes as well as increasing selectivity.¹⁴⁴

To have the possibility of obtaining fibres and membranes from PIMs opens doors into additional research topics such as capturing and deactivation of chemical warfare agents (CWAs), where an aspiration is to use fibres of PIMs that can be incorporated into textiles to produce protective personal equipment (PPE).

It is known that PIMs are highly efficient adsorbents of organic vapours. The work described in this thesis details the chemical modification of PIMs to prepare Lewis basic sites aiming to enhance adsorption capability and catalytical destruction of CWAs. Additionally, it investigates the effect of increasing Lewis basic sites for the enhancement of CO₂ uptake to improve selectivity for gas separations or the potential use of PIM solids as effective CO₂ adsorbents.

1.3 Chemical Warfare Agents

The United Nation Office for Disaster Risk Reduction (UNDRR) has defined Chemical Warfare Agents (CWAs) as “chemicals used to cause intentional death or harm through their properties. Munitions, devices and other equipment specifically designed to weaponised toxic chemicals also fall under the definition of chemical weapons.”¹⁴⁵ The use of CWAs was pioneered by Germany, who launched the first-ever large-scale chemical weapon (approximately 170 metric tons of chlorine gas) in Belgium on April 22nd 1915, during World War One (WWI), where the number of casualties was estimated to be more than 1,100 people.¹⁴⁶ The use of chemical weapons during WWI caused public outrage around the globe resulting in the Geneva Protocol being revisited in 1925 to prohibit the use of chemical and biological weapons as mass destruction weapons in wars. However, Zyklon B gas (hydrogen cyanide gas), developed by scientists of Nazi Germany, was used during World War II in gas chambers to claim the lives of more than one million civilians. Even with renewed protocols in place, we are still witnessing illegal and unauthorised use of CWAs in recent wars and even in the UK.

There are currently thousands of known toxic substances and CWAs form only a minor subgroup. CWAs are synthetic compounds with low molecular weight that are fast-acting

and intermittently lethal even at low concentration levels. The toxicity of these substances is determined by measuring the lethal concentration value, i.e. the vapour concentration leading to 50% death in humans within 60 seconds of inhalation and these are characterised based on their chemical and physical properties.¹⁴⁷

Choking agents are often dispersed as gas but could also be deployed as liquid and aerosol (**Figure 1.3a**). Upon inhalation, toxic choking gases cause damage to the respiratory tract, especially the lungs, by causing the alveoli and air sacs in the lung to secrete fluid leading to organ damage.^{148,149}

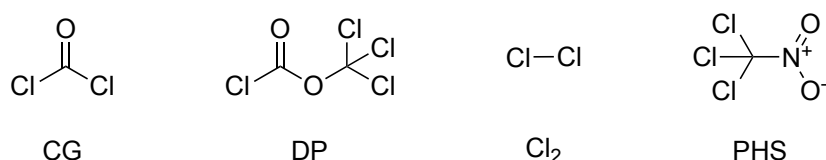


Figure 1.3a: Choking agents chemical structure, phosgene (**CG**), diphosgene (**DP**), chlorine (**Cl₂**), and chloropicrin (**PHS**).

Blood agents are dispersed as gas and are absorbed via lungs and skin (**Figure 1.3b**). They affect the cells ability to accept/load oxygen, and some blood agents also affect the ability of red blood cells to transfer oxygen causing the body to suffocate by inhibiting the Cytochrome C Oxidase enzymes.

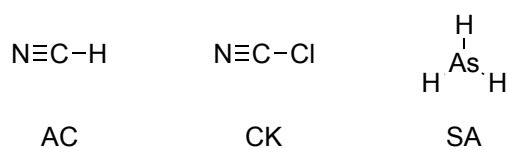


Figure 1.3b: Blood agent chemical structures, hydrogen cyanide (**AC**), cyanogen chloride (**CK**), and arsine (**SA**).¹⁵⁰⁻¹⁵²

Riot-control agents are dispersed as fine powder or aerosol due to low vapour pressure. The most used type of riot-control agents are pepper spray (OC) and tear gas (CS) shown in (**Figure 1.3c**). They cause a person to be temporarily incapacitated by irritating the eyes, mouth, throat, lungs, and skin. Although official organisations such as police force

and special units can legally acquire riot agents for domestic use, they are classified CWAs and organisations must report what type of riot agents they own.¹⁵³

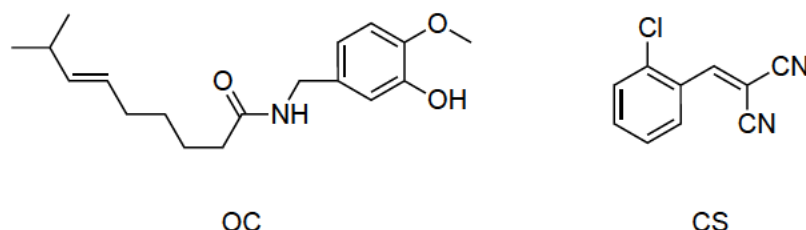


Figure 1.3c: Riot-control agent chemical structures: oleoresin capsicum (**OC**) and 2-chlorobenzal malonitrile (**CS**).

Blister agents are dispersed as liquids, aerosol, vapour, and dust (**Figure 1.3d**). Their mode of action is through inhalation and adsorption through the skin, causing damage to the eyes, skin, and respiratory tract. Blister agents inhibit mitosis and reduce tissue respiration resulting in cellular death through apoptosis or necrosis. Prolonged exposure can lead to systemic effects such as bone marrow suppression, leukopenia, gastrointestinal tract damage and in some cases carcinogenic.¹⁵⁴ Sulphur mustard is a blister and alkylating agent used during the First World War and other more recent conflicts. The victim will start to develop blisters around the second day of exposure which could increasingly worsen for up to two weeks after exposure.¹⁵⁵

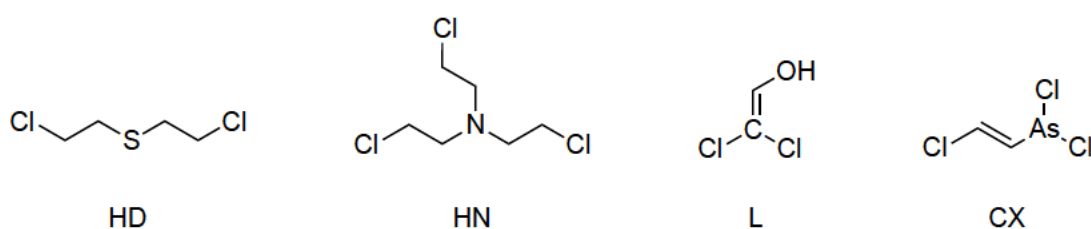


Figure 1.3d: Blister agent chemical structures: Sulphur mustard (**HD**), nitrogen mustard (**HN**), lewisite (**L**), and phosgene oxime (**CX**).

1.3.1 Nerve Agents

Gerhard Schrader, a German scientist, accidentally discovered nerve gas Tabun (named after German word Taboo) when attempting to develop new insecticides in the 1930s. Newly discovered Tabun possessed much higher toxicity levels compared to its other

organophosphate counterparts. Nerve agents are tasteless and odourless liquids and are considered the most toxic form of chemical warfare agents.^{156,157} Nerve agents are classified into two categories; the “non-persistence” G-series (**Figure 1.3.1a**) are liquids that possess the same density, vapour pressure and freezing point like water, with a slightly higher boiling point at 150 °C and can evaporate within 24 hours in the open air. Vapours produced from a G-series nerve agent can cause severe symptoms upon exposure. V-Series nerve agents were discovered by a British scientist Dr R. Ghosh (**Figure 1.3.1b**). Due to the viscous nature (resembling motor oil) of V-series they possess a much higher vapour pressure, hence, V-series are known to be more persistence and can contaminate an area for up to few weeks.

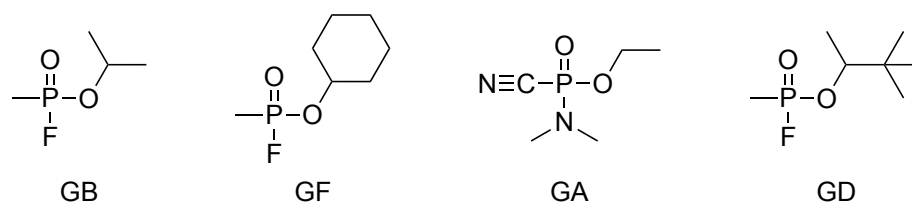


Figure 1.3.1a: Chemical Structures of G-series nerve agents; sarin (**GB**), cyclosarin (**GF**), tabun (**GA**), and soman (**GD**).

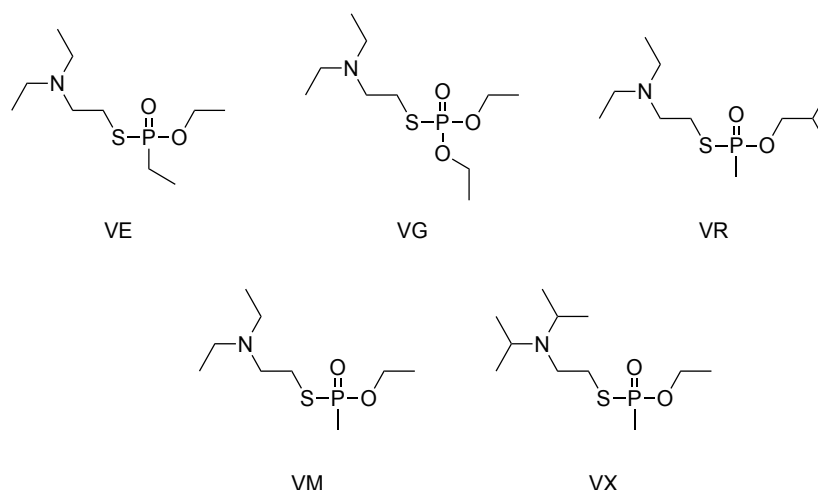
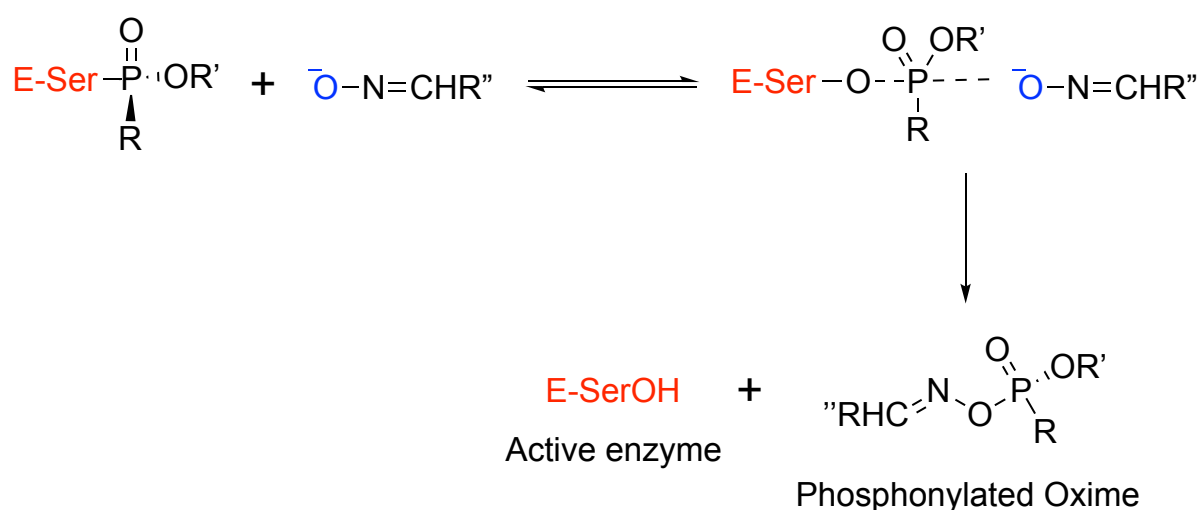


Figure 1.3.1b: Chemical structures of V-series nerve agents; (s-(dimethylamino) ethyl O-ethyl ethylphosphonothioate) (**VE**), Amiton (**VG**), Edemo (**VM**), R-33 (**VR**), and Ethyl N-2-diisopropylaminoethyl methylphosphonothioate (**VX**).

A nerve agent’s mode of action is to inhibit the enzyme acetylcholinesterase (AChE) by forming covalent bonds with the enzyme’s active site and prevent breaking down of acetylcholine (Ach). Inhibition of acetylcholinesterase active site by organophosphorus

compounds are irreversible under normal circumstances and cause a build-up of Ach in the synapses. Symptoms of organophosphorus poisoning includes muscarinic and nicotinic toxicity.¹⁵⁸ It is known that personal protective equipment such as breathing apparatus and protective suits can prevent exposure to toxic nerve gases; however, if nerve agent poisoning does occur the primary aim is to reduce the toxicity effect by:

1. administration of an anticholinergic drug such as atropine sulphate to reduce involuntary movements around the body such as lung contraction, gastrointestinal tract, and urinary tract.
2. Administration of benzodiazepine drugs to combat spasms and seizures.^{159–161}
3. Reactivation of acetylcholinesterase active site using oxime reactivators (**Scheme 1.3.1a**)¹⁶². The oxime mode of action for reactivation of AChE is used as an inspiration to design novel PIMs for adsorption and hydrolysis of organophosphate compounds. We aimed to synthesis polymers containing oxime groups to mimic the mechanism for activation of AChE active site to capture and detoxify nerve agents before they can enter the victim's body. Detoxification of nerve agents outside the body will reduce the change of enzyme blockage and thereby reduce fatality rate.



Scheme 1.3.1a: Nucleophilic reaction of organophosphate inhibited AChE (E-Ser).¹⁶³

Chapter 2: Background Theory of Adsorption

2.1 Determination of Surface Area

For porous materials there are factors such as specific surface area (SSA), pore size and pore size distribution that plays a very important part in their physical and chemical performances^{164, 164} IUPAC defines SSA as total SA of a material per unit mass ($\text{m}^2 \text{Kg}^{-1}$ or $\text{m}^2 \text{g}^{-1}$)¹⁶⁵ and it is a physical property that is dependent on particle size, structure, and porosity^{166, 166} therefore it will directly impact physical interactions with liquids and gases. SA analysis is particularly important for porous materials applied in adsorption, heterogenous catalysis, and surface reactions.¹⁶⁷ Unlike simpler mathematical 2D and 3D shapes, SA determination of porous materials with internal SA are more challenging and requires more sophisticated methods of analysis. Various analytical techniques are available for determination of internal SA of a material, for instance porosimetry techniques such as Mercury Intrusion Porosimetry (MIP) employing a non-wetting liquid method,^{168, 169} and optical methods.^{170, 171} (Figure 2.1a).^{172, 173}

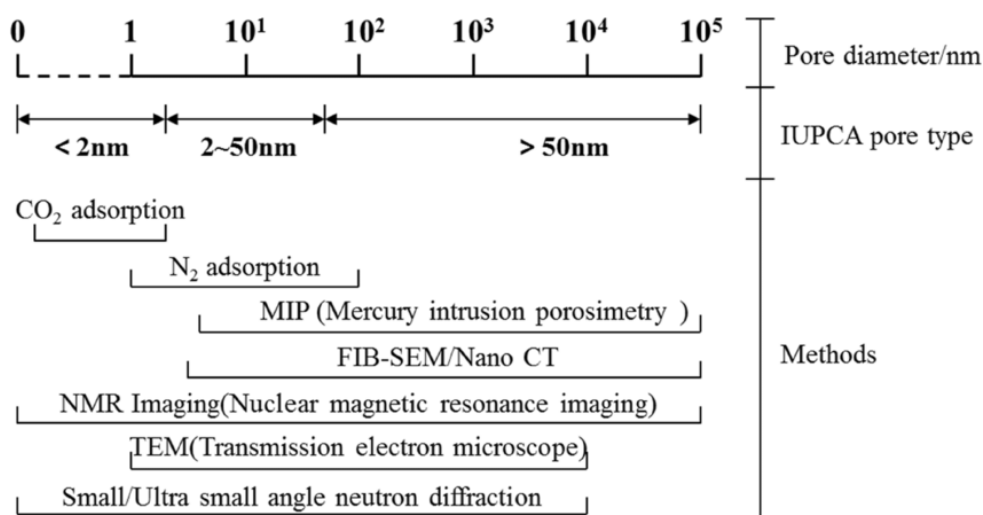


Figure 2.2a: Various analytical measurements for different pore sizes.

Adsorption plays a very important part in the chemical industry from hard water softening, dye removal, heterogeneous catalysis, and gas separation¹⁷⁴ to the characterisation of porous materials¹⁷⁵. Dewar was the first to report on adsorption of gases such as nitrogen at liquid air temperature (~ 77 K) in 1905¹⁷⁶ and now the adsorption is the most used technique for determination of surface area and pore size distribution.^{177,178} The fundamental theory of gas adsorption is based on adsorption characteristic of gas on solid surfaces¹⁷⁹ by reversible physisorption. The surface area of a porous material can be determined by adsorption of a gas with measured volume and known effective cross-section in a monolayer fashion. Countless physical and chemical procedures take place at the frontier between two phases. The change in concentration of a given substance at the interface compared to the neighbouring phase(s) is known as adsorption. Taking into consideration what type of phases are in contact we can categorise the processes into the following systems: liquid-liquid, liquid-gas, liquid-solid, and solid-gas. Key adsorption processes take place at liquid-solid^{180,181} and solid-gas^{182–185} interface, however all types of above interfaces can be applied in laboratory separation techniques.^{186–188}

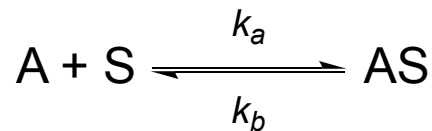
Adsorption can occur through two different pathways, physisorption (physical adsorption) and chemisorption (chemical adsorption).^{189–191} Chemisorption is a result of strong chemical interaction such as hydrogen bonding, covalent or ionic bonds between the adsorbate molecule and a specific site of the adsorbent surface known as the active site.¹⁹² Due to the strong interaction between the adsorbate species and the adsorbent surfaces this process tends to be irreversible as the adsorbate gases can form strong interactions with the adsorbing surfaces for long period of time or permanently bind to the active site causing what is called “poisoning”, which is commonly observed in heterogeneous catalysis.¹⁹³ Chemisorption is essentially limited to a monolayer adsorption due its “lock and key” mechanism of action; therefore, it is useful in characterisation of catalyst surfaces as well as the elucidation of chemical reaction mechanisms of heterogeneous catalysis.¹⁹⁴

Physisorption is a reversible process in a sense that the adsorbate species are adsorbed onto the adsorbent surfaces usually with only with weak van der Waals interactions and can temporarily interact with the adsorbent surface and break away through a process

called desorption.^{195,196} The most common method for surface area measurements is the gas adsorption method which heavily relies on desorption of adsorbed gas. Since the adsorbent gas has a specific cross-section area, the SA of a given material can be estimated by calculating the volume of adsorbed gas.¹⁹⁷ Nitrogen remains a popular choice amongst gases used in gas sorption analysis because of its ability to penetrate mesoporous and microporous surfaces as well as its low cost and availability in laboratories.¹⁹⁸

There are number of mathematical models used for calculating SSA, however most analysis is based on the adsorption isotherm and a model is applied for calculation of adsorption equilibrium¹⁹⁹ which assumes the ideal gas behaviour of the adsorbate. Classically, nitrogen gas is used for surface area analysis.^{200,201} However other gases such as Ar, CO₂, or in some instances organic vapours (dynamic vapor sorption) is used.^{202–205} To avoid confusion here, nitrogen gas is considered as the adsorbate gas.

A thermodynamic equilibrium equation can be written where free nitrogen molecule (A) is adsorbed onto available surfaces of porous material (S) to form a volume of adsorbed species (AS) at the rate k_a . Given that nitrogen species are adsorbed via weak interactions reverse mechanism is possible through a desorption mechanism at rate k_d to reform free N₂.



The functional surface coverage (θ) of a system can be expressed as a fraction of occupied sites i.e. volume of gas adsorbed divided by amount of gas in a monolayer.

$$\theta = \frac{\text{Sites occupied}}{\text{Sites available}} = \frac{V_a}{V_m}$$

Fractional coverage of a surface is dependent on the pressure (P) applied to the system. The adsorption/desorption isotherm is achieved from the change in fractional coverage at constant volume and temperature.

2.1.1 Langmuir Theory

Langmuir analysis is the simplest practical isotherm model which can be applied to both high- and low-pressure systems²⁰⁶ and was introduced by Irving Langmuir in 1916.²⁰⁷ This relates the area covered by adsorbate molecules on the adsorbent surface as a function of partial pressure or concentration at fixed temperature. As mentioned, the rate of adsorption depends on the pressure (P) and the number of available sites ($N(1 - \theta)$) and desorption rate depends on the occupied sites ($N\theta$). The rate of change of fractional surface coverage is given by the following equation²⁰⁸ where $K = \frac{K_a}{K_d}$.

$$\theta = \frac{KP}{1 + KP}$$

The above equation can be presented as a linear equation using $y = mx + c$ to deduce V_m from linear plot.

$$\frac{1}{V_m} = \frac{1}{KV_m} \left(\frac{1}{P} \right) + \frac{1}{V_m}$$

The Langmuir isotherm model was derived under the assumptions that **(a)** adsorption of free gases happens in monolayer; **(b)** all adsorbent surfaces are equal and can adsorb at least one adsorbate molecule; **(c)** there is no interaction or repulsion between adsorbate molecules; and **(d)** the adsorbate molecules interaction with the adsorbent surface are held sufficiently strongly with weak interactions and are therefore considered immobile.^{199,209}

In Langmuir's proposed model, these assumptions are rarely accurate and therefore this model gives less than reliable estimates of SA by causing an underestimation of adsorption enthalpy by disregarding the adsorbate – adsorbate interactions, while causing an over estimation of average adsorption enthalpy by overlooking the surface non-uniformity. Nevertheless, Langmuir isotherm tends to produce more acceptable results than expected from the model as often the two primary limitations cancel each other out.²¹⁰

2.1.2 Brunauer-Emmett-Teller Theory

The Brunauer-Emmett-Teller (BET) model is an extension of the Langmuir model in that it considers the multilayer adsorption that was previously overlooked by Langmuir isotherm while upholding Langmuir's other theories.²¹¹ The BET theory suggests the following new assumptions:

- Adsorbate molecules can adsorb to a surface in an infinite number of layers.
- No interaction will occur between individual adsorption layers.
- Langmuir theory is applied to each individual layer.

From these assumptions a new set of equation is deduced:

$$V_a = \frac{V_m CP}{P_0 - P \left(1 + \frac{(c-1)P}{P_0} \right)}$$

Hence, the BET equation can then be rearranged into the $y = mx + c$ to give the linear equation:²¹²

$$\frac{P}{V_a(P - P_0)} = \frac{C - 1}{CV_m} \left(\frac{P}{P_0} \right) + \frac{1}{CV_m}$$

where V_m = volume of adsorbate gas in a monolayer (mL), V_a = volume of adsorbed gas (mL), P = partial vapour pressure of the adsorbate molecule in surface equilibrium at 77K (P_a), P_0 = saturation pressure of the adsorbate molecule (P_a). Parameter C is directly affected by monolayer adsorption.²¹³ hence determine the shape of the isotherms and it is represented by:

$$C = \exp \left(\frac{E_1 - E_L}{RT} \right)$$

Where E_1 = the heat of adsorption of the initial layer and E_L = the heat of adsorption beyond the first layer.

Using the linear BET equation above, plotting $P/V_a(P - P_0)$ against P/P_0 should theoretically produce a linear graph.²¹¹ Linearity is observed at lower P/P_0 , however, a deviation from the linear equation is observed at higher P/P_0 caused by multilayer adsorption happening as the partial pressure is reaching saturation pressure of the adsorbate. It has experimentally been proven that plotting $P/V_a(P - P_0)$ against P/P_0

will produce a linear graph for the P/P_o range of 0.05 – 0.35. The intercept (i) and gradient (m) obtained from this plot can be used to calculate the BET constant (C) and the volume of the monolayer.

$$V_m = \frac{1}{m + i}$$

$$C = \left(\frac{m}{i}\right) + 1$$

Specific BET surface area, S_{BET} (m^2g^{-1}), of a porous sample can then be calculated from (V_m) using the equation:

$$S_{BET} = \frac{V_m N_A \sigma}{M V_{STP}}$$

where V_{STP} = molar volume (22414 mL) occupied by a gas at ambient temperature (273.15 K) at 1 atm, M = mass of sample, σ = Effective cross-sectional area of one diatomic nitrogen molecule ($16.2 \text{ \AA}^2$), N_A = Avogadro's constant ($6.022 \times 10^{23} \text{ mol}^{-1}$).²¹¹

Specific BET surface area of a given porous sample is calculated from three or more points collected within the P/P_o range of 0.05 – 0.35, giving the ability to automatically calculate the surface area and the total pore volume using a simple surface area analyser based on gas adsorption. It is important to note that the values obtained from BET analysis are estimated and might have slight (or even large) differences to the actual values due to human error in sample preparation and over estimation of BET surface area caused by the micropore filling effect.

2.1.3 Types of Adsorption Isotherms

Brunauer and his co-workers Emmett and Teller²¹⁴ also categorised the basis shape of potential physical adsorption isotherms into six types depicted in **(Figure 2.1.3a)**.^{215,216}

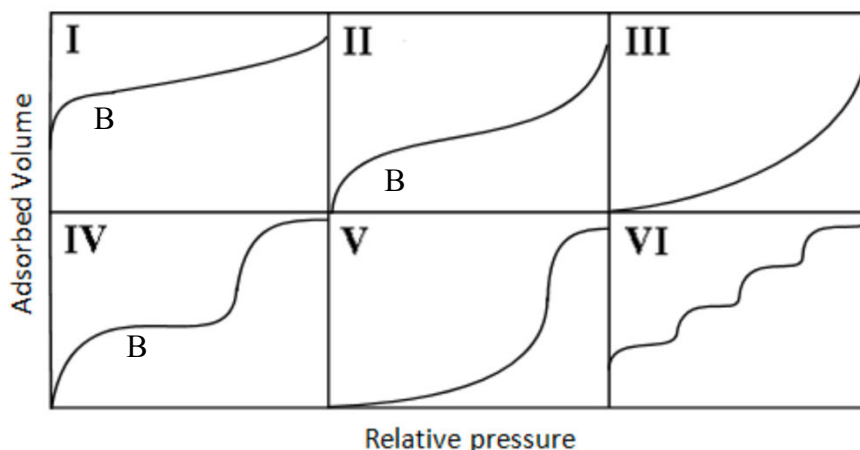


Figure 3.1.3a: The six types of physical adsorption isotherms described by Brunauer, Emmett, and Teller.

BET physical adsorption isotherms are characterised as follows:²¹⁷ Reversible Type I is the typical shape of isotherm for microporous materials containing micropores below ≈ 1 nm as well as mesopores (> 2 nm). Reversible Type II isotherm is related to materials that are predominantly non-microporous. For Type I and II the point **B** on the isotherm corresponds to monolayer coverage, here if the monolayer coverage is completed, a sharp curvature is observed whereas a more gradual curvature is seen it indicates the beginning of multilayer formation. Type III isotherm is achieved when the interactions between the adsorbate and the adsorbent is weak resulting in lack of information from the monolayer coverage. Type IV isotherm is commonly observed from mesoporous materials and usually show hysteresis between adsorption and desorption at higher values of P/P_0 . Type V isotherm is achieved at low P/P_0 ranges like that of type III isotherm, where the adsorbate-adsorbent interaction is weak. Hysteresis may be observed for this isotherm at higher relative pressures. Type VI isotherm is a typical multilayer adsorption isotherm obtained from materials that contain uniform nonporous surfaces. The shape of the step curve depends on the material, the adsorbate gas, and the temperature.

Chapter 3: Functionalisation of Polyacrylonitrile

3.1 Hydrolysis of PNPA with PAN/PANOX

Prior to initiating the synthesis and analysis of novel PIMs for adsorption and catalytic deactivation of CWAs model compound, it was essential to review the study carried out by Chen et. al. (2007). This study highlights the investigation of the catalytic hydrolysis of *p*-nitrophenyl acetate (PNPA) using electrospun polyacrylamidoxime (PANOX) nanofibers. Chen et. al.'s study depicts the capability of PANOX nanofibers for adsorption and catalytic deactivation of CWAs. This finding provides better insights into the design and development of novel PIMs with enhanced adsorption and catalytic properties.²¹⁸ This study is specifically important for the development and synthesis of novel PIMs due to a multitude of reasons. As mentioned earlier, this study looks at PNPA as a non-toxic model compound for ester hydrolysis, displaying key structural features of nerve agents such as soman or VX allowing safe experimental study to better understand the hydrolysis behaviour of nerve agents. Chen et. al. also covers the importance of functionalising the active sites of porous polymeric materials with functional groups such as Lewis bases, nucleophiles and amidoxime groups to improve catalytic hydrolysis properties of these materials. During this Study Chen et. al. also looked at producing electrospun nanofibers from PANOX to incorporate into protective equipment such as vests and masks.

Note, as a safety measure PNPA was chosen for measurements of its rate of hydrolysis of CWAs as it mimics that of more toxic organophosphate presents in nerve agents and the insecticide Paraoxon (**Figure 3.1a**).

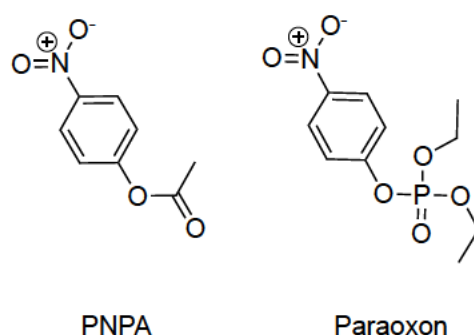
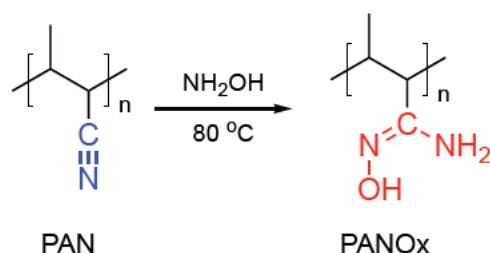


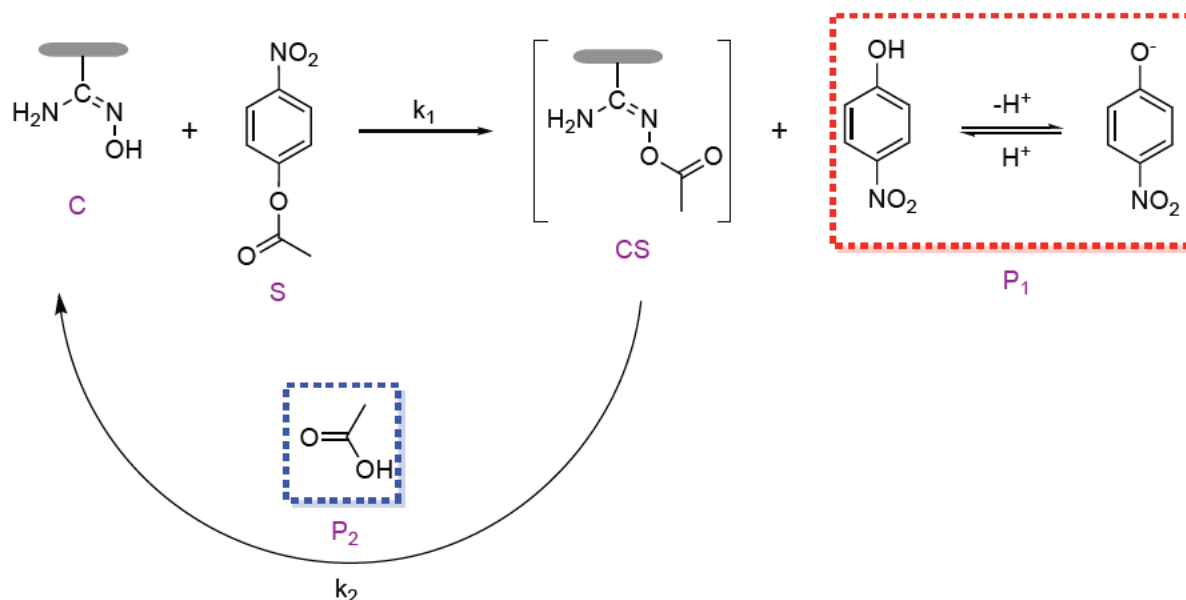
Figure 3.1a: Chemical structures of PNPA and Paraoxon.

Polyacrylonitrile (PAN) is a synthetic polymer widely recognised for its exceptional properties, including high malleable strength, chemical resistance, and thermal stability. PAN can undergo amidoximation, a chemical modification process involving the conversion of nitrile (-CN) groups to amidoxime (-C(NH₂)=NOH) groups to obtain catalytic PANOx (Scheme 3.1a). This functionalization process can be achieved through the reaction of PAN with hydroxylamine (NH₂OH) under basic conditions (Scheme 3.2a).²¹⁸



Scheme 3.1a: Modification of polyacrylonitrile to polyacrylamidoxime.

The proposed reaction scheme illustrates the cleavage of PNPA by nucleophiles in solution (Scheme 3.1b), where a base is required to regenerate the amidoxime active site by removing the acetate group.^{219,220}



Scheme 3.1b: Catalytic hydrolysis of PNPA by acrylamidoxime groups of the nanofibers. Where PNPA substrate (S), acrylamidoxime groups (C), amidoxime functional group bonded to the polymer (CS), pH dependant product (P₁), acetate (P₂), rate constant of hydrolysis (k₁) and rate constant of deacetylation (k₂).²¹⁸

As reported by Chen and his group, the use of PAN/PANOX nanofibers as heterogeneous catalysts appears to increase the hydrolysis rate of PNPA (**Figure 3.1b**). They have conducted the experiment using three sets of buffers with pH 7, 8, and 9. It was described that introducing PAN/PANOX nanofibers as heterogeneous catalysts to the reaction system with increasing pH increased the rate of hydrolysis (3 – 7-fold) compared to that of the control experiment which used non-catalytic PAN nanofibers but under same buffer range. It was suggested by the authors that slower hydrolysis was observed from the control experiment; this trend is the same across both experiments as higher pH level showed higher hydrolysis rates compared to lower pH levels. Evaluating the data further suggested that the rate of conversion in both experiments at pH 9 appears to be much the same and ~95% conversion happens at approximately the same time. It is already disclosed that the catalytic PAN/PANOX nanofibers have negligible solubility in common organic solvent and therefore will act only as a heterogeneous catalyst. When measuring the hydrolysis rate *via* UV-vis absorption spectroscopy the solution should be free of any solid. *i.e.* the nanofibers are filtered out of the solution and no longer act as a catalyst, hence, this raises the question as to how large a role the base is playing in the hydrolysis of PNPA versus the active PANOX nanofibers.

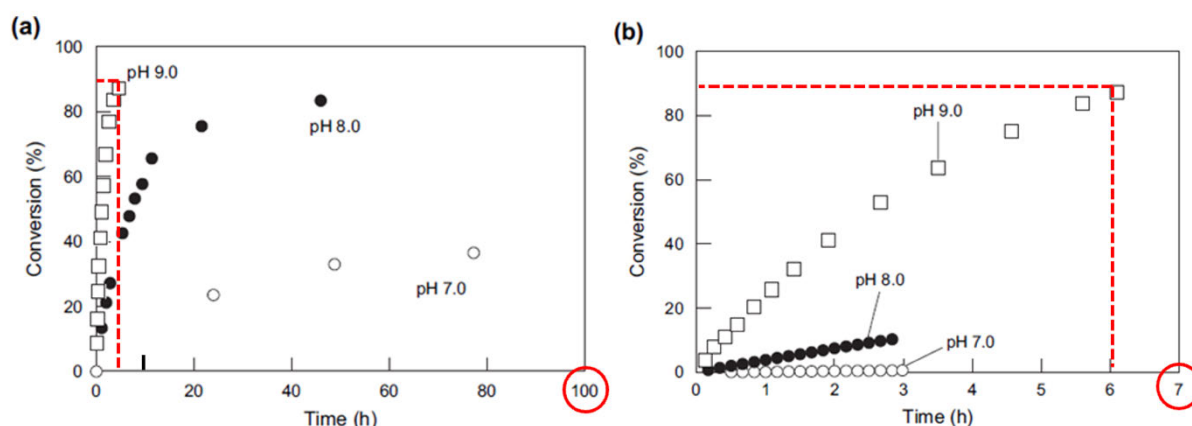


Figure 3.1b: Graphs representing the kinetics of PNPA conversion (a) with, and (b) without PAN/PANOX nanofiber as a function of pH.²¹⁸

Other extensive studies have been carried out investigating the hydrolysis of 4-nitrophenyl acetate between pH 6 and 9 in various buffers including tris(hydroxymethyl)aminomethane (*i.e.* Tris buffer). These studies indicate that

hydrolysis could be achieved via an acid-catalysed, base-catalysed, or pH-independent mechanism. As before, the rate constants were measured spectrophotometrically from the initial disappearance of 4-nitrophenyl acetate at 270 nm and the appearance of 4-nitrophenol at 313 nm and 4-nitrophenolate at 400 nm.²²¹ As mentioned the hydrolysis of 4-nitrophenyl acetate (an ester) can take place through three reaction pathways; acid-catalysed, base-catalysed and pH-independent.²²² Hine has established that these three reaction pathways are independent of one another.²²³ Therefore, it can be said that the pseudo-first-order rate constant consists of the sum of the products of the catalyst concentration and second-order rate constant. Where the second-order rate constant indicates the fundamental ability of the catalyst to cause hydrolysis. For hydrolysis reactions of esters taking place in distilled water the rate constant (k_0^{water}) is expressed as:

$$k_0^{water} = k_{H_2O} + k_{H^+}[H_3O^+] + k_{OH^-}[HO^-]$$

Where k_{H_2O} is the pH-independent rate constant, k_{H^+} is the second-rate constant for acid-catalysed reaction, k_{OH^-} is the second-rate constant for base-catalysed reaction, $[H_3O^+]$ and $[HO^-]$ are hydronium ion and hydroxide ion concentrations respectively.²²⁴ If the hydrolysis of 4-nitrophenyl acetate occurring in neutral pH the pseudo-first-order rate constant can be described as:^{224–227}

$$k_0^{water} = k_{H_2O} + k_{OH^-}[HO^-]$$

3.2 Replication and Verification of Literature Results on PNPA Hydrolysis

Initial research focused on replicating the results presented by Chen et al. to provide a benchmark for the comparison for future studies involving novel PIMs. PANOX was synthesised *via* functional group modification of PAN with excess hydroxylamine hydrochloride in DMF for 24 h at 80 °C, the resulting white powder was washed with water, methanol and acetone. Conversion of acrylonitrile group to amidoxime was monitored by reduction of nitrile peak at 2260 cm⁻¹ and appearance of amidoxime group C=N stretch at 1670 cm⁻¹, NH₂ bend at 1610 cm⁻¹, NH₂ and H₂O vibration at 3100–3600

cm^{-1} (Figure 3.2a). Samples of PAN/PANOx was sent to our collaborator Prof. Maria-Chiara Ferrari and Dr. Elsa Lasseguette of the School of Engineering, University of Edinburgh, for nanofiber processing (Figure 3.2b) using the method previously described by Chen et al.²¹⁸

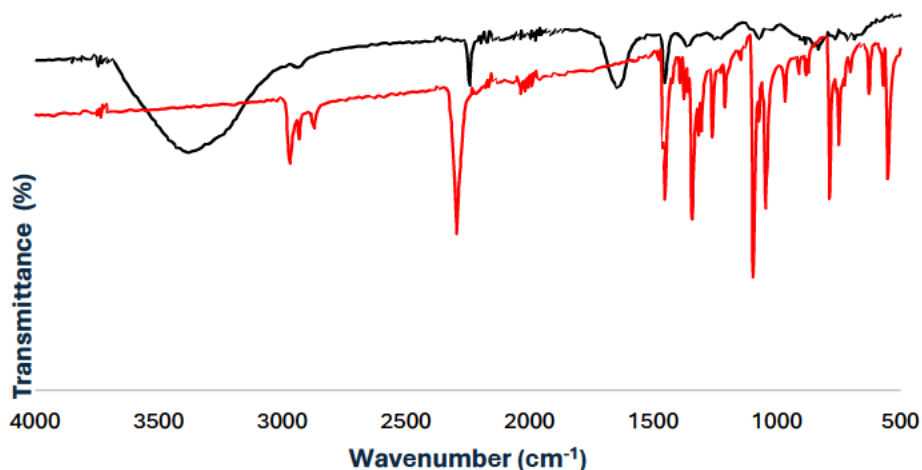


Figure 3.2 a: FT-IR spectrum of acrylonitrile group conversion of PAN (Red) to amidoxime of PAN/Ox (Black).

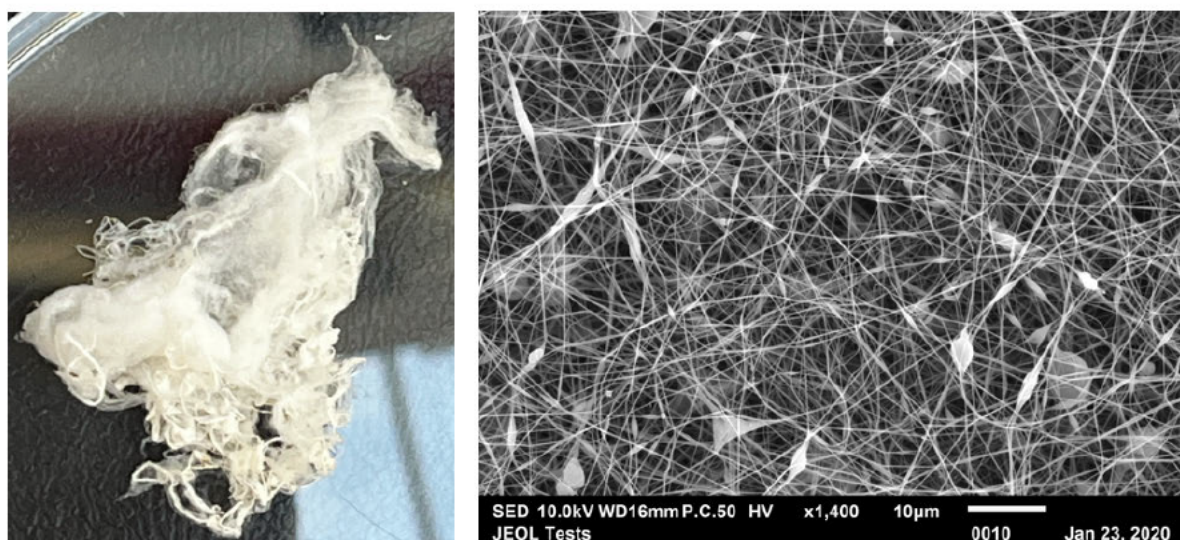


Figure 3.2b: (Left) Electrospun PAN/PANOx nanofibers, (right) SEM image of PAN/PANOx nanofibers (average fibre diameter: $230 \pm 20 \text{ nm}$, scale bar: $10 \mu\text{m}$).

A series of experiments was then performed following the literature procedure to qualitatively analyse the formation of 4-nitrophenolate in basic reaction medium. Samples were analysed using a Shimadzu UV-1800 spectrometer, with 4-nitrophenol

(colourless compound) absorbing at 313 nm and 4-nitrophenolate (bright yellow compound) absorbing at 400 nm (**Figure 3.2c**).

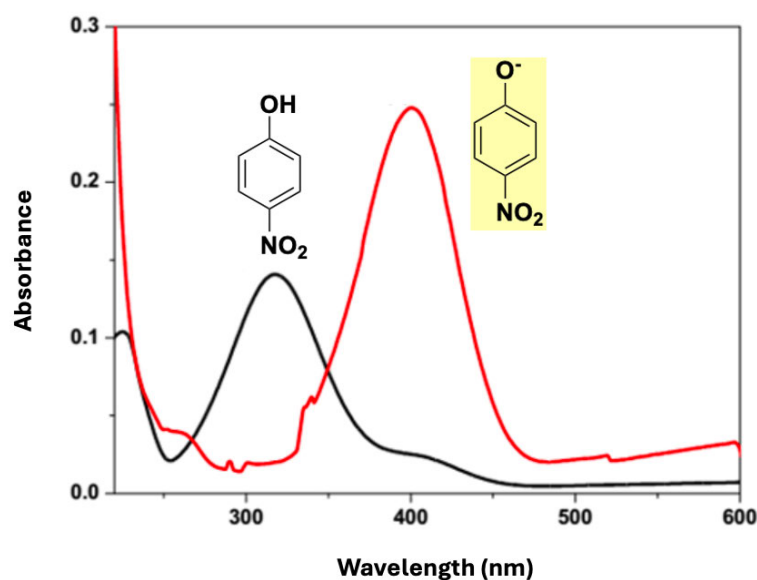


Figure 3.2c: UV absorption spectra of 4-nitrophenol at 313 nm (black) and 4-nitrophenolate at 400 nm (red).

PNPA was dissolved in ethanol^[228]

All sample preparation was done in accordance with Chen et. al. except that ethanol is used to compensate for the low solubility of PNPA in water as well as low wettability of PAN/PANOx nanofibers. Control samples were analysed to observe the effect of ethanol in the hydrolysis of PNPA.

Sample **A** was prepared by dissolving PNPA (~200 mg) in absolute EtOH (25 mL) and stirring the mixture for 3 hours. Sample **B** was prepared by dissolving PNPA (~200 mg) in a mixture of EtOH and water (1:1 v/v% total volume of 25 mL). After 3 hours no sign of visual changes were observed from sample **A** as the solution stayed colourless indicating the absence of 4-nitrophenolate: this was confirmed by UV spectrometry where no absorption was observed at 400 nm and the presence of 4-nitrophenyl acetate peak at 270 nm for sample **A**. Sample **B** had change colour to clear pale yellow after 3 hours and UV analysis confirmed the appearance of a peak at 400 nm, indicating the presence of 4-nitrophenolate (**Figure 3.2d**).

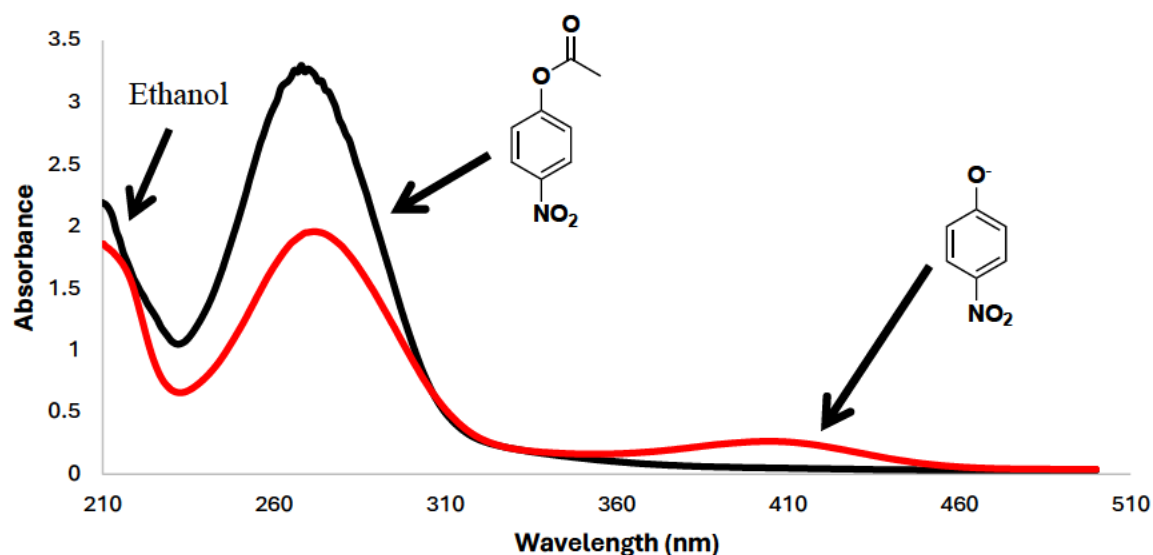


Figure 3.2d: UV spectra of sample **A** (Black) and sample **B** (Red).

To compare our findings with literature a series of samples were prepared containing PNPA and the catalytic PAN/PANOx nanofibers. A typical sample was prepped by suspending 100 mg of PAN/PANOx nanofibers in a 9 mL solution of Tris buffer/ethanol (1:1 v/v%), to which 1 mL of freshly prepared PNPA/ethanol solution was added and the pH monitored using a pH meter, solutions were stirred at room temperature. Prior to UV-vis analysis aliquots (200 μ L) were taken from the stock solutions at different time intervals, filtered using a 17 mm PTFE 0.22 μ m syringe filter to remove solid residue, transferred into a standard macro quartz cuvette cell and made up to 3000 μ L using ethanol.

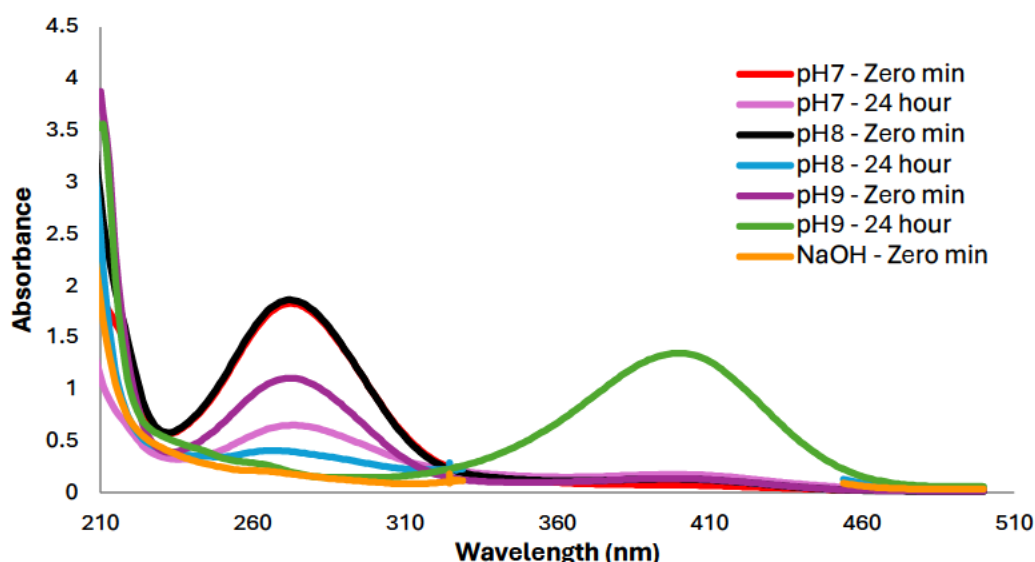


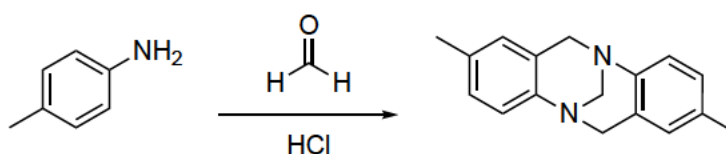
Figure 3.2e: UV-vis spectra of PNPA hydrolysis with PAN/PANOx in different pH value buffer solution. Sample tested with NaOH does not contain catalytic PAN/PANOx nanofibers.

This analysis verified the hydrolysis of PNPA in the presence of catalytic PAN/PANOx nanofibers, where at higher pH an increase in the rate of 4-nitrophenolate was observed (Figure 3.2e). The reaction in pH 7 buffer showed the least amount of conversion compared to those carried out in pH 8 and 9, this observation is linear in both initial samples (zero min) and samples analysed after 24 hours. The highest conversion (in the presence of PAN/PANOx nanofiber) was observed from pH 9 buffer solution in both the initial and 24-hour sample. A sample containing PNPA with 0.1 M NaOH in the absence of PAN/PANOx nanofibers was also analysed, displaying complete and instantaneous hydrolysis of PNPA to 4-nitrophenolate, proving that the hydrolysis reaction of the ester PNPA is more effective with a base. As observed, PAN/PANOx does not contain any basic sites along its polymeric structure making it very difficult to provide the necessary conditions for hydrolysis of PNPA with PAN/PANOx in the absence of a base in the form of buffer. This result confirmed that the proposed AO-modified PIMs will require base either in buffer form or incorporated into the system as a component of the PIM. The following chapters describe attempts to incorporate basic amine (and potentially basic amide) units into PIM with AO functionality.

Chapter 4: Synthesis of PIMs Containing Tröger's Base

4.1 Tröger's Base

As an initial objective, the concept of incorporating a simple basic unit in a form of Tröger's Base (TB) monomer, which has been proven to act as a useful rigid structural unit for making PIMs, was investigated. TB was discovered in the 1887 by the German chemist Julius Tröger while studying the reaction of *p*-toluidine with formaldehyde²²⁹ (Figure 4.1a) where he discovered this reaction yields a product with a molecular formula of C₁₇H₁₈N₂.



Scheme 4.1a: Synthesis of Tröger's Base.

Tröger was never able to explain the exact structure of the compound he had isolated. It was not until much later that Spielman was able to assign the correct structure in 1935²³⁰ and it would take another 51 years for the structure of TB to be fully confirmed using single crystal X-ray diffraction.²³¹ The structure of TB consists of two aromatic rings fused to a bridged bicyclic ring system. The benzene rings are twisted relative to each other, resulting in a chiral molecule with two enantiomeric forms (Figure 4.1b).



Figure 4.1b: MMFFs-Optimized geometry of the two enantiomers of Tröger's Base.²³²

Wepster's research was initially focused on understanding the stereochemical and electronic properties of Tröger's base molecule concerning its rigid V-shaped structure creating steric hindrance, chirality arising from the rigidity of the molecule, and basicity which is the direct result of limited delocalisation and interactions of nitrogen lone pairs. According to Wepster's initial claims, TB is believed to be a weak base,²³³ however, a study was conducted in 2004 where the hydrogen bonding acceptor strength of TB was measured, and it was reported that TB is strongly basic in comparison to other aromatic amines ($pK_{HB}(N) = 1.15$).²³⁴ The moderately high basicity of TB is believed to be the result of its rigid structure pushing the nitrogen lone pairs of electrons into an orientation where there are little to no orbital overlap with the associated aromatic ring system and therefore disturbing the π -conjugation.²³⁵

The basic nature and the contorted geometry of TB molecule makes a very interesting choice to explore as a potential monomer for the synthesis of PIMs. By introducing TB to the polymeric structure of PIMs the rigid structure essential to PIMs performance as a microporous material can be maintained as well as introducing basicity to the polymeric structure. By introducing a basic unit to the polymer, we can explore different avenues such as exploring its effect on gas permeability specially gas separation of acidic gases such a carbon dioxide as well looking at the effect on hydrolysis of PNPA (and organophosphate CWAs) without the need to introduce an external base in the form of buffer solutions.

From the time of its discovery many procedures have been reported for TB synthesis, all of which remain very similar to that of the original procedure. A general method for TB synthesis can be described as such; an aromatic amine derivative is reacted with a CH_2 source such as DMSO²³⁶, formaldehyde²²⁹ or paraformaldehyde²³⁷ under acidic conditions. As such, common acids used for TB synthesis are hydrochloric acid²²⁹, methanesulfonic acid²³⁸ and trifluoroacetic acid²³⁹, which can act both as solvent medium and as well as catalyst for the reaction. A reaction mechanism for TB synthesis has been proposed by Wagner,^{240,241} and Farrar²⁴² (**Figure 4.1c**) which is backed by Eberlin and Coelho²⁴³ who studied the reaction mechanism by identifying the reaction intermediates using mass spectrometry.

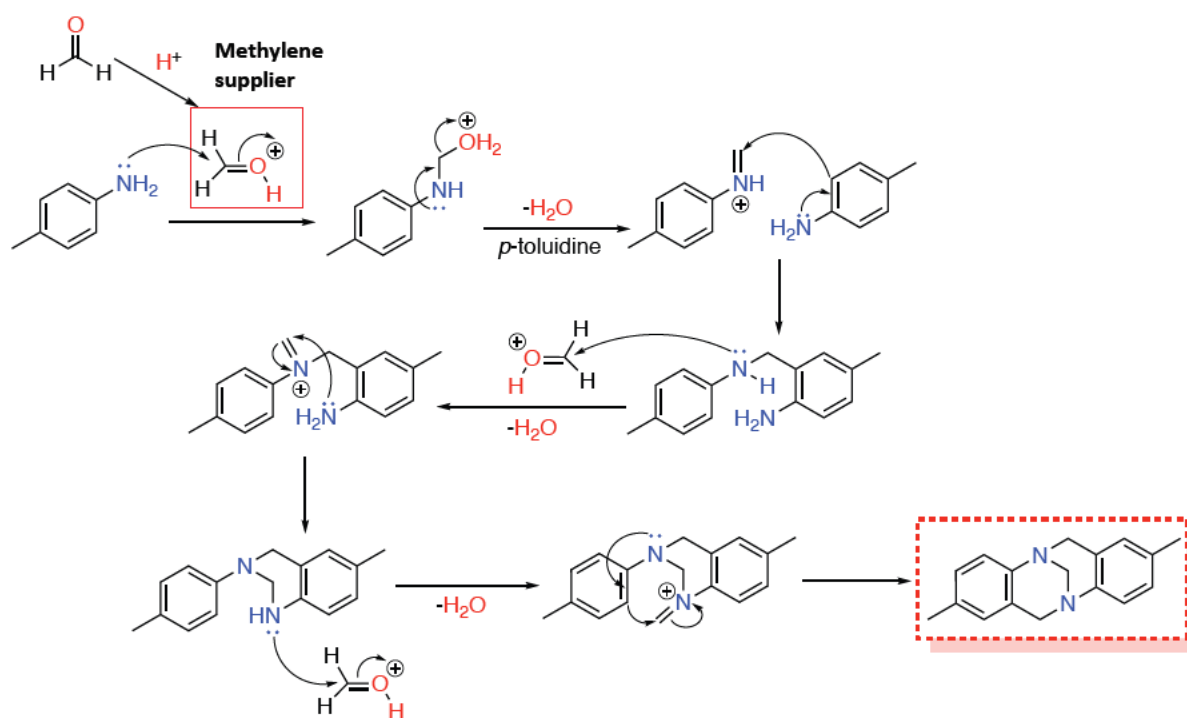


Figure 4.4c: Wagner and Farrar's proposed mechanism of Tröger's base formation using formaldehyde.

4.2 TB-Based PIM

4.2.1 Tetramethoxy-TB Precursor

The reaction procedure for the synthesis of TB analogue used for polymerisation in this section has been taken from the reported work of former McKeown research group member Dr. Mariolino Carta.²⁴⁴



Figure 4.2.1a: Synthesis of a tetramethoxy Tröger's Base derivative.

2,3,8,9-Tetramethoxy-6H,12H-5,11-methanodibenzo[1,5]-diazocine (**1**) was synthesised (Figure 4.2.1a) by gradual addition of 3,4-dimethoxyaniline and excess *p*-formaldehyde to ice cold solution of trifluoroacetic acid resulting in a light purple powder with 65% yield. Recrystallisation from methanol yielded plate like crystals used for single crystal X-ray analysis (Figure 4.2.1b).

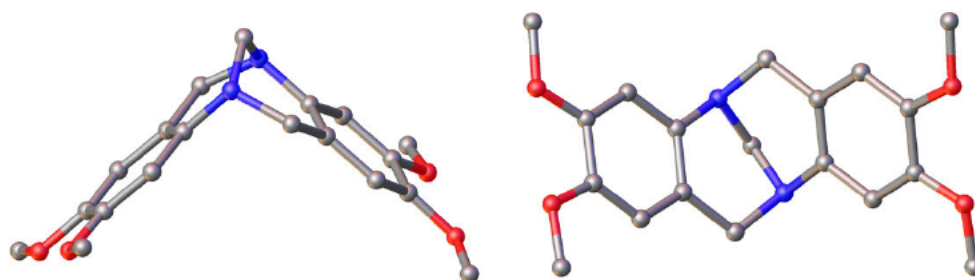


Figure 4.2.1b: Crystal structure of tetramethoxy-TB (**1**), side view (left) and top view (right). Crystals obtained from slow evaporation of methanol.

4.2.2 Demethylation of Tetramethoxy-TB

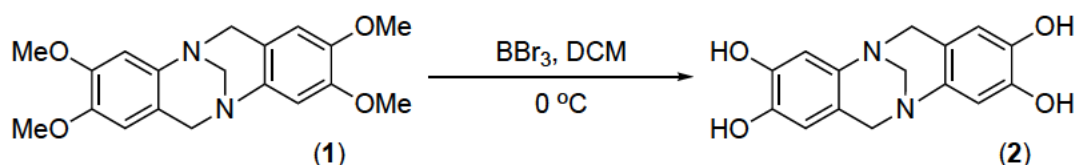


Figure 4.2.1c: Demethylation reaction of tetramethoxy-TB (**1**).

Compound (**1**) was demethylated using BBr_3 to give a white product (**2**) in 20% yield. FT-IR analysis was used to monitor the reaction by observing the disappearance of CH stretch ($3205 - 3371 \text{ cm}^{-1}$) and appearance of broad OH band at 3228 cm^{-1} (Figure 4.2.2a). Sample purity was confirmed by NMR and the product was dried in a vacuum oven for 12 hours at 30°C to give the desired tetrahydroxy-Tröger's Base (biscatechol) product (**2**).

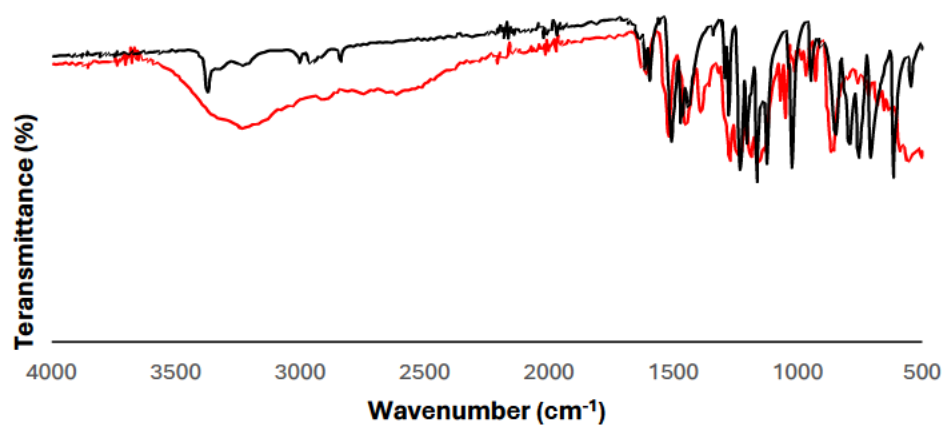


Figure 4.2.2a: FT-IR spectra of tetramethoxy-TB (black) and biscatechol-TB (red).

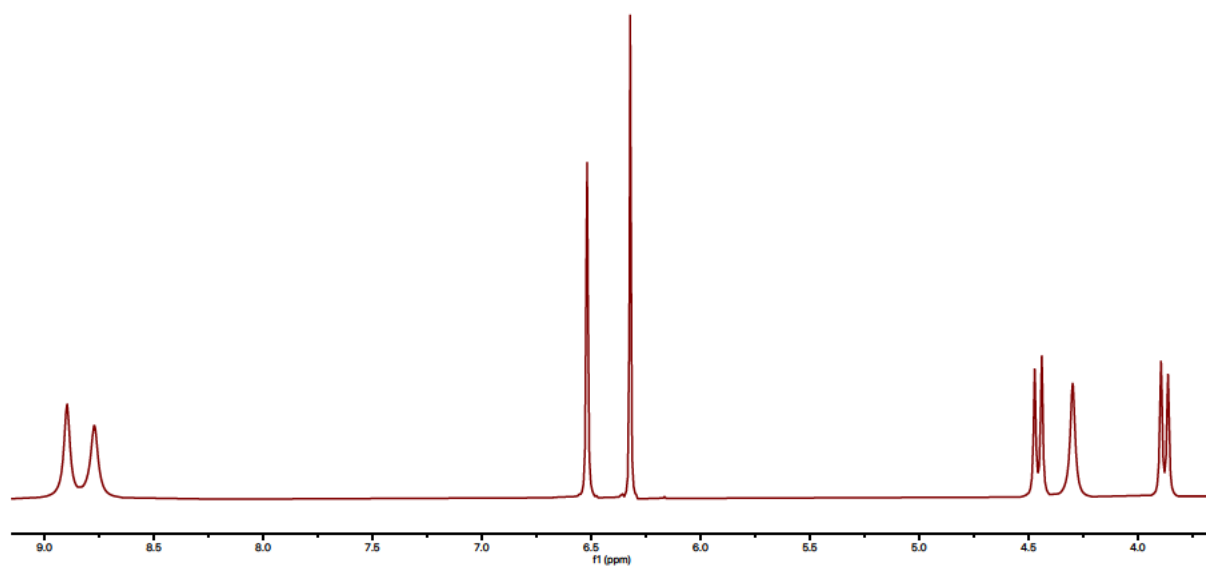


Figure 4.2.2b: ¹H NMR spectrum of biscatechol-TB dissolved in DMSO d⁶.

4.2.3 TFTTSBI Synthesis (ABA-Type Monomer)

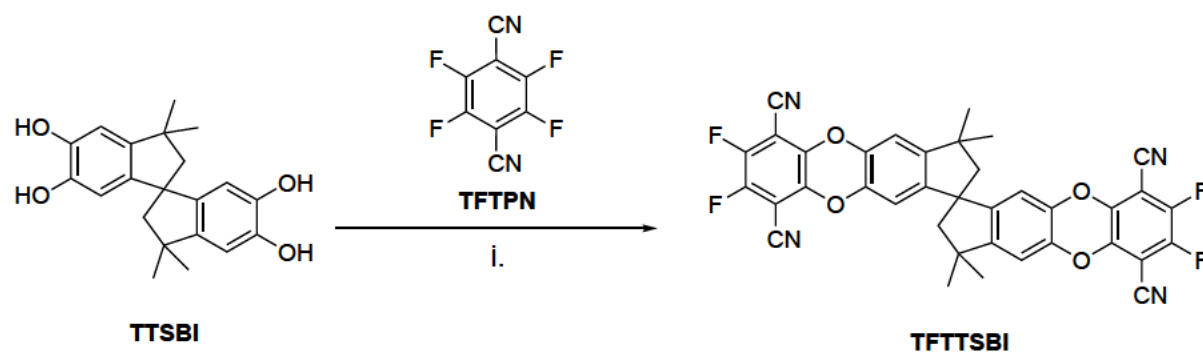


Figure 4.2.5a: Synthesis of **TFTTSBI**. i) K_2CO_3 , DMAc, 80 °C.

The tetrafluoro monomer **TFTSBI** is a useful building block commonly used in PIM polymerisation to give alternating copolymers and its synthesis was achieved according to a literature procedure.²⁴⁵ **TTSBI** was reacted with tetrafluoroterephthalonitrile **TFTP** (1:2 molar equivalent with **TFTP** in excess) in the presence of base under nitrogen atmosphere to obtain compound **3** with 88% yield. Its structure was confirmed by ^1H NMR analysis.

4.2.4 The Synthesis of TB-PIM

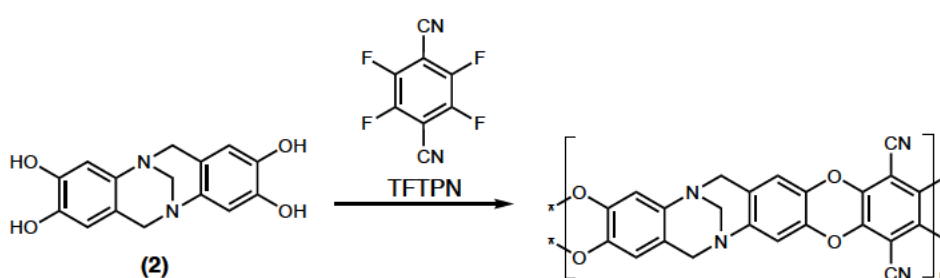


Figure 4.2.4: Polymerisation reaction of **PIM-TB**.

Following the literature procedure **PIM-TB** was successfully synthesised in 87% yield by reaction of TB monomer **2** with **TFTP**. However, due to poor solubility of the polymer full characterisation of the polymer was only achieved using MAS ^{13}C NMR spectroscopy

(magic angle spinning) where the nitrile groups appear at around 124 ppm and the bridging carbons are observed at approximately 65 ppm (**Figure 4.2.4b**).

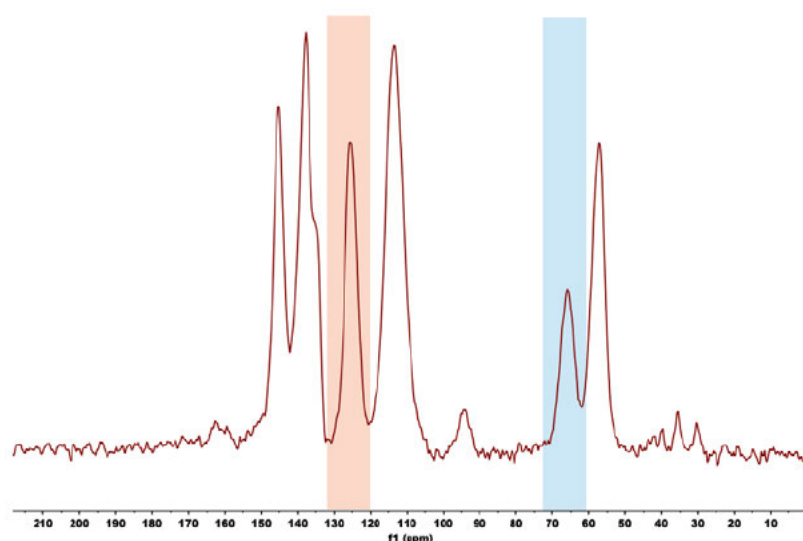


Figure 6.2.4b: MAS ^{13}C NMR spectra of **PIM-TB**, nitrile group (orange) and bridging carbons (blue).

4.2.5 Preparation of Alternating TB-PIM Copolymer

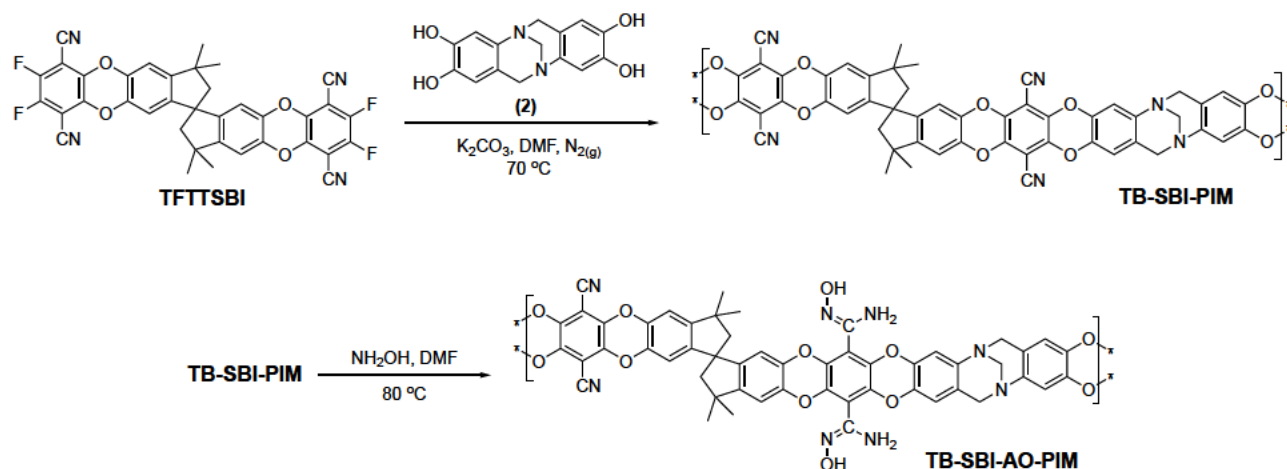


Figure 4.2.7a: Synthesis of **PIM-1** and Tröger's Base co-polymerisation (top) and its AO modification (bottom).

TB-SBI-PIM copolymerisation was carried out by reacting TB monomer **2** with TFTTSBI in a 1:1 molar ratio in basic conditions under a nitrogen atmosphere for 48 hours. The resulting polymer was washed and refluxed in methanol to remove low molecular weight chains. The polymer was insoluble in organic solvents therefore no deuterated solvent was suitable for ^1H NMR characterisation, hence the resulting polymer was also

characterised by solid-state cross-polarisation magic-angle spinning carbon-13 nuclear magnetic resonance spectroscopy (solid-state CP/MAS ^{13}C NMR), which is consistent with its structure showing a combination of peaks associated with both TB and SBI (**Figure 4.2.5b**).

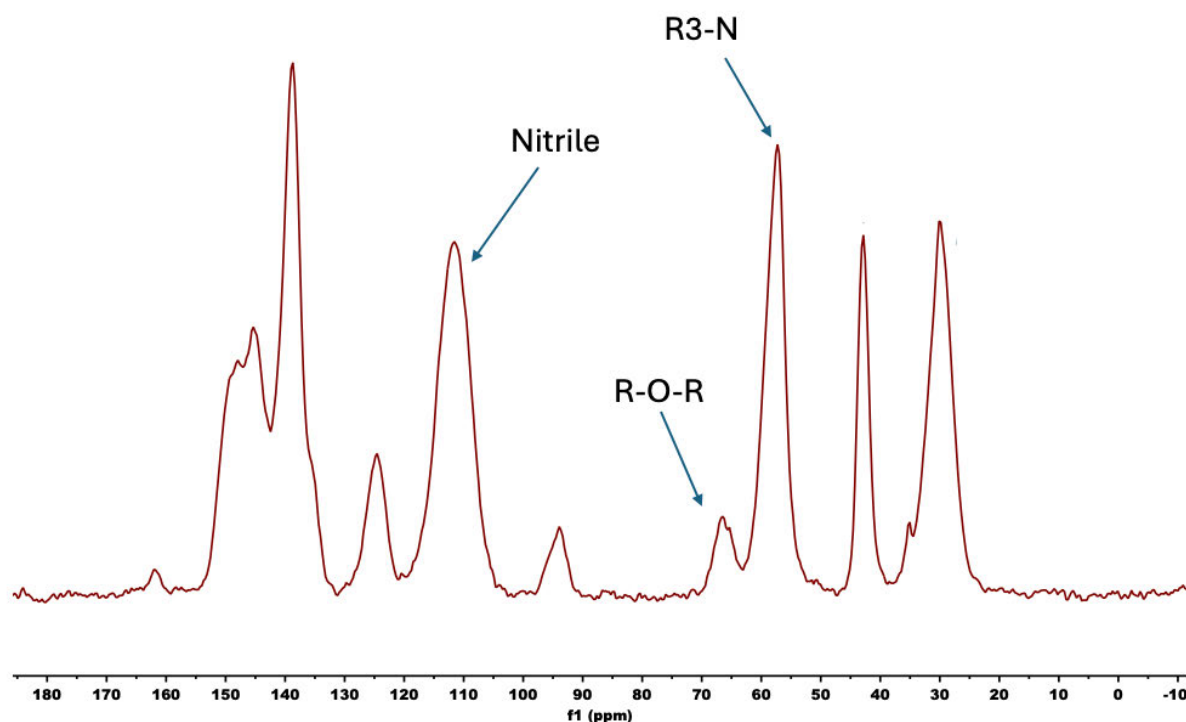


Figure 4.2.5b: MAS ^{13}C NMR spectra of **TB-SBI-PIM**.

TB-SBI-PIM was then reacted with excess of hydroxylamine chloride to convert the nitrile group to amidoximes to obtain **TB-SBI-AO-PIM**. The functional group modification was confirmed with FT-IR analysis: the disappearances of nitrile group at 2237 cm^{-1} and the appearance of OH/NH peak at 3609 cm^{-1} along with C=N at 1670 cm^{-1} and NO at 874 cm^{-1} .

PIMs containing **TB** monomers can suffer from poor solubility in organic solvents. This was initially observed in **TB-PIM**, leading to synthesis of copolymers containing **TTSBI** monomers. **TTSBI** is a soluble monomer and the building block of PIM-1 (known for its high solubility and processability) and by copolymerisation of this monomer with **TB** the polymeric backbone rigidity decreases compared to a **PIM** synthesised from pure **TB** monomer. **TTSBI** increases the chain flexibility and in turn increase the solubility of polymer. Incorporating **TTSBI** with **TB** in a 1:1 ratio, however, did not drastically improve

the solubility of the copolymers and both **TB-SBI-PIM** and **TB-SBI-AO-PIM** copolymers displayed little to no solubility in organic solvents when synthesised in a 1:1 ratio. The solubility of these copolymers could potentially be further enhanced by adjusting the monomer ratio, for example the ratio of monomers can be adjusted to 75:25 ratio of **TTSBI:TB** monomers.

4.2.6 TB-PIM Analysis

The N_2 gas adsorption and desorption isotherm plots of **PIM-TB**, **TB-SBI-PIM** and **TB-SBI-AO-PIM** were obtained at 77K (Figure 4.2.6a). **TB-SBI-PIM** (green) and **PIM-TB** (purple) isotherms obtained displayed Type I behaviour characteristic of microporous materials and **TB-SBI-AO-PIM** (blue) displayed an isotherm of an essentially non-porous material.

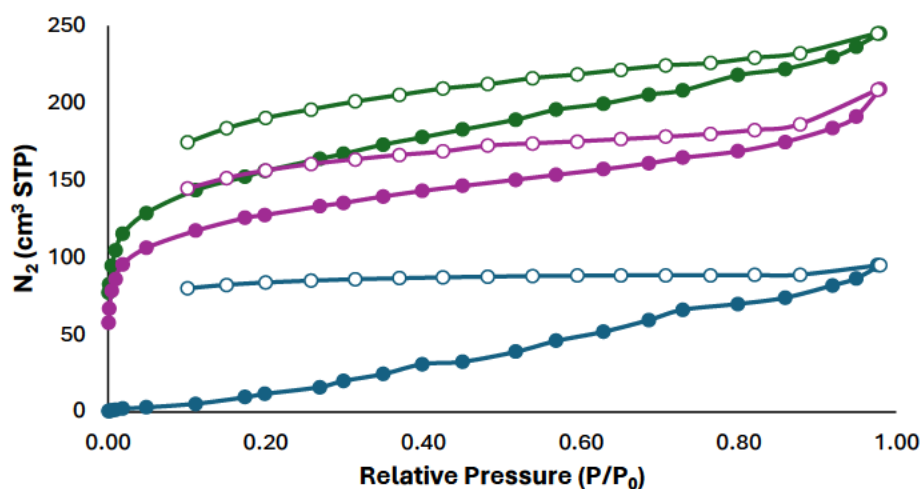


Figure 4.2.6a: N_2 adsorption isotherm measure at 77 K, adsorption (solid filled circles) and desorption (empty circles). **PIM-TB** (purple), **TB-SBI-PIM** (green) and **TB-SBI-AO-PIM** (blue).

From the obtained N_2 isotherms, BET surface area and total pore volume of the three polymers were calculated (Table 4.2.6a). By incorporating the **TTSBI** unit, a drastic improvement in surface area was observed from **TB-SBI-PIM** compared to that of **PIM-TB** due to the additional sites of contortion along the polymer backbone. We observe a decrease in surface area for **TB-SBI-AO-PIM** which could potentially be a direct result of

AO modification from the nitrile group. Amidoximes are a flexible functional group creating a less rigid polymeric backbone allowing for much more compressed folding of the polymeric chain resulting in loss of intrinsic microporosity. They are much larger functional group compared to nitriles blocking the micropores and reducing free volume of the polymer causing decrease in surface area. **AO** functional groups will also form hydrogen bonds introducing additional intermolecular and intramolecular interactions and forcing polymeric chains closer together, which causes PIMs to lose their intrinsic microporosity characteristic and reduces the surface area even further.

Table 4.2.6a: Gas adsorption properties of **PIM-TB**, **TB-SBI-PIM** and **TB-SBI-AO-PIM**.

Polymer	Solubility	SA_{BET}^a ($m^2 g^{-1}$)	V_{Total}^b ($mL g^{-1}$)	CO_2 uptake ^c ($cm^3 g^{-1}$)
PIM-TB	-	451	0.324	38.8
TB-SBI-PIM	-	550	0.380	43.6
TB-SBI-AO-PIM	-	42	0.147	33.4

^aBET surface area was obtained from N₂ adsorption at 77 K. ^bTotal pore volume was calculated from N₂ uptake at $P/P_0 = 0.98$. ^cCO₂ uptake was measured at 1 bar, 273 K.

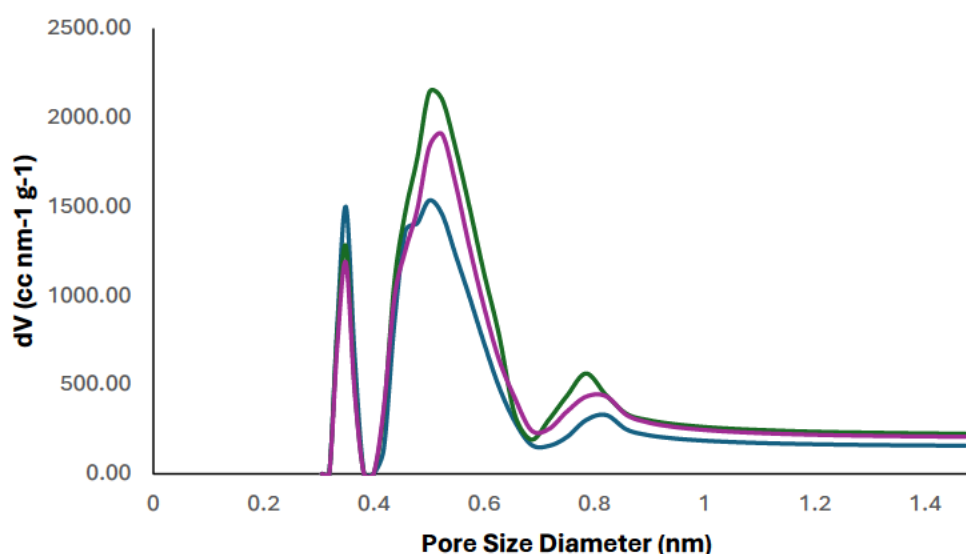


Figure 4.2.6b: Pore Size Distribution (PSD) calculated from CO₂ adsorption data using non-local density functional theory (NLDFT): **PIM-TB** (Purple), **TB-SBI-PIM** (green) and **TB-SBI-AO-PIM** (Blue).

The CO₂ adsorption isotherm for the polymers were also obtained, from which the CO₂ uptake at 1 bar, 273 K could be calculated (**Table 4.2.6a**). The pore size distribution within the polymers was also calculated from these isotherms, using non-local density functional theory (NLDFT) (**Figure 4.2.6b**). This indicated that the polymers possess a mixture of ultra-micropores (pore diameter < 0.7 nm) and micropores (pore diameter < 2 nm), where the AO-modified polymers presented higher volume of ultra-micropores with diameter less than 0.4 nm.

4.3 Hydrolysis of PNPA with TB- PIMs

In order to synthesize PIMs with basic properties, we have incorporated Tröger's Base as the building block for a series of TB polymers. These polymers were then assessed as heterogenous catalysts for the hydrolysis of PNPA in a simple UV-vis experiment. For consistency and to test the true ability of the polymers to catalyse the hydrolysis of PNPA (basicity of the polymers) the hydrolysis experiments were performed in buffer pH 7. It is also very important to develop PIMs that are capable of hydrolysing CWAs effectively at pH lower than pH 9 or more ideally at pH 7. The aim is to incorporate these polymers into personal protective equipment as nanofibers for clothing or in protective masks where they are in contact with human skin and the use of highly basic solutions to activate the hydrolysis process is not practical.

A typical sample was prepared by suspending 100 mg of **TB-PIM** as powder in a 9 mL solution of tris-buffer/ethanol (1:1 v/v%), to which 1 mL of freshly prepared PNPA/ethanol solution was added and the pH monitored using a pH meter. The solutions were stirred at room temperature then, prior to UV-vis analysis, aliquots (200 μ L) were taken from the stock solutions at different time intervals, filtered using 17 mm PTFE 0.22 μ m syringe filter to remove solid residue, transferred into a standard macro quartz cuvette cell and made up to 3000 μ L using ethanol.

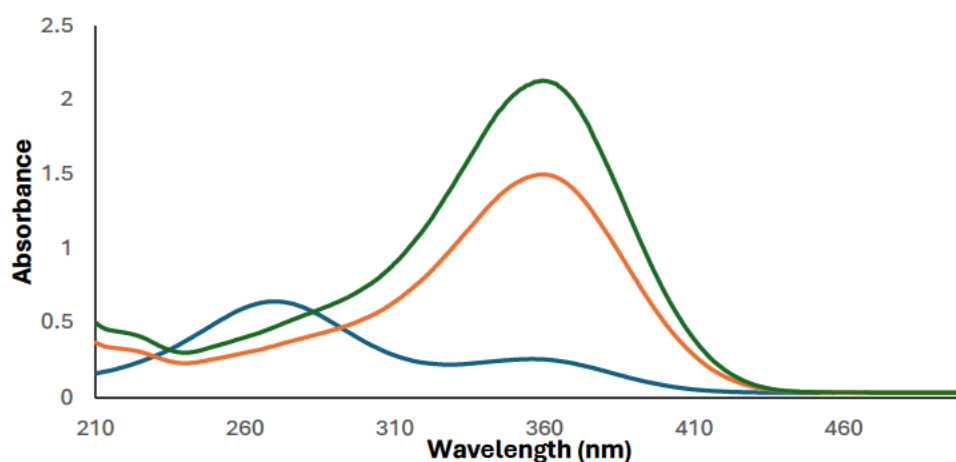


Figure 4.3a: UV-vis spectra of PNPA hydrolysis by **PIM-TB** (blue), **TB-SBI-PIM** (orange) and **TB-SBI-AO-PIM** (green) 24 hour at pH 7 (buffer solution).

As shown in (Figure 4.3a), PIM-TB shows the least amount of catalytic activity in producing the phenol anion via hydrolysis, this could be due the lack of surface area displayed by PIM-TB as well as absence of AO functional groups to act as nucleophiles. In contrast, both **TB-SBI-PIM** and **TB-SBI-AO-PIM** cause an increase in the overall hydrolysis of PNPA after 24 hours with the greater activity of **TB-SBI-AO-PIM** showing the benefit of combining AO and TB functionality.

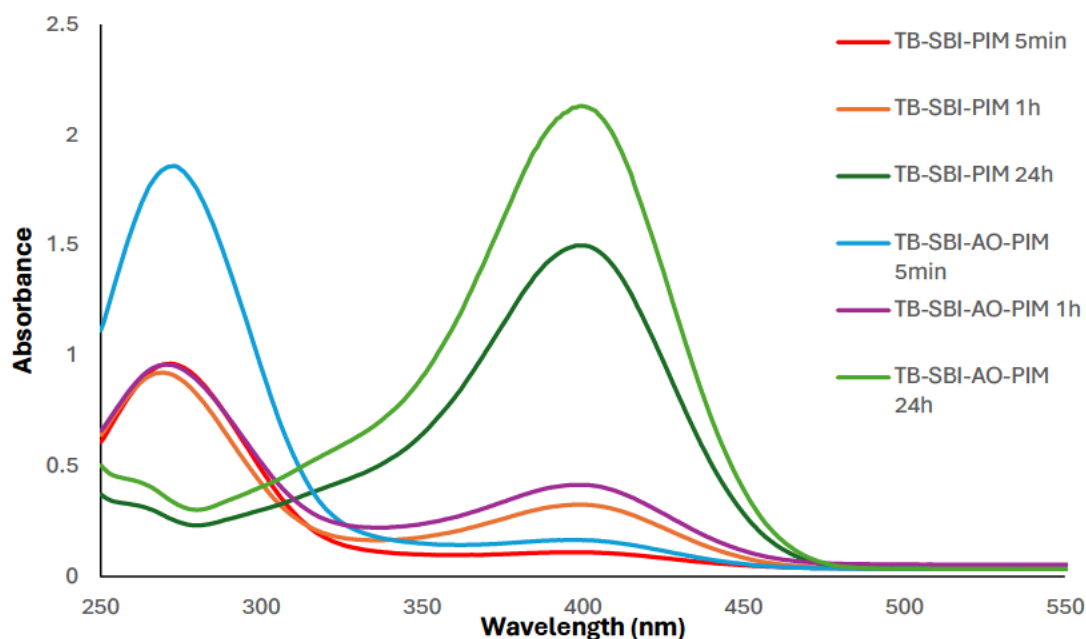


Figure 4.3b: UV-Vis Spectra of PNPA by **TB-SBI-PIM** and **TB-SBI-AO-PIM** in pH 7 at different time intervals as indicated.

As noted, although both polymers showed an improve catalytic performance when hydrolysing PNPA at pH 7, the catalytic ability of **TB-SBI-AO-PIM** is slightly enhanced compared to that of **TB-SBI-PIM**. This could be interpreted as the presence of AO functional group assisting as a strong nucleophile. Unfortunately, the hydrolysis of PNPA with **TB-SBI-AO-PIM** is slow and takes 24 h to reach completion (**Figure 4.3b**). In addition, **TB-SBI-PIM** and **TB-SBI-AO-PIM** are both completely insoluble in organic solvents and hence, are not solution processable for fabricating into films or nanofibers and can only be used as a heterogenous catalyst in the form of a powder. This not ideal for the application of these polymers as fibrous CWA destruction materials, where they are needed to be incorporated into PPEs either a membranes or nanofibers. A couple of different methods could be used to potentially resolve the solubility issue of these polymers. One method is to adjust the copolymer ratio to favour a greater contribution of SBI structural units to enhance solubility. Another applaudable method of increasing solubility is to employ the use of mixed matrix membrane (MMMs). This method consists of amalgamating inorganic or hybrid fillers, such as MOFs, zeolites, or graphene-based materials with PIMs. MMMs have porous structures which can enhance the gas adsorption, selectivity and permeability of PIMs and some cases they can improve solubility.

Chapter 5: Novel Nitrogen-Containing Spiro-Based PIMs

Spirobiindane (SBI) is a bicyclic structure containing two indane rings fused together at a single carbon-carbon bond (**Figure 5a**). The term "spiro" indicates that the rings share a single atom. Such structures are of interest as scaffolds in medicinal chemistry, catalysis, and organic materials due to its unique features, which can impart specific properties (*i.e.* chirality and solubility).

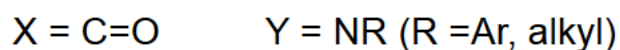
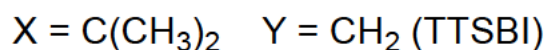
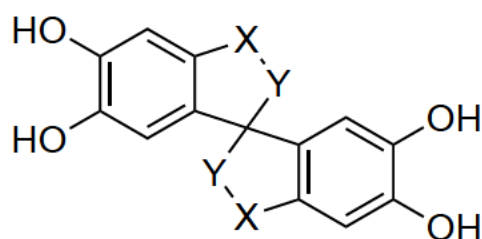
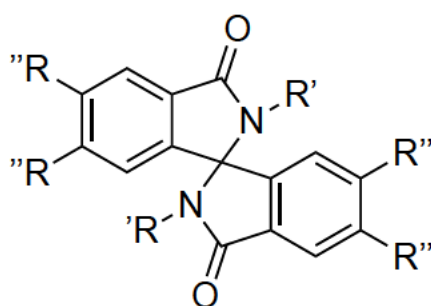


Figure 5a: General structure of SBI compound.

It is now well established that polymers containing SBI exhibit high free volume that can even result in intrinsic porosity, making it a promising structural unit for making polymers with applications such as gas storage, separation, and catalysis. The unique properties of the polymers with spirobiindane-based backbone stem from the combination of rigidity and microporosity. It was anticipated that spiro-based precursors could be synthesised from different starting materials to allow for the addition of heteroatoms such as nitrogen into their molecular structure, hence introducing a degree of basicity to the resulting polymer. These features make such nitrogen-containing PIMs candidate materials for addressing challenges in areas such as gas purification and carbon capture. They are also ideal for investigation for their potential in the catalysis of the hydrolysis reaction of organophosphate CWAs under ambient conditions. Initial target monomers were spirobilactams (**Figure 5b**), which could be readily reduced to amine functionality.



R' = Analine, 3,4-dimethoxyaniline, *n*-butylamine

R'' = H, OMe

Figure 5b: General Structure of spirobilactams.

5.1 Spirobilactam Monomer Synthesis

5.1.1 Spirobilactam Derivatives

The first step towards the target spirobilactam monomer was the synthesis of the precursor 2,2'-benzophenone dicarboxylic acid **4** by the oxidation of commercially available dibenzosuberone.

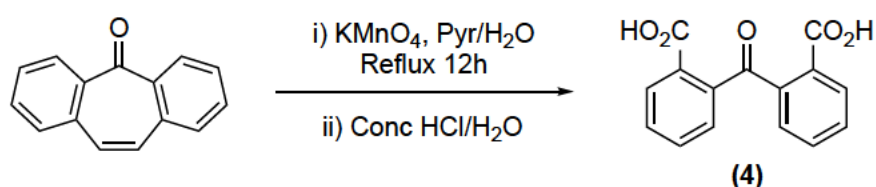


Figure 5.1.1a: Synthesis of 2,2'-benzophenone dicarboxylic acid.

Following a literature procedure (Ohtsuka et al. 2019),²⁴⁶ compound **4** was prepared by adding an excess of potassium permanganate in two portions (10 molar equivalents for each group undergoing oxidation) to a mixture of dibenzosuberone in 50/50 v/v% mixture of pyridine and water followed by reflux for 12 hours. Pyridine and manganese dioxide were removed by hot vacuum filtration then the pale-yellow filtrate was collected, and the solvent was evaporated under reduced pressure. It was ensured that pyridine was entirely removed as the presence of pyridine can lead to reduced yield due

to possible formation of water-soluble pyridine/carboxylate salts. The milky powder was then redissolved in water and reprecipitation with concentrated hydrochloric acid to give **4** in 65% yield.

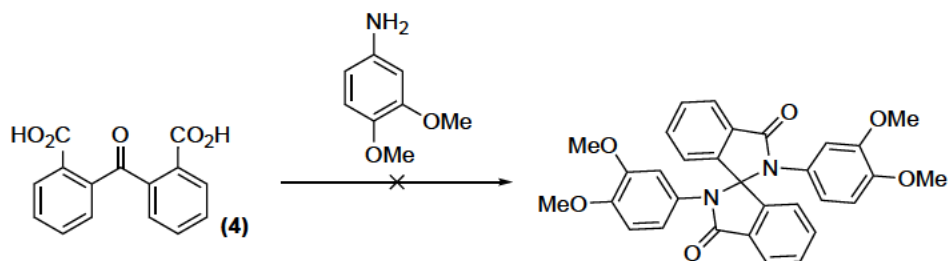


Figure 5.1.1b: Proposed synthesis of 2,2'-bis(3,4-dimethoxyphenyl)-1,1'-spirobi[isoindole]-3,3'(2H,2'H)-dione from 2,2'-benzophenone dicarboxylic acid.

In the attempt to prepare the desired spirobilactam precursor, 2,2'-benzophenone dicarboxylic acid **4** was reacted with 3,4-dimethoxyaniline in various high boiling point polar solvents such as NMP, DMF and DMSO and triethylamine (TEA) under reflux. The limitation faced with this reaction lies with the very low decomposition temperature of 3,4-dimethoxyaniline at approximately 98 °C, which was below the high boiling points of the aprotic solvents, used for this reaction which led to many attempts that resulted in the decomposition of the reaction mixture. Some dark purple solids were obtained from performing the reaction below reflux temperatures, however, the isolated product in each case was the mono-adduct, which was confirmed by single crystal XRD (**Figure 5.1.1c**).

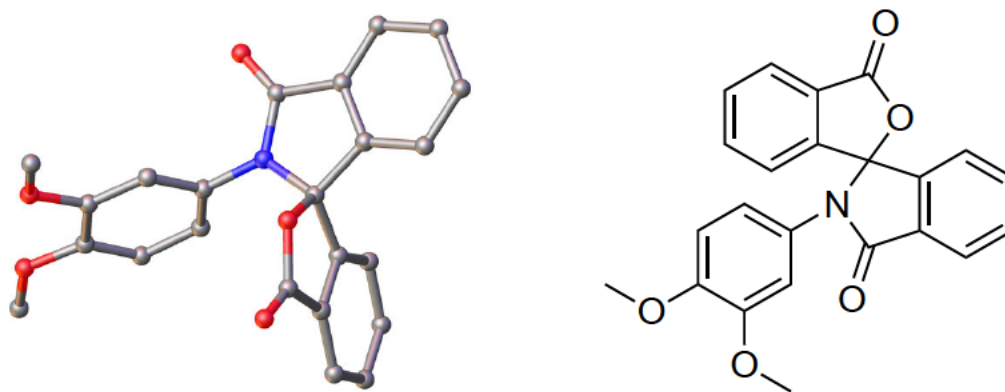


Figure 5.1.1c: Molecular structure of the mono-adduct 2,2'-bis(3,4-dimethoxyphenyl)-1,1'-spirobi[isoindole]-3,3'-(2H,2'H)-dione, single crystal XRD (left), ChemDraw (right).

5.1.2 Attempt at Spiro Compound from 2,2'-(oxomethylene)dibenzoyl chloride

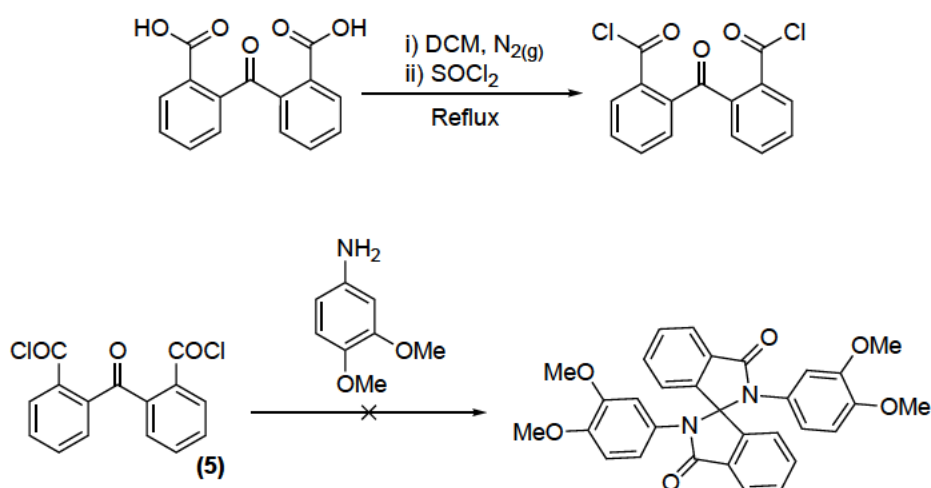


Figure 5.1.2a: Carboxylic acid functional group conversion to acid chlorides (top). Synthesis of 2,2'-bis(3,4-dimethoxyphenyl)-1,1'-spirobi[isoindole]-3,3'-(2H,2'H)-dione by 2,2'-(oxomethylene)dibenzoyl chloride **5** with aprotic solvents and TEA (bottom).

Due to the limitations faced by low decomposition temperature of 3,4-dimethoxyaniline, the carboxylic acid functional groups of compounds (**4**) were converted to the more reactive acid chloride by dissolving compound (**4**) in DCM and adding 3 molar equivalents of thionyl chloride (SOCl_2). Due to the sensitivity of the resulting acyl chloride (**5**) towards hydrolysis, this reaction was carried in a closed system under nitrogen atmosphere to yield 82% of product (**5**): this structure was confirmed by NMR. However, the reaction of compound (**5**) with 3,4-dimethoxyaniline also failed to produce the desired 2,2'-bis(3,4-

dimethoxyphenyl)-1,1'-spirobi[isoindole]-3,3'(2H,2'H)-dione with every reaction leading to decomposition of the starting materials.

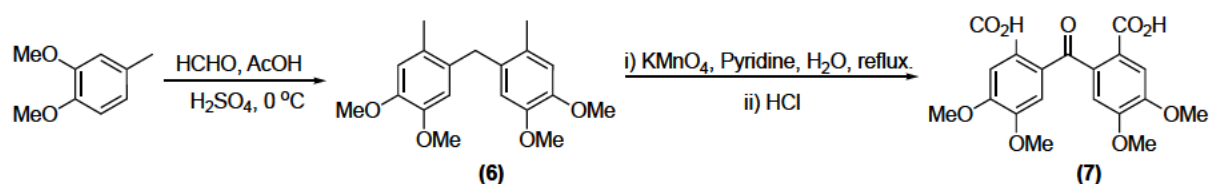


Figure 5.1.2b: Synthesis of precursor 4,4',5',5'-tetramethoxybenzophenone-2,2'-dibenzoic acid (**7**) from 3-methylveratrol.

Due to these limitations, a new synthetic route was designed for the synthesis of spirobis lactams. The condensation reaction of 1,2-dimethoxy-4-methylbenzene with formaldehyde in acidic conditions resulted in 1,1'-methylenebis(4,5-dimethoxy-2-methylbenzene) (**6**) in approximately 90% yield. Compound (**6**) was oxidized with excess potassium permanganate to give 4,4',5',5'-tetramethoxybenzophenone-2,2'-dibenzoic acid (**7**) and its structure was confirmed by NMR and FT-IR, which showed the appearance of the broad carboxylic peaks at 3305 cm^{-1} (O-H stretch), 1678 cm^{-1} (C=O stretch) and 1272 cm^{-1} (C-O stretch).

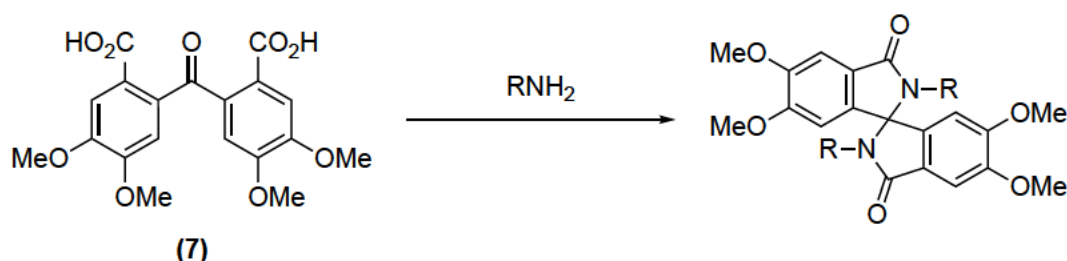
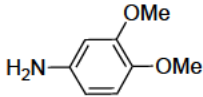
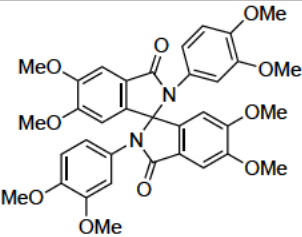
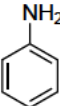
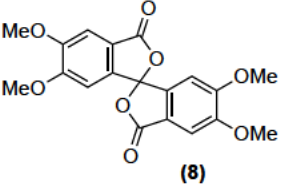


Figure 5.1.2c: Proposed general synthesis for 2,2'-bis(R)-1,1'-spirobi[isoindole]-3,3'(2H,2'H)-dione.

Spiro-cyclisation reactions were attempted by reacting 4,4',5',5'-tetramethoxybenzophenone-2,2'-dibenzoic acid (**7**) with an excess amount of various amine compounds (aniline, 3,4-dimethoxyaniline and butylamine) in an aprotic solvent under reflux for 72 hours. All reactions were quenched in water and HCl was added to reaction mixtures containing triethylamine to neutralise the base. The initial reaction was carried out in *N*-methyl-2-pyrrolidone (NMP) with 3,4-dimethoxyaniline at $202\text{ }^{\circ}\text{C}$, however this reaction failed and no product was obtained as a result of the decomposition of the reactant. The reaction was repeated with the more stable aniline.

Triethylamine was also added as a base to aid deprotonation of the carboxylic group and produce a more reactive intermediate (-COO^-). However, single crystal X-ray analysis confirmed the product obtained as that from a double dehydration as 5,5',6,6'-tetramethoxy-3*H*,3'*H*-1,1'-spirobi[[2]benzofuran]-3,3'-dione (**8**) (Fig. 5.2.1c). This reaction was carried out at 125 °C due to aniline decomposing at temperatures above 190 °C. To eliminate the risk of decomposition, the solvent for the reaction was changed to dimethylformamide (DMF), another aprotic solvent with lower boiling point (153 °C) compared to that of NMP (202 °C). Future scaled up preparations of compound (**8**) were carried out in the absence of aniline, where 2,2'-(oxomethylene)bis(4,5-dimethoxybenzoic acid) was refluxed in quinoline in the presence of TEA. To decrease the steric hindrance around the spiro centre, butylamine was used as nucleophile in excess. As confirmed by single crystal XRD analysis, the mixed lactam/lactone 2'-butyl-5,5',6,6'-tetramethoxy-3*H*-spiro[[2]benzofuran-1,1'-isoindole]-3,3'(2'*H*)-dione (**9**) was obtained in good yield (Figure 5.1.2c), (Table 5.1.2a).

Table 5.1.2 a: Spirocompounds obtained from 4,4',5'5'-tetramethoxybenzophenone-2,2'-dibenzoic acid in reaction with various amine reagents.

Amine-reagent	Spirobiindane derivative	%Yield
		0
		81

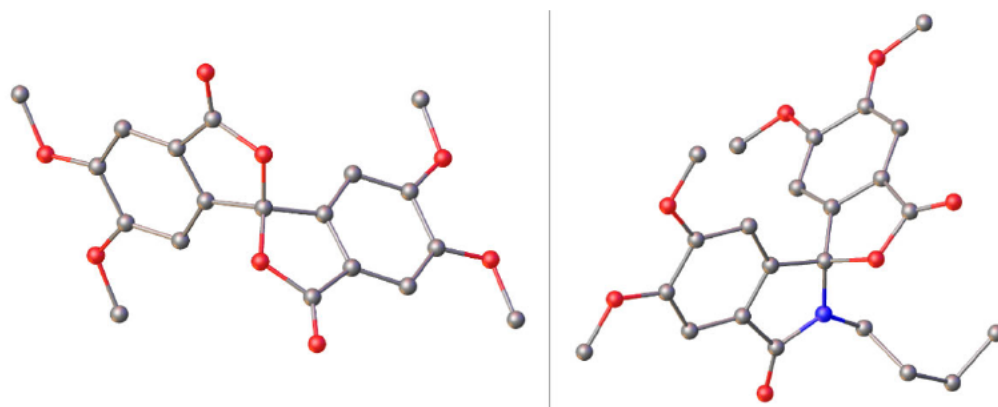
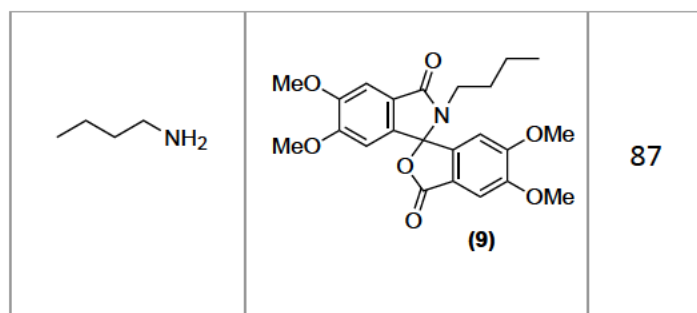


Figure 5.1.2c: Crystal structures of *spiro*-compound **8** (left) and compound **9** (right).

5.2.1 Spiroilactam Monomer Synthesis Using Aniline Melt Reaction

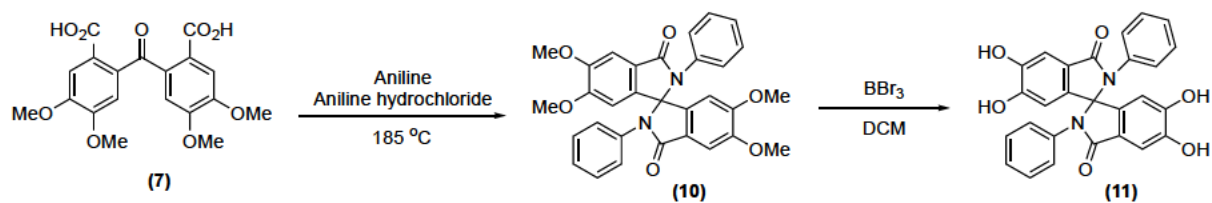


Figure 5.2.1a: Melt reaction to give 5,5',6,6'-tetramethoxy-2,2'-diphenyl-1,1'-spiro[isoindole]-3,3'-(2H,2'H)-dione (**10**) and synthesis of the demethylated monomer (**11**).

Based on a procedure adapted from the literature²⁴⁷ compound **7** was reacted with a mixture of aniline (10 equivalent) and an excess of aniline hydrochloride at 185 °C. The reaction mixture, a dark purple liquid, was quenched with a mixture of ice/HCl under vigorous stirring until a light purple precipitate formed. The product was purified by reprecipitated from methanol to give 5,5',6,6'-tetramethoxy-2,2'-diphenyl-1,1'-

spirobi[isoindole]-3,3'(2H,2'H)-dione **10** with 70% yield. Due to the extremely sensitive nature of the product towards oxidation, compound (**10**) was immediately reacted with excess BBr_3 at 0°C in a closed system under nitrogen atmosphere for 12 hours. After quenching with iced water to remove unreacted BBr_3 , the final product was collected under nitrogen atmosphere by evaporation of the reaction solvent (anhydrous DCM) to give 5,5',6,6'-tetrahydroxy-2,2'-diphenyl-1,1'-spirobi[isoindole]-3,3'(2H,2'H)-dione (**11**). The success of the demethylation reaction was confirmed by observing the appearance of O-H peak at 3035 cm^{-1} from the FT-IR spectrum (Figure 5.2.1b).

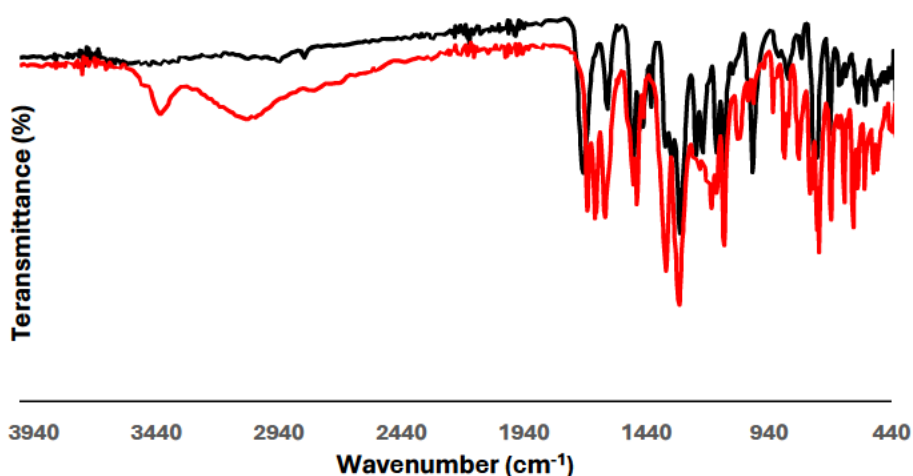


Figure 5.2.1b: FT-IR spectra of compound **10** (black) and compound **11** (red).

5.3 Spirobilactam Polymerisation

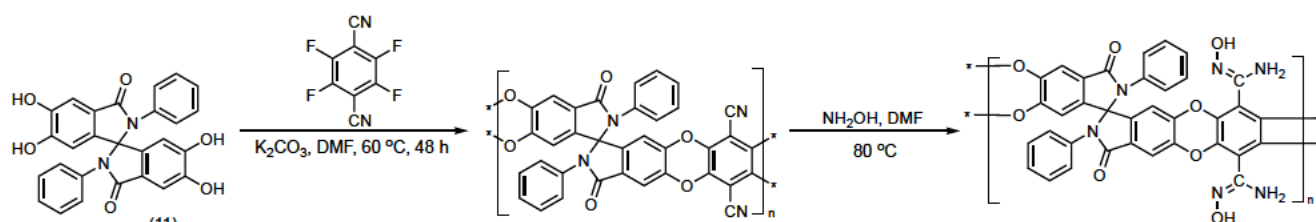


Figure 5.3a: Synthesis of **SBL-PIM** and its AO modified derivative (**SBL-AO-PIM**).

Polymer **SBL-PIM** was synthesised from compound **11** by reaction with **TFTPN** in basic conditions (excess amount of dry K_2CO_3) in anhydrous DMF in a close system under nitrogen atmosphere to prevent its oxidation. The reaction mixture was heated for 48

hours under stirring to give a viscous yellow solution which was quenched with water and acid to neutralise the excess base. The final product was collected by filtration and then washed with water, then acetone and methanol to remove any oligomers and to provide **SBL-PIM** in 69% yield. The **SBL-PIM** structure was confirmed by ^1H NMR spectroscopy by observing the severely broadened aromatic peaks between 6.6 – 8.0 ppm.

The AO modification of the nitrile groups was achieved by suspending **SBL-PIM** in DMF and heating the reaction mixture to 80 °C followed by the addition of hydroxylamine hydrochloride and stirring overnight. The resulting precipitate was filtered and washed with water and methanol to collect **SBL-AO-PIM** in 98% yield.

The adsorption and desorption isotherm plots of **SBL-PIM** and **SBL-AO-PIM** was obtained by N_2 gas adsorption at 77K (Figure 5.3b). All obtained isotherms were of Type V and showed evidence of kinetically restricted adsorption, with the desorption curve increasing in value compared to the uptake at P/P_0 .

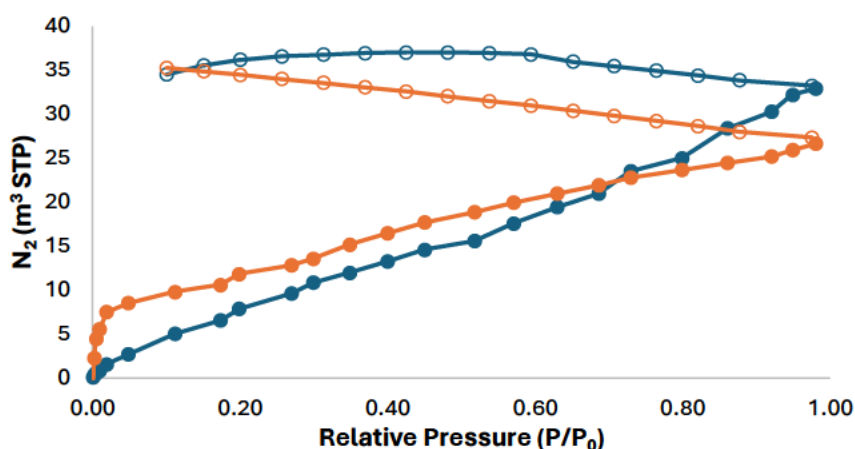


Figure 5.3b: N_2 adsorption isotherm measure at 77 K, adsorption (solid filled circles) and desorption (empty circles). **SBL-PIM** (blue) and **SBL-AO-PIM** (orange).

From these N_2 isotherms, BET surface area and total pore volume of the polymers were calculated (Table 5.3a). **SBL-PIM** displayed a very low surface area ($35 \text{ m}^2 \text{ g}^{-1}$) indicating that there are strong intermolecular interactions between polymer chains resulting in a denser solid. Additionally, the bulky phenyl substituents protruding out from the body of the polymer chain could contribute to filling the intrinsic microporosity. A small improvement in surface area ($65 \text{ m}^2 \text{ g}^{-1}$) was observed with **SBL-AO-PIM**, displaying

unexpected from behaviour for AO modified polymer. AO groups tend to introduce additional intermolecular interactions, therefore decreasing porosity.

Table 5.3a: Gas adsorption properties of SBL-PIM and SBL-AO-PIM.

Polymer	Solubility	SA_{BET}^a ($m^2 g^{-1}$)	V_{Total}^b ($mL g^{-1}$)	CO_2 uptake ^c ($cc g^{-1}$)
SBL-PIM	DMSO	35	0.057	41.49
SBL-AO-PIM	DMSO	64	0.163	37.23

^aBET surface area was obtained from N₂ adsorption at 77 K, ^btotal pore volume was calculated from N₂ uptake at $P/P_0 = 0.97$, and ^cCO₂ uptake was measured at 1 bar, 273 K.

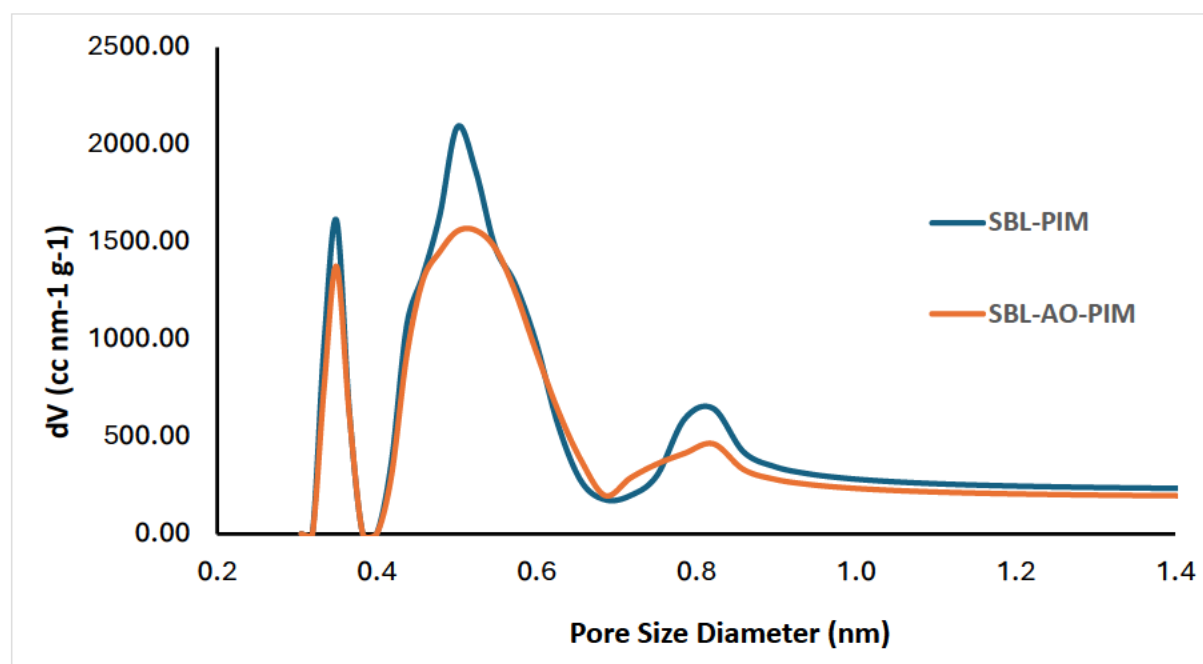


Figure 5.3c: Pore Size Distribution (PSD) calculated from CO₂ adsorption data using non-local density functional theory (NLDFT)

The CO₂ adsorption isotherm for these polymers were also obtained, from which the CO₂ uptake at 1 bar, 273 K could be calculated (Table 5.3c). The pore size distribution of the polymers was also calculated from this isotherm, using non-local density functional

theory (NLDFT) a pre-set model used by BET software to determine the porosity, pore size and pore size distribution of a sample from the measured gas adsorption isotherm (**Figure 4.2.6b**). The pore size distribution analysis indicated that all polymers contain a mixture of ultra-micropores (pore diameter < 0.7 nm) and micropores (pore diameter < 2 nm), with the AO-modified polymers presented higher volume of ultra-micropores with diameter less than 0.4 nm.



*Figure 5.3a: Membrane casted from **SBL-PIM** (left) and **SBL-AO-PIM** (right) with DMSO*

Attempts were made at casting membranes from **SBL-PIM** and **SBL-AO-PIM** by fully dissolving each polymer in DMSO. Initially a glass petri dish was chosen for membrane casting however upon solvent evaporation the membranes cracked and broke apart (**Figure 5.3a**). This was thought to be caused by high level of hydrogen bonding interaction between the polymers and polar surface of the glass petri dish, therefore, a Teflon petri dish was used to reduce the surface interaction. However, similar results were observed and therefore no membranes were obtained for gas permeability analysis.

UV-vis analysis of **SBL-PIM** and **SBL-AO-PIM** was carried out in accordance with the methods described in the previous chapter. PNPA solutions were freshly prepared as needed to prevent premature hydrolysis prior to UV experiment.

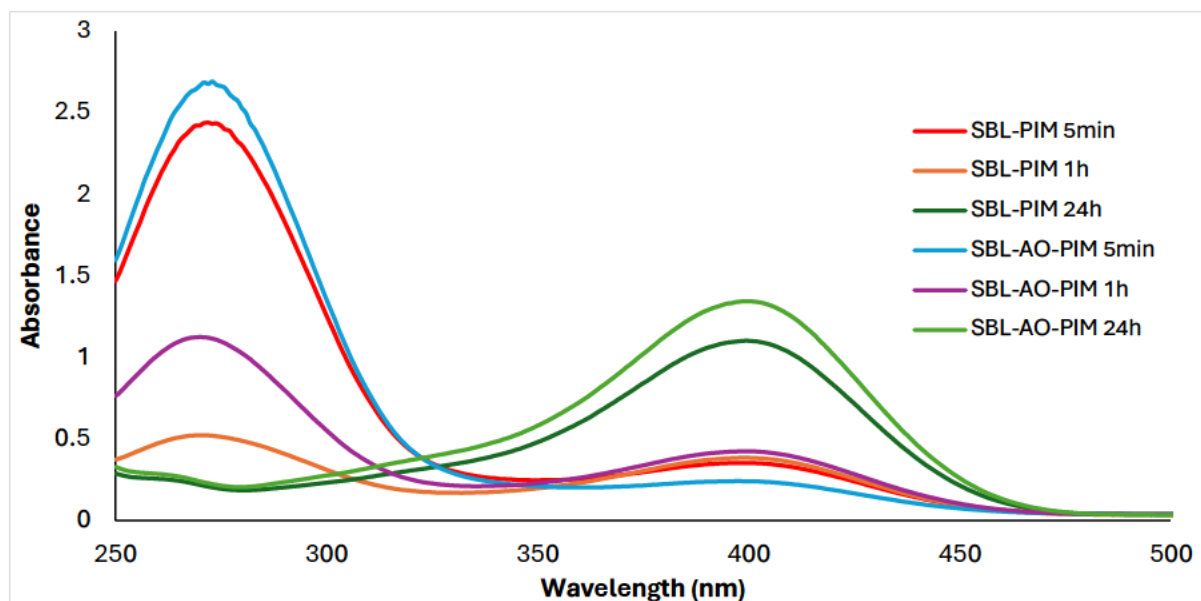


Figure 3.5b: UV spectra of PNPA hydrolysis by **SBL-PIM** and **SBL-AO-PIM** in pH 7 at various time intervals.

The overall trend shown by both **SBL-PIM** and **SBL-AO-PIM** follows the pattern previously observed for PIMs (Figure 3.5b). Very little hydrolysis caused by either polymer during the first 5 minutes of their introduction. However, it is noteworthy that **SBL-AO-PIM** had an overall better performance compared to **SBL-PIM** counterpart, indicating that AO group is acting as an active site for PNPA adsorption, hence increasing the rate of hydrolysis. This may be due to the presence of amidoxime functional group which acts as an active site and allows the interaction of the base with PNPA molecules. The rate of hydrolysis increased with prolonged interaction of the heterogenous catalysts and the PNPA remaining within the solution. After 1 hour **SBL-AO-PIM** showed approximately 90% hydrolysis of PNPA into 4-nitrophenolate.

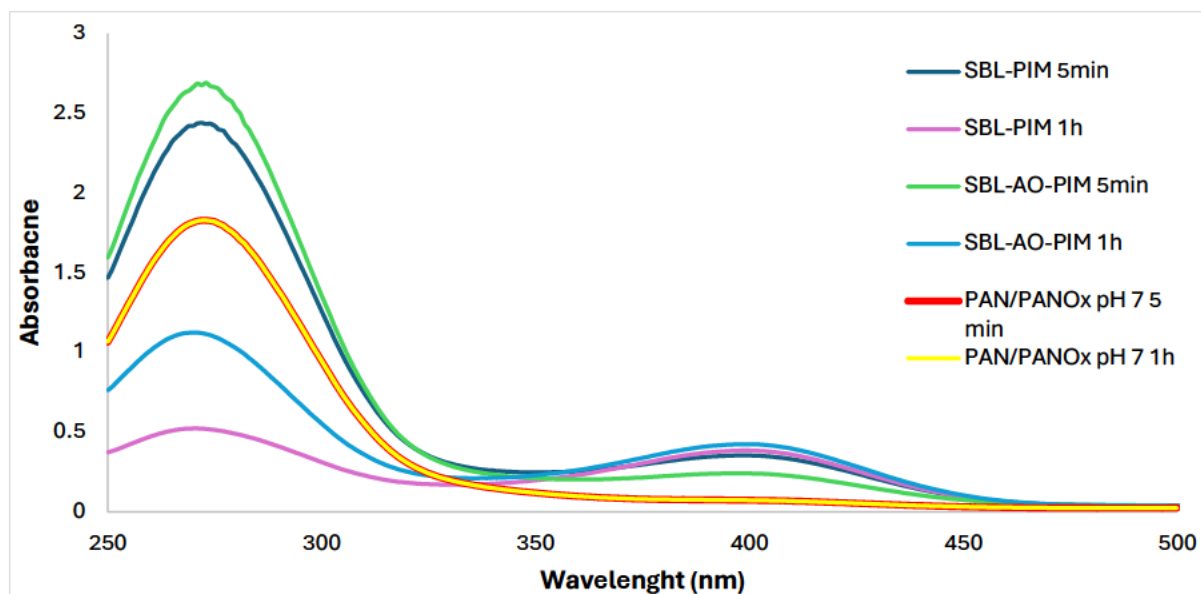


Figure 3.5c: UV spectra of performance comparison between PAN/PANOx and newly synthesised **SBL-PIM** and **SBL-AO-PIM** in pH 7 at different time intervals.

In comparison of PAN/PANOx nanofiber discussed in Chapter 3, the newly synthesised PIMs, **SBL-PIM** and **SBL-AO-PIM**, appear to be more active towards PNPA hydrolysis. This is evident from the initial reading after 5 min where both **SBL-PIM** and **SBL-AO-PIM** have catalysed the hydrolysis process whereas no activity is observed from PAN/PANOx nanofiber one hour after its introduction into the PNPA solution. UV-vis analysis was carried out qualitatively and the rate of hydrolysis was compared to the initial reading of PAN/PANOx at pH 7.

Chapter 6 Propellane Inspired PIMs

Propellanes are a class of organic compound characterized by their unique three-dimensional shape, resembling a propeller. These molecules possess interesting chemical properties due to their unusual geometry and hence their synthesis and study have been of great interest to chemists due to potential applications in materials science and organic chemistry.

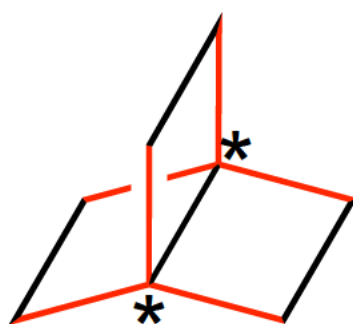
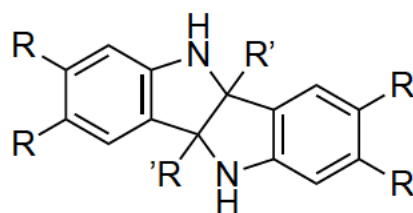


Figure 6a: A general structure of propellanes with both bridgehead positions marked by an asterisk.

6.1 Bisindoline-Based Monomers



R = OMe, OH

R' = Butandione, cyclohexadione, nihydrine

Figure 6.1a: General structure of bisindoline.

Bisindolines are a class of organic compounds, which contains two indoline rings. Indole itself is a heterocyclic compound composed of a benzene ring fused to a pyrrole ring (Figure. 6.1b). Based on an excellent literature precedent, in which substituted bisindolines are prepared from 3,5-dimethoxyaniline in a one-step reaction with 2,3-

butandione,²⁴⁸ it was anticipated that a similar bisindolines product would form from 3,4-dimethoxyaniline. Furthermore, it was anticipated that reactions with cyclic diones, such as the readily available 1,2-cyclohexanedione would provide a simple route to propellane monomers. A summary of the initial assessment of this reaction using 3,4-dimethoxyaniline and a range of commercially available diones is given in Table 6.1a.

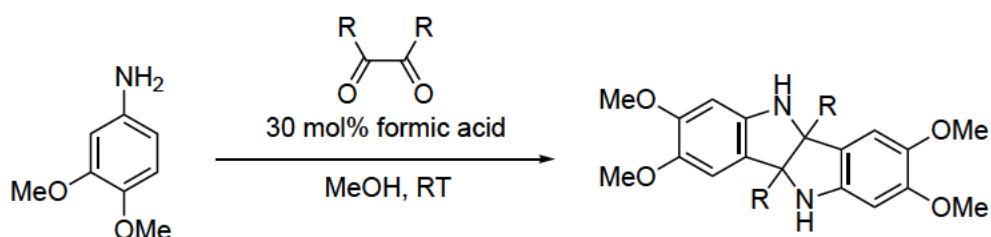
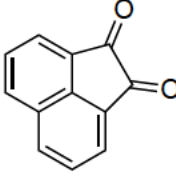
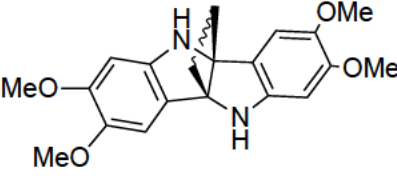
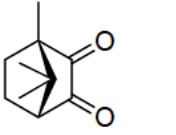
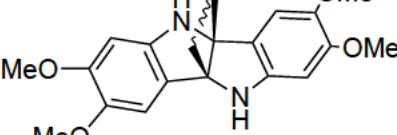
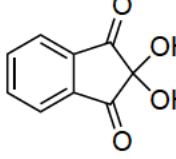
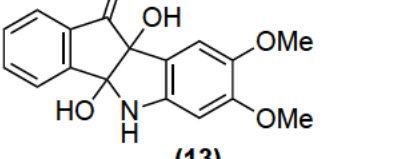
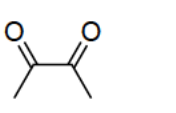
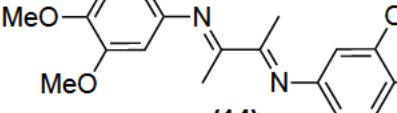


Figure 6.1b: Summary of reactions of 3,4-dimethoxyaniline with various diones.

Table 6.1a: List of diketone compounds used for synthesis of bisindoline monomers and resulting yields.

Dione-reagents	bisindoline derivative	%Yield
	 (12)	89
		0
		0

		0
		0
	 (13)	92
	 (14)	93

A proposed mechanism for the successful reaction of 3,4-dimethoxyaniline with 1,2-cyclohexanedione is given in **Figure 6.1c** and involves a series of acid mediated imine formations and aromatic electrophilic ring closures promoted by the electron-donating methoxy groups.

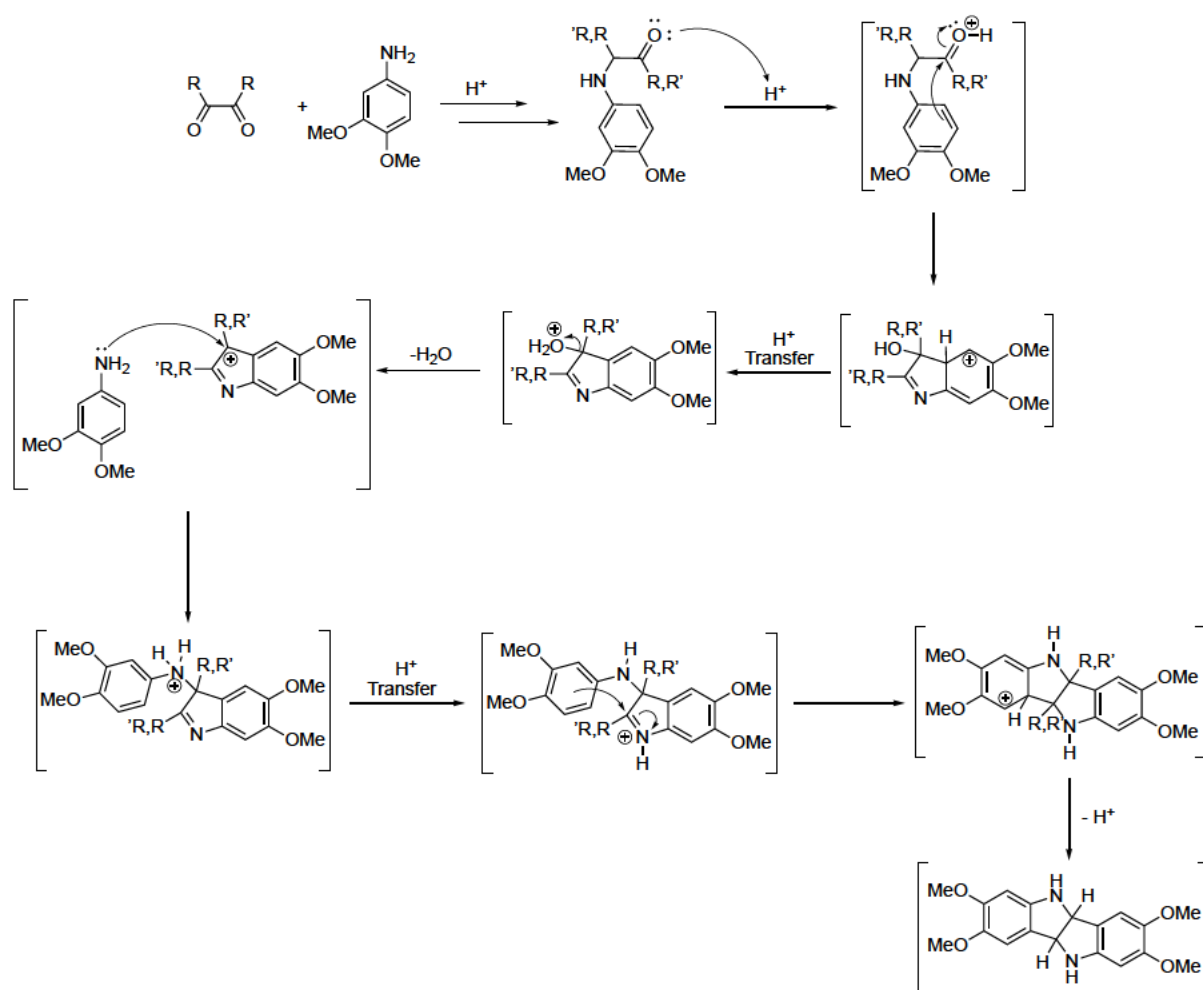


Figure 6.1c: Proposed reaction mechanism for formation of bisindolines from 3,4-dimethoxyaniline with a dione

6.2.1 The Reaction Between 2,3-Butanedione and 3,4-Dimethoxyaniline.

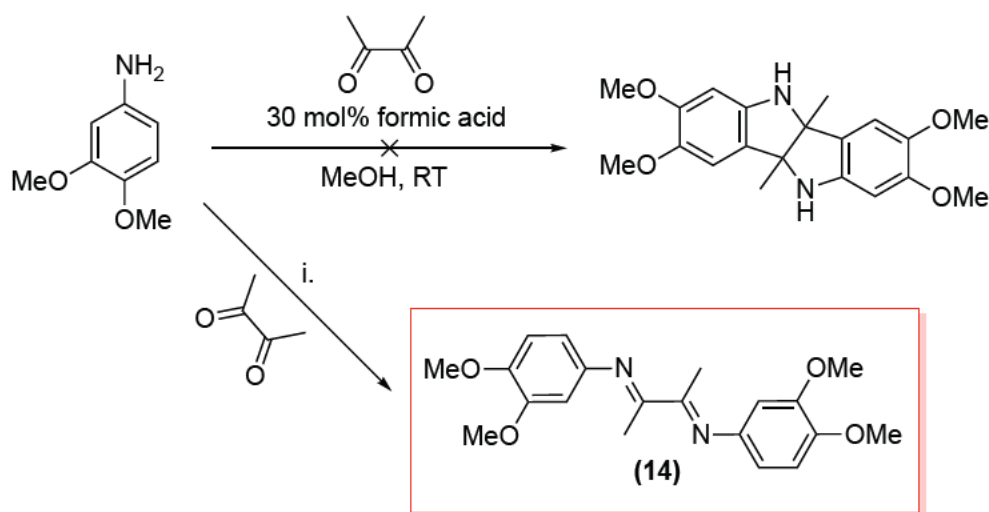


Figure 6.2.1a: Reaction scheme for 3,4-dimethoxyaniline and 2,3-butanedione. i) 30 mol% formic acid, MeOH, RT.

The reaction between 3,4-dimethoxyaniline and 2,3-butanedione did not produce the desired bisindoline heterocyclic product. Instead, imine formation occurred on each attempt even with variation in reactions conditions. The product (2E,3E)-N²,N³-bis(3,4-dimethoxyphenyl)butane-2,3-diimine (**14**), which was fully characterised by single crystal XRD (Figure 6.2.1b), formed instantly upon addition of the formic acid and precipitated from solution. Even prolonged heating of the reaction failed to produce the desired bisindoline product. Although Compound **14** appears to be novel, very similar compounds have been described in the literature for use as ligands for metal catalysts.²⁴⁹

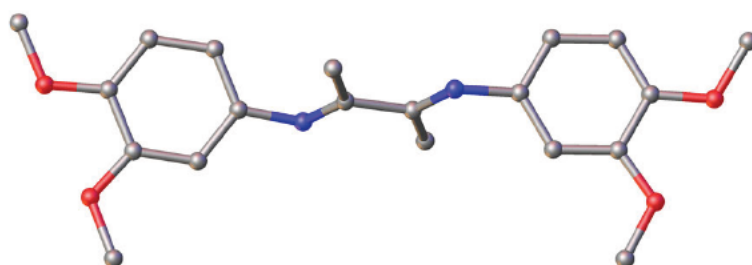


Figure 6.2.1b: Structure of compound **14** confirmed by single crystal X-ray crystallography.

6.2.2 Reaction Between 2,3-Cyclohexanedione and 3,4-Dimethoxyaniline.

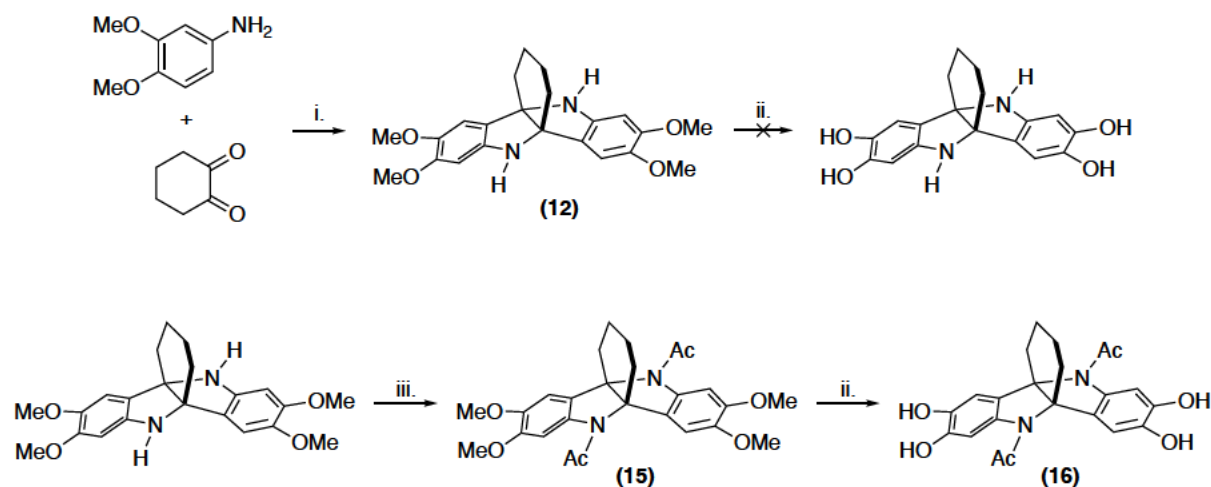


Figure 6.2.2a: Reaction scheme depicting the synthetic route taken to synthesis the desired catechol compound **16**. i) 30 mol% formic acid, MeOH, RT, 24h. ii) BBr₃, DCM, N₂, 0°, 12h. iii) Ac₂O, anhydrous sodium acetate, RT, 8h.

(4*bR*,9*bR*)-2,3,7,8-tetramethoxy-5*H*,10*H*-4*b*,9*b*-butanoindolo[3,2-*b*]indole (**12**) was successfully synthesised from the reaction between 3,4-dimethoxyaniline and 1,2-cyclohexadione in acidic conditions. The crude product was recrystallised from methanol to give 89% yield. The chemical structure of compound **12** was confirmed using single crystal X-ray diffraction analysis (Figure 6.2.2b). In order to produce a monomer suitable for PIM synthesis, the methyl groups need to be removed, which is usually carried out using BBr₃. Unfortunately, attempts with this reagent resulted in degradation of the ring system presumably due to the nitrogen atoms present in compound **12** acting as a Lewis base and reacting with BBr₃ (a Lewis acid). To prevent this undesired side reaction, compound **12** was reacted with excess anhydrous sodium acetate and acetic anhydride in order to protect the nitrogen atoms with an acetyl group, resulting in 1,1'-[(4*bR*,9*bR*)-2,3,7,8-tetramethoxy-5*H*,10*H*-4*b*,9*b*-butanoindolo[3,2-*b*]indole-5,10-diyl]di(ethan-1-one) (**15**). Variable temperature ¹H NMR was performed to confirm the structure of compound **15** as the acetyl group possesses highly restricted degree of freedom of rotation causing peak broadening when performing ¹H NMR at room temperature. VT ¹H NMR shows sharpening of NMR peaks specifically the R-COCH₃ peak (highlighted in orange) at high temperatures as shown in Figure 6.2.2c. VT ¹H NMR was performed with

DMSO- d_6 as the solvent to allow for sufficient temperature increase so that data could be collected at room temperature, 300 K (27 °C), 323 K (50 °C) and 343 K (67 °C).

Once the nitrogen atoms were protected by an acetyl group, the demethylation reaction was carried out on compound **15** without resulting in decomposition and the desired bis-catechol monomer 1,1'-[(4*bR*,9*bR*)-2,3,7,8-tetrahydroxy-5*H*,10*H*-4*b*,9*b*-butanoindolo[3,2-*b*]indole-5,10-diyl]di(ethan-1-one) (**16**) was obtained.

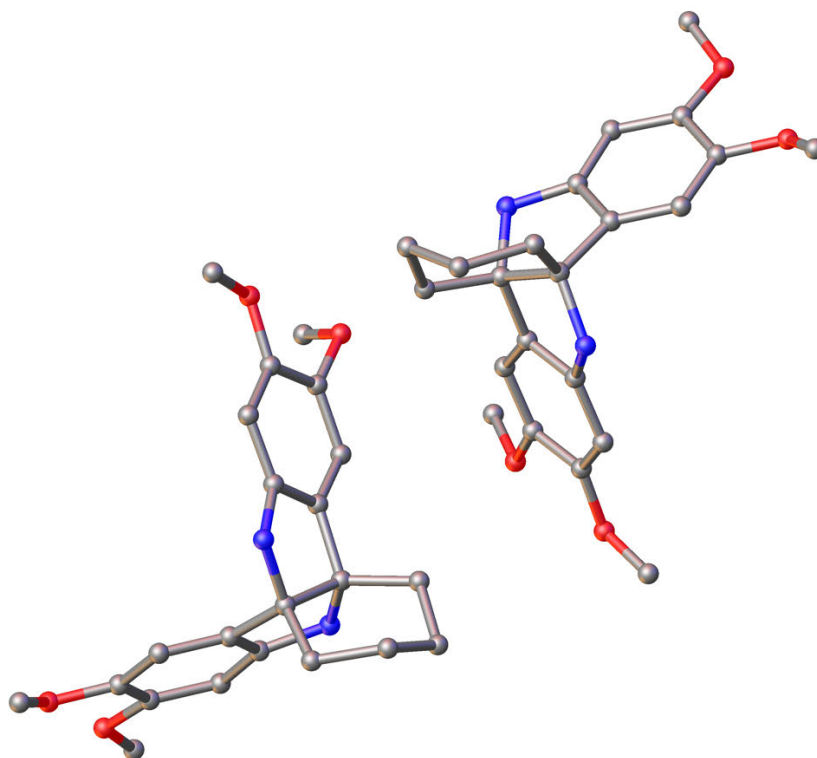


Figure 6.2.2b: Chemical structure of Compound **12** confirmed by crystallography (hydrogens not shown for clarity).

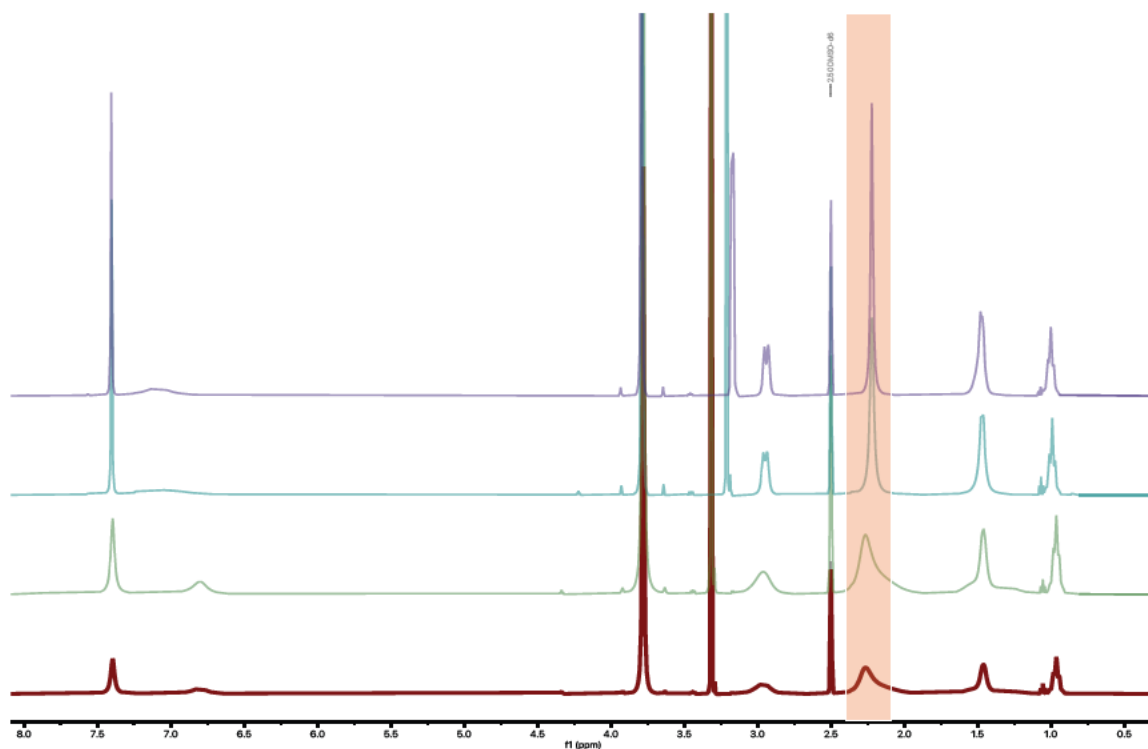


Figure 6.2.2c: VT ^1H NMR spectra of compound **15** obtained at RT (red), 300 K (green), 323 K teal blue and 343 K (purple).

6.2.3 Reaction Between Ninhydrin and 3,4-Dimethoxyaniline.

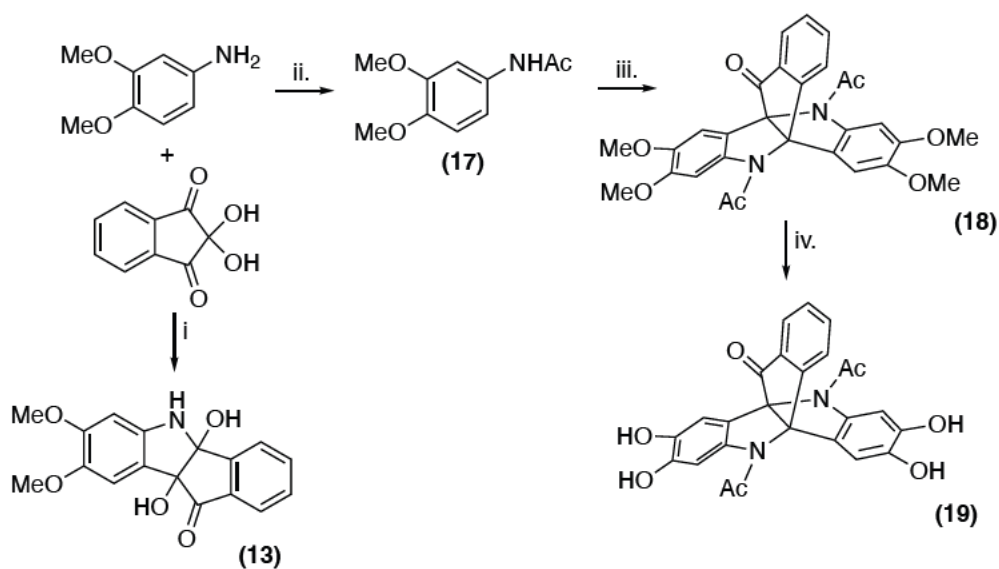


Figure 6.2.3a: Reaction scheme showing the synthesis of ninhydrin-based monomer. i) 30 mol% formic acid, MeOH, 70 °C, 24h. ii) aqueous NaOH, acetic acid. iii) ninhydrin, 30 mol% formic acid, MeOH, 70 °C. 24h. iv) BBr_3 , DCM, 0 °C, 12h.

Direct reaction of 3,4-dimethoxyaniline and ninhydrin lead only to the synthesis of the mono-adduct compound **13**, although in good yield. The formation of compound **13** has been previously described in the literature using a similar reaction.²⁵⁰ Once the mono-adduct compound was obtained, no further reaction conditions were found that would encourage addition of the second 3,4-dimethoxyaniline and ring closure to form the desired bisindoline compound. Therefore, other synthetic routes were explored in order to prepare the desired compound **18**. It was discovered that by first protecting the amine group of 3,4-dimethoxyaniline with acetate to produce *N*-(3,4-dimethoxyphenyl)acetamide (**17**) enabled the reaction with ninhydrin to proceed as desired to give compound **18**. This method also removed the requirement for performing acetate protection of compound **18** prior to the demethylation reaction with BBr₃ and this was successfully performed to give monomer **19**. The structure of compound **13** and **18** was confirmed with ¹H NMR (Figure 6.2.3b), where it was also confirmed that the protective acetyl group placed on nitrile group of precursor compound **17** (2.00 ppm) was present on compound **18** and not cleaved during the reaction. This confirmation allowed for direct demethylation on compound **18** to obtain the final bis-catechol product.

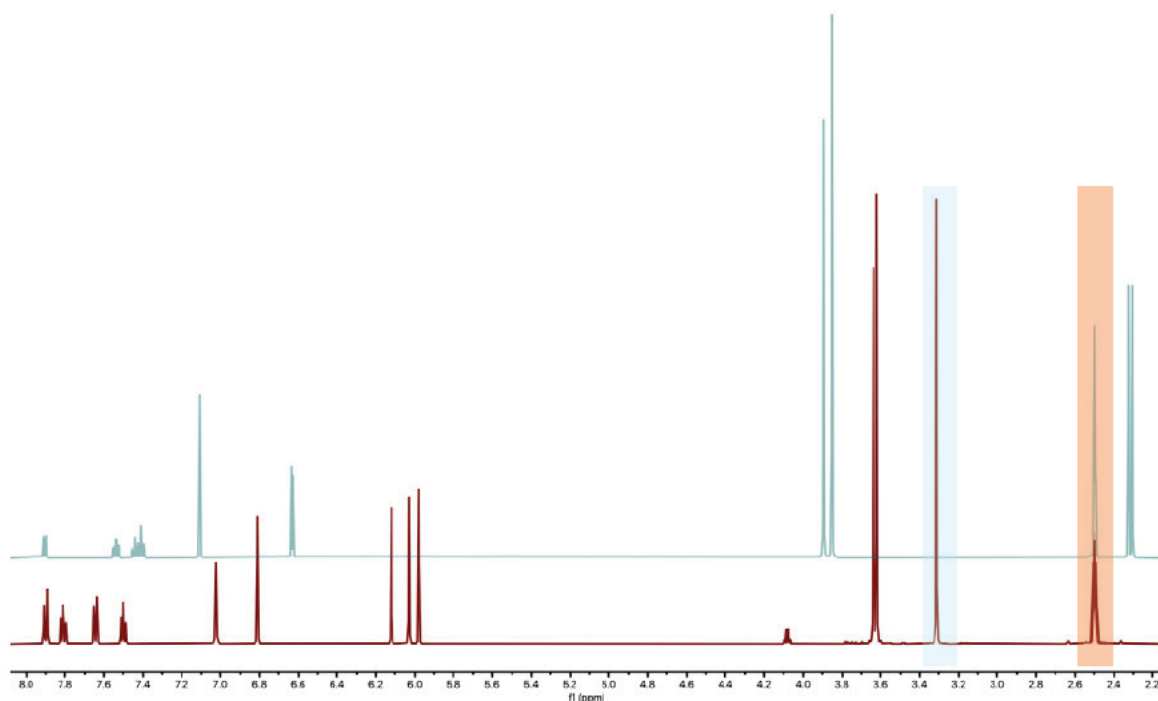


Figure 6.2.3b: Stacked ¹H NMR spectra of compound **13** (red, monoadduct) and compound **18** (blue, diadduct). DMSO-d₆ (highlighted in orange) was used as NMR solvent, water peak is highlighted in blue.

6.3 Polymerisations Using Bisindole Monomers

6.3.1 The Synthesis of Bisindole-Based PIMs

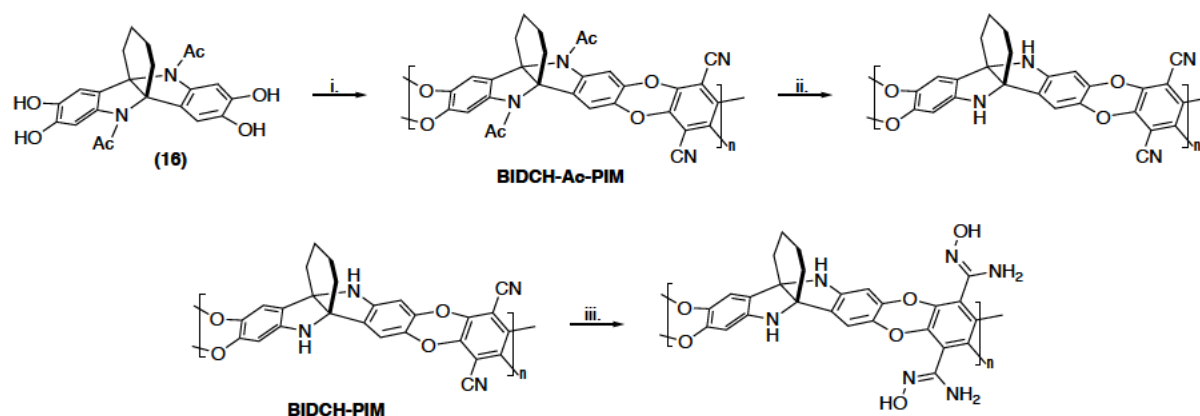


Figure 6.3.1a: Synthetic route describing the polymerisation process of **BIDNH-AO-PIM**. i) TFTP, K₂CO₃, DMF, 70 °C, N₂. ii) Conc HCl, EtOH, reflux. iii) NH₂OH, 80 °C.

As shown in **Figure 6.3.1a**, compound **16** was reacted with TFTP in basic conditions under nitrogen atmosphere at 70 °C for 72 hours until a viscous bright yellow solution was formed. The reaction mixture was quenched with cold water and concentrated HCl was added to the reaction mixture to neutralise the base after which pale-yellow precipitates were formed. The resulting polymer was collected under vacuum and washed with water, acetone, and methanol to remove low molecular weight polymer chains to give **BIDCH-Ac-PIM**. In order to remove the acetate protecting groups, **BIDCH-Ac-PIM** was then refluxed in a solution of ethanol and concentrated HCl to give bisindole-cyclohexane PIM (**BIDCH-PIM**). This polymer **BIDCH-PIM** was then reacted with hydroxylamine hydrochloride in order to convert the nitrile group into amidoxime functional group to give **BIDCH-AO-PIM** (**Figure 6.3.1a**).

Figure 6.3.1b shows the N₂ adsorption and desorption isotherms of **BIDCH-Ac-PIM** (blue), **BIDCH-PIM** (orange) and **BIDCH-AO-PIM** (green) obtained at 77K. **BIDCH-Ac-PIM** and **BIDCH-PIM** display Type I isotherms, the later with evidence of kinetically restricted

adsorption, and **BIDCH-AO-PIM** displays Type III isotherm due to the lack of significant porosity.

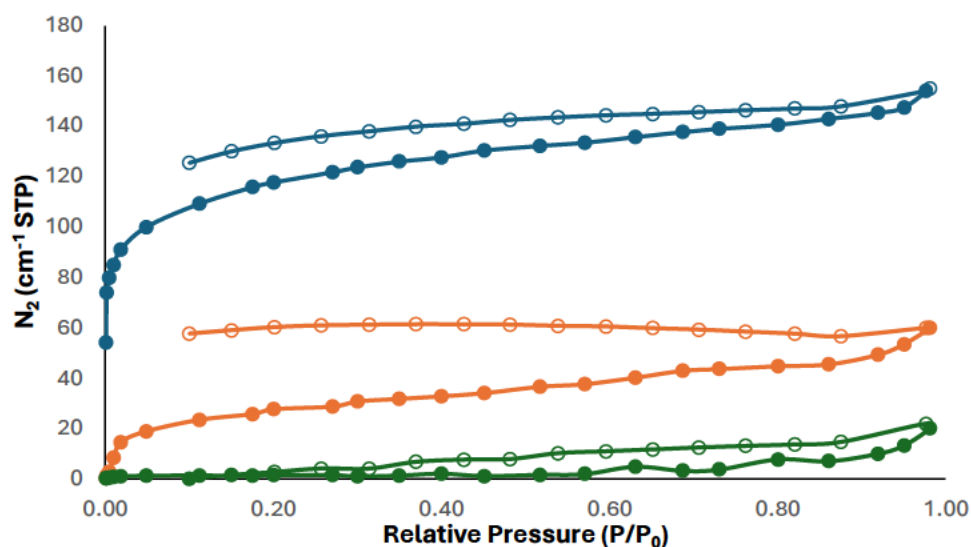


Figure 6.3.1b: N_2 adsorption isotherm measure at 77 K, adsorption (solid filled circles) and desorption (empty circles). **BIDCH-Ac-PIM** (blue), **BIDCH-PIM** (orange) **BIDCH-AO-PIM** (green).

From the obtained N_2 isotherms, BET surface area and total pore volume of the polymers were calculated (Table 6.3.1b). **BIDCH-Ac-PIM** showed a greater surface area ($415 \text{ m}^2 \text{ g}^{-1}$) compared to **BIDCH-PIM** ($24 \text{ m}^2 \text{ g}^{-1}$) and **BIDCH-AO-PIM** ($5 \text{ m}^2 \text{ g}^{-1}$), where in both cases a large decrease in surface area was observed. This could suggest that the acetyl group was providing a degree of hinderance around the chain preventing strong intermolecular interactions resulting in higher surface area. The most extreme surface area loss was shown by **BIDCH-AO-PIM**, however this is expected from polymers containing amidoxime groups as these groups can interact strongly by forming hydrogen bonding, forcing the polymer chains closer together and reducing the porosity.

Table 6.3.1a: Properties of **BIDCH-Ac-PIM**, **BIDCH-PIM**, and **BIDCH-AO-PIM**.

Polymer	Solubility	SA_{BET}^a ($m^2 g^{-1}$)	V_{Total}^b ($mL g^{-1}$)	CO_2 uptake ^c ($cc g^{-1}$)
BIDCH-Ac-PIM	$CHCl_3$	415	0.24	79.0
BIDCH-PIM	NMP	24	0.19	45.2
BIDCH-AO-PIM	DMSO	5	0.03	18.7

^aBET surface area was obtained from N_2 adsorption at 77 K. ^bTotal pore volume was calculated from N_2 uptake at $P/P_0 = 0.97$. ^c CO_2 uptake was measured at 1 bar, 273 K.

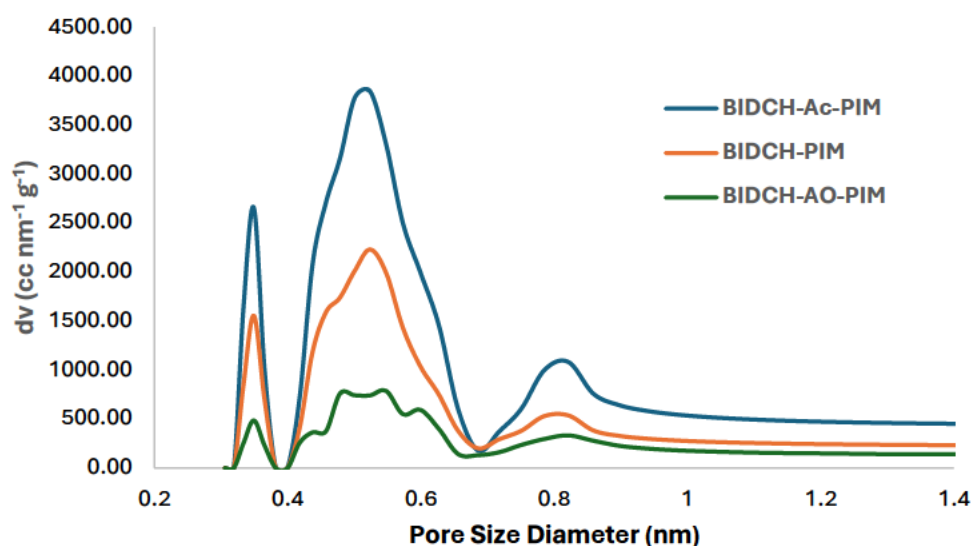


Figure 6.3.1c: Pore Size Distribution (PSD) calculated from CO_2 adsorption data using non-local density functional theory (NLDFT)

The CO_2 adsorption isotherm for the polymers was also obtained, from which the CO_2 uptake at 1 bar, 273 K could be calculated (Table 6.3.1a). The pore size distribution of the polymers was also calculated from this isotherm, using non-local density functional theory (NLDFT) (Figure 6.3.1.c). The pore size distribution analysis indicated that the porosity of all the polymers comprised a mixture of ultra-micropores (pore diameter < 0.7 nm) and micropores (pore diameter < 2 nm).

Free standing and flexible films of **BIDCH-Ac-PIM** were cast from CHCl_3 solution and films from **BIDCH-PIM** were cast from NMP solution. Unfortunately, attempts to cast a film from **BIDCH-AO-PIM** from DMSO solution resulted in a broken film not suitable for gas permeability measurements. Samples of **BID-Ac-PIM** and **BIDCHC-PIM** were provided to the Institute on Membrane Technology (ITM) for single gas permeability measurement and data collected and compared to that from PIM-1.

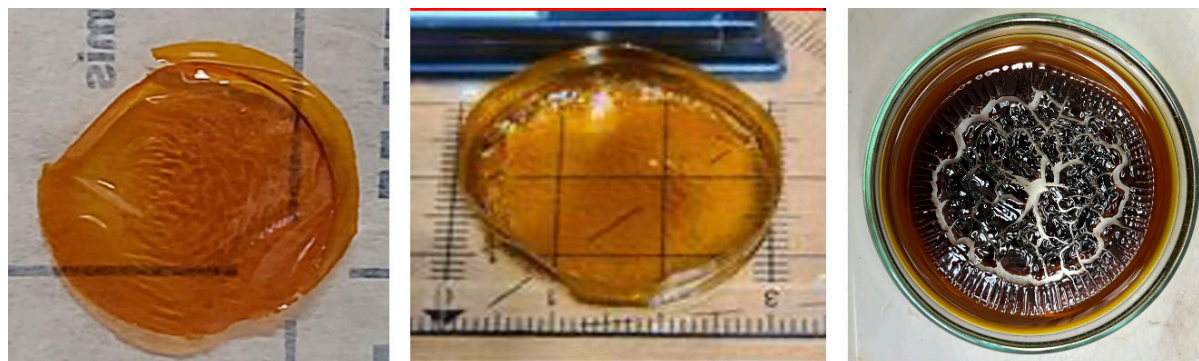


Figure 6.3.1d: **BIDCH-Ac-PIM** cast from CHCl_3 solution (left), **BIDCH-PIM** membrane cast from NMP solution (middle), failed attempt to form a **BIDCH-AO-PIM** film from DMSO solution (right).

Single gas permeabilities of **BIDCH-Ac-PIM** and **BIDCH-PIM** films were measured to study the effects of the different functional groups. It should be noted that the gas permeabilities of glassy polymers such as the PIMs are dependent on their film histories and thickness. Methanol treatment of membranes was carried out prior to measurement to reverse the effects of physical aging, allowing the direct comparison of different polymers. Membranes were also analysed after methanol treatment to investigate the effect of physical aging on gas permeability and selectivity of the polymers (**Table 6.3.1e**). Both freshly methanol treated films of **BIDCH-Ac-PIM** and **BIDCH-PIM** displayed high gas permeability. The acylated and non-acylated membranes possessed different trends of gas permeability. Fresh methanol treated and aged membrane of **BIDCH-Ac-PIM** have the permeability trend of $\text{H}_2 > \text{He} > \text{CO}_2 > \text{O}_2 > \text{CH}_4 > \text{N}_2$. This can be compared with fresh methanol treated and aged samples of **BIDCH-PIM**, which show the trend $\text{H}_2 > \text{CO}_2 > \text{He} > \text{O}_2 > \text{N}_2 > \text{CH}_4$. For aged **BIDCH-PIM** there is a higher permeability of He compared to CO_2 , this could be because of higher density of ultra-micropores present.

Table 6.2.1e: Membrane thickness (L , μm), ideal gas permeabilities (P_x , Barrer) of freshly methanol treated and aged films measured at 25 °C and 1 bar of feed pressure.

Polymer	L (μm)	P_{N_2}	P_{O_2}	P_{CO_2}	P_{CH_4}	P_{H_2}	P_{He}
BIDCH-Ac-PIM							
MeOH	135	238	918	5423	307	3482	1458
(38)	135	135	572	3170	153	2521	1066
(92)	135	73	336	1931	82	1657	767
BIDCH-PIM MeOH	37	47	303	5108	39	2650	1294
(29)	37	22	136	687	20	1122	614
(85)	37	21	130	675	20	1492	578

Numbers in parentheses are the number of days of membrane aging after methanol treatment.

As expected, diffusivity of H_2 and He for all freshly methanol treated and aged samples of **BIDCH-Ac-PIM** and **BIDCH-PIM** are relatively high (Table 6.3.1f). No significant changes were observed from solubility coefficient for freshly methanol treated and aged **BIDCH-Ac-PIM** and **BIDCH-PIM** (Table 6.3.1g).

Table 6.3.1f: Membrane thickness (L , μm), diffusivity coefficients (D_x , $10^{-12} \text{ m}^2/\text{s}$) of freshly methanol treated and aged films measured at 25 °C and 1 bar of feed pressure.

Polymer	D_{N_2}	D_{O_2}	D_{CO_2}	D_{CH_4}	D_{H_2}	D_{He}
BIDCH-Ac-PIM						
MeOH	44	918	5423	307	3482	1458
(38)	29	126	40	8	4008	10462
(92)	17	75	23	5	2918	4316
BIDCH-PIM MeOH	10	63	16	3	1507	7435
(29)	5	31	8	1	2068	1160
(85)	5	27	7	1	1492	8342

Numbers in parentheses are the number of days of membrane aging after methanol treatment.

Table 6.3.1g: Membrane thickness (L , μm), solubility coefficient (S_x , $\text{cm}^3_{\text{STP}} \text{ cm}^{-3} \text{ bar}^{-1}$) of freshly methanol treated and aged films measured at 25 °C and 1 bar of feed pressure.

Polymer	S_{N_2}	S_{O_2}	S_{CO_2}	S_{CH_4}	S_S	S_{He}
---------	-----------	-----------	------------	------------	-------	----------

BIDCH-Ac-PIM	4	4	71	17	1	0.1
MeOH						
(38)	3	3	60	14	0.5	0.1
(92)	3	3	63	13	0.4	0.1
BIDCH-PIM MeOH	4	4	69	12	1	0.1
(29)	3	3	66	12	0.4	0.4
(85)	3	4	68	12	0.5	0.1

Numbers in parentheses are the number of days of membrane aging after methanol treatment.

Significantly, most data points lie above the 2008 Robeson upper bounds for technologically important gas pairs. Indeed, some data points lie close to 2015 upper bound for O_2/N_2 , H_2/N_2 , H_2/CH_4 and CH_4/CO_2 with the permeability of freshly methanol treated **BIDCH-PIM** being particularly promising.

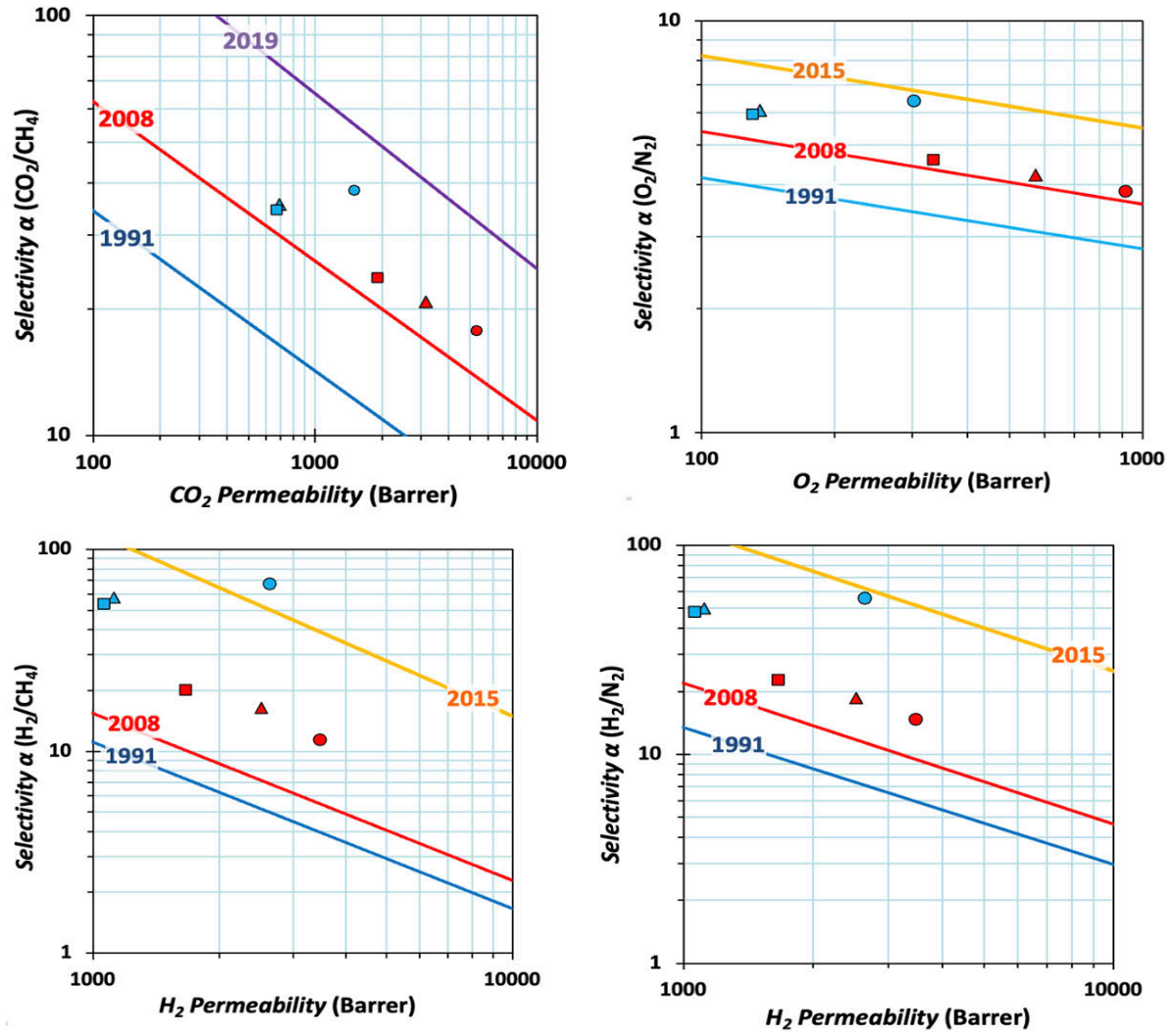


Figure 8: Robeson plots of selected gas pairs for BIDCH-Ac-PIM and BIDCH-PIM with 1991 (—), 2008 (—), 2015 (—) and 2019 (—). BIDCH-Ac-PIM: MeOH (●), 38 days (▲), 92 days (■) and BIDCH-PIM: MeOH (●), 29 days (▲) and 85 days (■).

6.3.2 BIDNH-PIMs

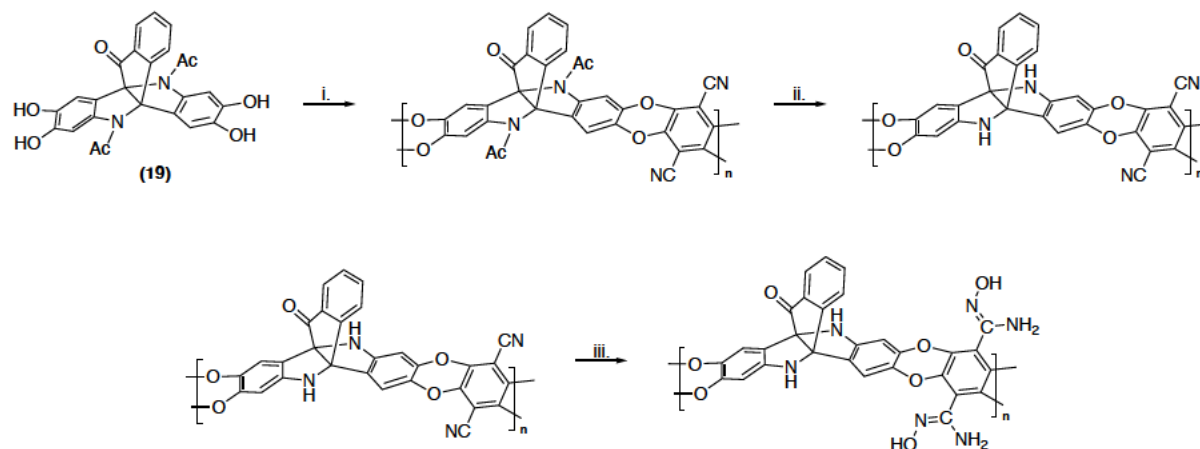


Figure 6.3.2a: Polymerisation of BIDNH-Ac-PIM and its AO modification. i) TFTPn, K₂CO₃, DMF, 70 °C, N₂. ii) Conc HCl, EtOH, reflux. iii) NH₂OH, 80 °C.

Polymerisation of **BIDNH-Ac-PIM** was attempted by reacting compound **19** with 1 molar equivalent of **TFTPn** in basic condition under a nitrogen atmosphere at 70 °C under constant stirring until a viscous yellow solution was obtained. The resulting solution was cooled then quenched with cold water and neutralised with hydrochloric acid to form a light-yellow precipitate. The crude product was collected under vacuum and washed with water, methanol, and acetone to remove low molecular weight polymer chains to give 45% yield. **BIDNH-Ac-PIM** was then refluxed in a mixture of ethanol and concentrated HCl to deprotect the nitrogen atoms. The precipitate was filtered and used to carry out the amidoxime conversion by reacting solid **BIDNH-PIM** with hydroxylamine hydrochloride at 80 °C overnight to convert the nitrile groups into AO. The final product was collected by filtration and washed with methanol to give **BIDNH-AO-PIM**.

The adsorption and desorption isotherm plots of **BIDNH-Ac-PIM**, **BIDNH-PIM** and **BIDNH-AO-PIM** were obtained by N₂ gas adsorption at 77K (**Figure 6.3.2b**). Surprisingly, all obtained isotherms show very small amounts of gas uptake that is consistent with the polymers being non-porous materials.

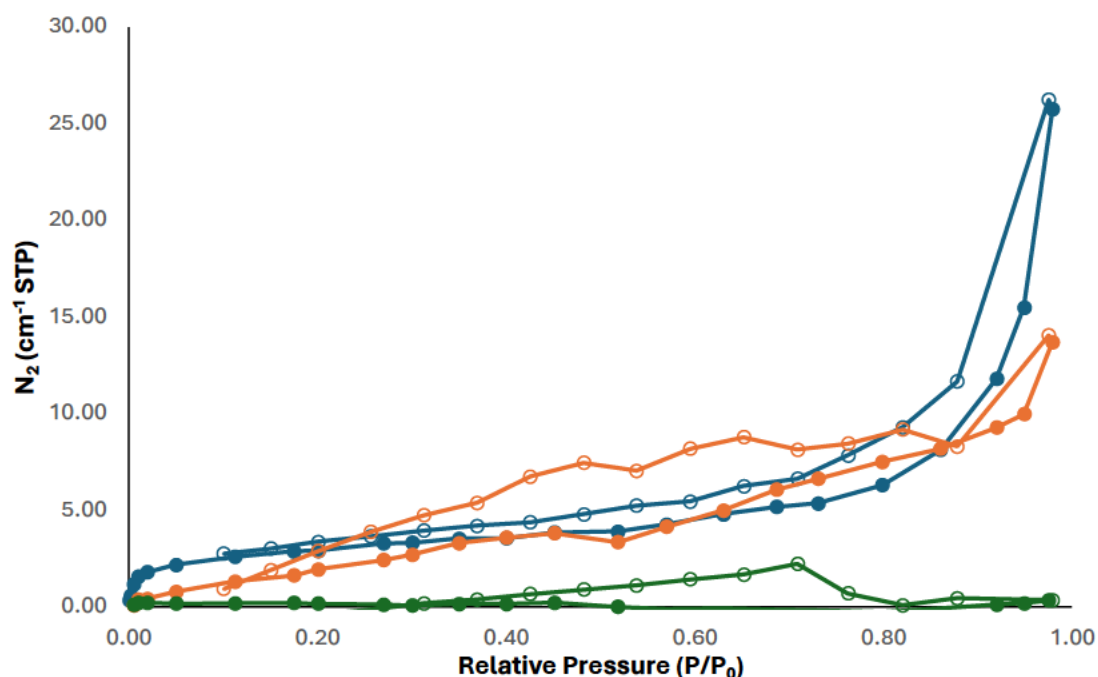


Figure 6.3.2b: N_2 adsorption isotherm measure at 77 K, adsorption (solid filled circles) and desorption (empty circles). **BIDNH-Ac-PIM** (blue), **BIDNH-PIM** (orange), **BIDNH-AO-PIM** (green).

From the obtained N_2 isotherms, BET surface area and total pore volume of the polymers were calculated (Table 6.3.2b). **BIDNH-Ac-PIM** shows a greater surface area ($10 \text{ m}^2 \text{ g}^{-1}$) compared to **BIDNH-PIM** ($6 \text{ m}^2 \text{ g}^{-1}$) and **BIDNH-AO-PIM** ($1 \text{ m}^2 \text{ g}^{-1}$).

Table 6.3.2a: Gas adsorption properties of **BIDNH-Ac-PIM**, **BIDNH-PIM** and **BIDNH-AO-PIM**.

Polymer	Solubility	SA_{BET}^a ($\text{m}^2 \text{ g}^{-1}$)	V_{Total}^b (mL g^{-1})	$CO_2 \text{ uptake}^c$ (cc g^{-1})
BIDNH-Ac-PIM	-	10	0.04	7.48
BIDNH-PIM	-	6	0.02	2.36
BIDNH-AO-PIM	-	1	0.003	-

^aBET surface area was obtained from N_2 adsorption at 77 K, ^btotal pore volume was calculated from N_2 uptake at $P/P_0 = 0.97$ (**BIDNH-AO-PIM** = 0.45), and ^c CO_2 uptake was measured at 1 bar, 273 K.

The CO₂ adsorption isotherm for these polymers was also obtained, from which the CO₂ uptake at 1 bar, 273 K could be calculated (**Table 6.3.2a**), which were also consistent with non-porous solids.

6.4 UV Analysis of PNPA Hydrolysis Using BIDCH-PIMs and BIDNH-PIMs

Thus far, the effect of incorporating basic components within the body of the PIM backbone on the rate of catalysis of PNPA hydrolysis. As discussed in Chapter 3 PAN/PANOx nanofibers did not provide the necessary catalytical activity for hydrolysis of PNPA in the absence of a basic component such as NaOH solution. In Chapter 4 the effectiveness of Tröger's Base in aiding the hydrolysis of PNPA was investigated and it was established that TB could not act as a strong base in hydrolysing PNPA. And finally, in Chapter 5 the novel bispirolactam PIM was investigated which showed improved performance in catalytical activity at pH 7.

For completeness, the effectiveness of **BIDNH-PIMs** and **BIDCH-PIMs** towards PNPA hydrolysis was investigated. All sample preparations were carried out as described in previous chapters. The absorbance spectra for the hydrolysis reaction using both series of propellane based polymers (**Figures 6.4a and 6.4b**) demonstrates that by introducing sufficient basicity into the polymeric structures of the PIM we are able to prepare catalytic polymers for hydrolysis of PNPA, where the absence of an external source of a basic compound was not a limiting factor.

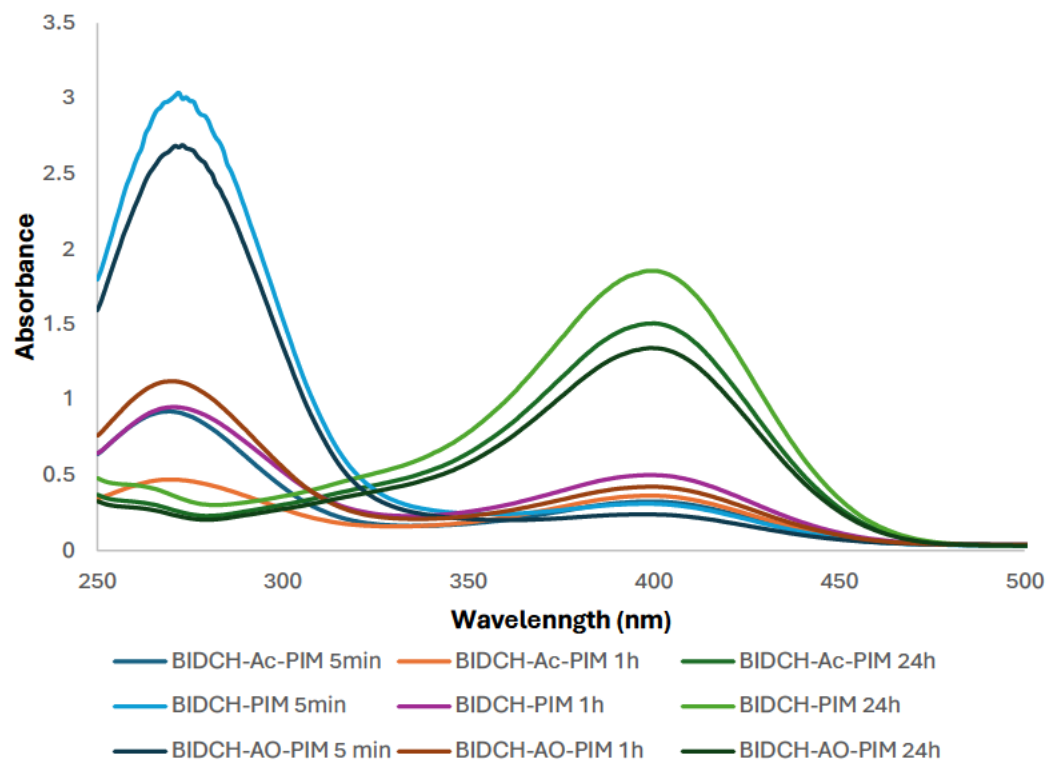


Figure 6.4a: UV spectra of PNPA hydrolysis by **BIDCH-Ac-PIM**, **BIDCH-PIM** and **BIDCH-AO-PIM** in pH 7 at various time intervals.

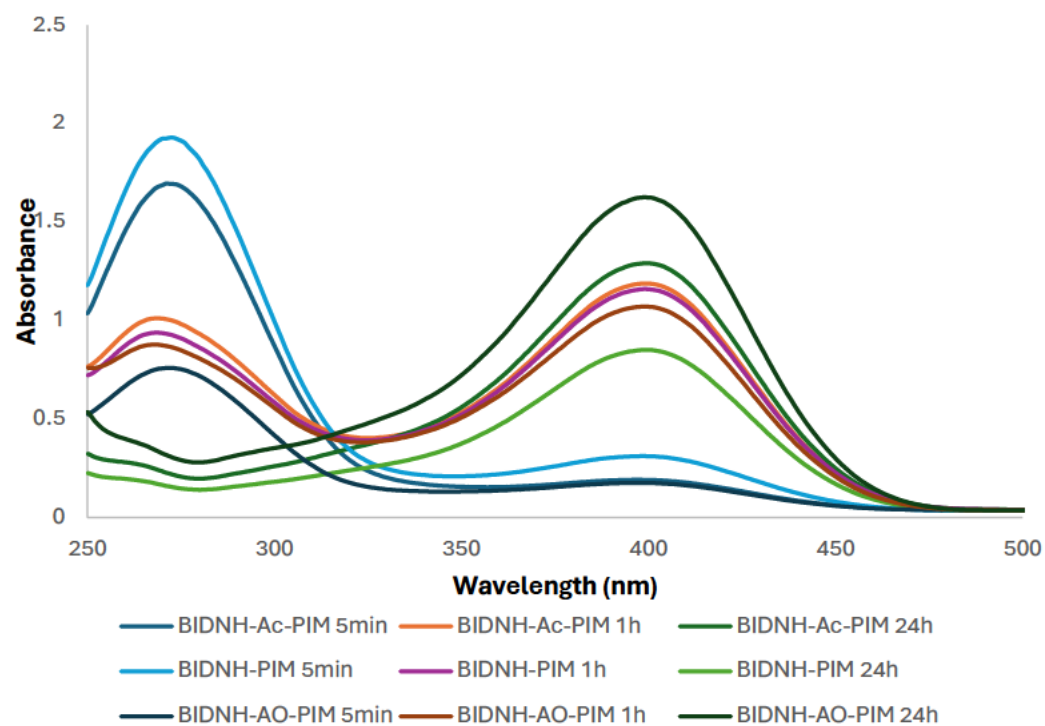


Figure 6.4b: UV spectra of PNPA hydrolysis by **BIDNH-Ac-PIM**, **BIDNH-PIM** and **BIDNH-AO-PIM** in pH 7 at various time intervals.

Conclusions

Chapter 3 of this thesis introduces the concept of using modifying polymeric structures as catalysts in deactivation of organophosphates (CWAs). It was also highlighted in that chapter that it is important to have a polymeric structure armed with functional groups such as amidoxime to bind to organophosphates and therefore act as a catalytic active site, however, it is of the essence to have a polymer that is capable of regenerating these active sites to avoid so called catalytic poisoning. To achieve this, we have dedicated this research to synthesising Polymers of Intrinsic Microporosity (PIMs) that are efficient at adsorbing and hydrolysing PNPA (a safe alternative to Paraoxon as a model compound for CWAs). For these polymers to be effective in personal protective equipment they should preform hydrolysis reactions under ambient conditions *i.e.* without the need an aid from basic sources. With this in mind, a series of novel amine and amide containing PIMs introducing basic site onto the body of these novel PIMs were designed and prepared. The hydrolysis abilities of these polymers were assessed, and the results showed that by making the polymers more basic we eliminate/reduce the need to use a source of base.

During the course of this research, different routes were explored in order to optimise the adsorption and hydrolysis of organophosphate compounds. Exploring the addition of Tröger's base (TB) as a monomer to synthesis a copolymer PIM did not aid in adsorption and hydrolysis of PNPA as TB did not provide sufficient basicity. Recognising that the PIMs synthesised for the purpose of hydrolysing organophosphate compound needed to contain a stronger basic site to eliminate the need to use basic solution such as buffers to assist with deactivation of CWAs. To do so secondary amines were introduced to the main-chain of novel PIMs and, therefore, a new series of nitrogen-containing PIMs was prepared.

Analytical UV-vis experiments of novel PIMs: **BIDCH-Ac-PIM**, **BIDCH-PIM**, **BIDCH-AO-PIM**, **BIDNH-Ac-PIM**, **BIDNH-PIM** and **BIDNH-AO-PIM** shows amidoxime (OA) modified PIMs of both groups of novel PIMs were the best performing when challenged in the hydrolysis of PNPA in the absence of basic buffers.

The **BIDNH-PIM** family synthesised from monomers containing ninhydrin show significant reduced in solubility, this did not cause any disadvantages in UV-vis analysis of this series of PIMs as they were used heterogeneously during the experiments. The reduced in solubility, means that no films could be casted from these polymers, hence, no gas permeability data could be collected.

PIMs synthesised from monomers derived from cyclohexadione, specifically **BIDCH-Ac-PIM** and **BIDCH-PIM** were readily soluble in chloroform allowing films to be cast from these polymers. Gas permeability data of these polymers showed plausible permeability towards methanol with good selectivity for H₂/CH₃ experiment, even with ageing of the polymers. **BIDCH-AO-PIM** however was insoluble in common organic solvents and therefore could not be analysed for gas permeability.

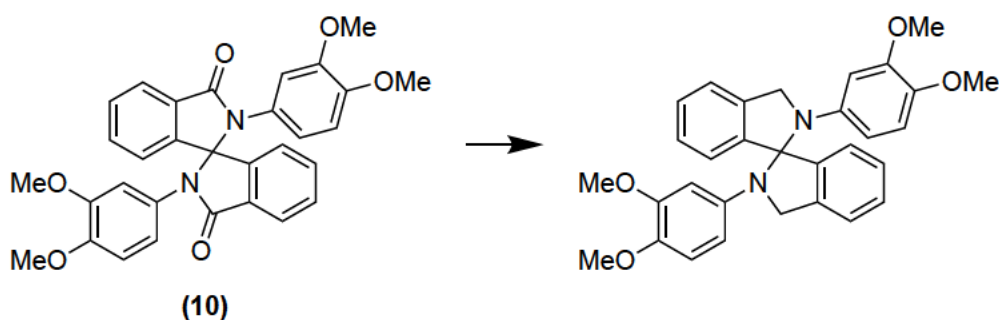
Future work

This thesis demonstrates the synthesis of novel PIMs with the ability to hydrolyse PNPA in neutral pH, however this research has just scratched the surface of what these polymers could achieve. Only a few examples of these series of polymers were synthesised where is still room for further modifications to enhance their catalytic potential.

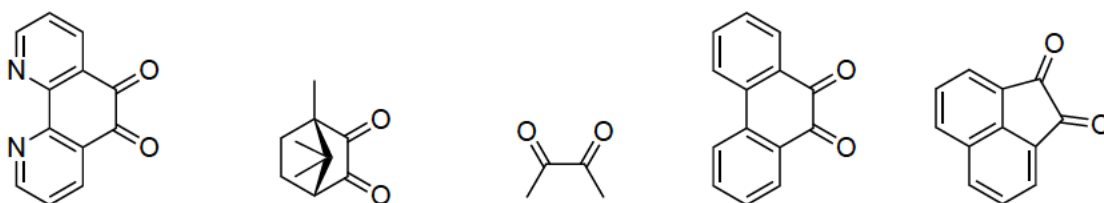
The novel **BIDNH-PIM** polymer family provides an encouraging set of polymers which display a promising catalytical activity against hydrolysis of organophosphate CWAs. However, this series of polymer shows low solubility in organic solvents. This can be further improved, and the polymerisation method can be optimised further to improve the molecular weight of the polymers in attempt to increase solubility. With improved solubility, membranes of these polymers could be cast in order to obtain gas permeability data which can be advantageous for obtaining preliminary data for different applications of these novel polymers.

Although **TB-PIMs** did not provide a promising activity against hydrolysis of PNPA as heterogeneous catalysis, its potential gas permeability has not been explored due to its insoluble nature when using 1:1 of Tröger's base and TFTP. The solubility was slightly improved by incorporating SBI monomer into the copolymer to achieve 1:1 of Tröger's base and SBI structural units. By further tuning the ratio to 1:2 Tröger's base to SBI it would likely lead to a significant improvement in solubility of the polymer allowing membranes to be cast from organic solvents.

SBL-PIM offered a reasonable catalytical activity towards hydrolysis of PNPA in the absence of external basic buffer compared to **TB-PIM**, where no significant catalytical activity was observed. In their current state **SBL-PIMs** made up of amide containing monomers where the tertiary nitrogen atom of amide displays a reduced basic activity compared to that of an amine group. To improve basic activity of **SBL-PIMs** the amide group present in this structure can be reduced to obtain more basic tertiary amines.



The novel polymers **BIDNH-PIMs** and **BIDCH-PIMs** show greater catalytic activity for PNPA hydrolysis. Although ninhydrin and cyclohexadione precursors have been successfully used to produce **BIDNH-PIMs** and **BIDCH-PIMs** respectively, attempts at synthesising monomers with other dione molecules have been unsuccessful, to date. The reaction between other diones and 3,4-dimethoxyaniline to form the bisindoline ring system may be achieved by using stronger acid conditions and these studies are currently being performed in the McKeown Group.



It would be intriguing to explore the possibility of using other amine sources (depicted below) to investigate the effect of the ring size on basicity of the monomer/polymer. By using 3,4-dimethoxybenzylamine and dopamine we may be able to increase the size of the propellane ring systems from 5 to 6 or 7.



Experimental

General procedures

All reagents used in this work were purchased from commercial suppliers and used without further purification. Anhydrous NMP, DMAc and DMF solvents were purchased from commercial suppliers and used as supplied. Anhydrous DCM was acquired from a PureSolv MD 7 solvent purification system (SPS). All reaction using air and/or moisture sensitive chemicals were carried out with oven-dried glassware under nitrogen flow. All reaction progresses were monitored by thin layer chromatography (TLC) using aluminium-backed plates coated with Merck TLC silica gel 60 F₂₅₄.

Characterisation Methods and equipment

Melting Point (Mp)

Melting points were recorded using Stuart SMP 10 equipment and are uncorrected.

Nuclear Magnetic Resonance (NMR)

¹H NMR, ¹³C NMR and variable temperature (VT) ¹H NMR data were obtained from Bruker AVA500, Pro500 (500 MHz).

Solid State ¹³C NMR data were collected using AVA300 at (76 Hz) and referenced to adamantane.

Fourier-transform Infrared Spectroscopy (FT-IR)

IR data obtained using ATR crystal Perkin-Elmer 660 Plus instrument.

Ultraviolet-visible light Spectroscopy (UV-Vis)

UV-vis analysis was carried out using Shimadzu UV-1800 with 10 mm path length quartz cuvette. Insoluble materials were filtered using PUURE TM Syringe Filter, 17 mm PTFE 0.2µm.

Mass Spectroscopy (MS)

Small molecule (Mw < 1000 g mol⁻¹) low resolution (LRMS) and high resolution (HRMS) mass spectroscopy was performed using a Fison VG Platform II quadrupole instrument plus Thermo Finnigan. MAT 900 XP, Electron Ionisation Sector MS utilising electron impact (EI).

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using thermal analysis SDT Q600 instrument. Samples were analysed up to 800 °C with temperature ramping of 10 °C min⁻¹ under air flow.

Brunauer-Emmett-Teller (BET) Surface Area

Nitrogen (77 K) and carbon dioxide (273 K) gas adsorption/desorption isotherms were obtained using Quantachrome Quadrasorbevo automated surface area analyser. All samples were degassed overnight at 100 °C prior to analysis.

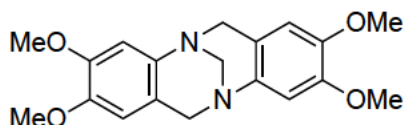
Single X-ray crystallography

Single crystal structures were obtained using Bruker Smart Apex CCD diffractometer with MoK α radiation λ = 0.71073 Å at 150 K. Oxford Diffraction SuperNova diffractometer with CuK α radiation λ = 1.5405 Å at 120 K.

Monomer Synthesis

2,3,8,9-Tetramethoxy-6H,12H-5,11-methanodibenzole[1,5]-diazocine (1)

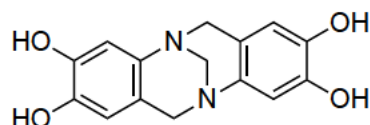
(Based on literature procedure²⁴⁴)



3,4-Dimethoxyaniline (30.00 g, 195.84 mmol) and paraformaldehyde (11.70 g, 391.60 mmol) were added in portions and under vigorous stirring to trifluoroacetic acid (200 mL) at 0 °C. The mixture was allowed to reach room temperature and left stirring for 16 h. The dark purple mixture was quenched with water and 35% aqueous NH₃ solution was added until pH 9 was obtained. The resulting precipitate was collected under suction and repeatedly washed with water and MeOH to obtain a purple powder. Product was purified by recrystallisation from methanol and was dried under vacuum to obtain light purple powder (21.78g, 65%, Lit²⁴⁴ 78%). Mp: 138–140 °C (Lit²⁴⁴ 198 – 200 °C). ν_{max} (cm⁻¹): 2929, 1608, 1504, 1433, 1224. ¹H NMR (500 MHz, CDCl₃) δ 6.78 (s, 2H, ArH), 6.42 (s, 2H, ArH), 4.73 (d, 2H, NCH₂), 4.39 (s, 2H, NCH₂N), 4.15 (d, 2H NCH₂), 3.88 (s, 6H, CH₃). ¹³C NMR (126 MHz, CDCl₃) δ 150.2, 147.4, 140.3, 123.4, 112.02, 109.7, 67.1, 57.13, 56.2, 56.0. TOF-HRMS (EI, m/z): calculated C₁₉H₂₂N₂O₄ 342.1564 found: 342.1563 [M⁺].

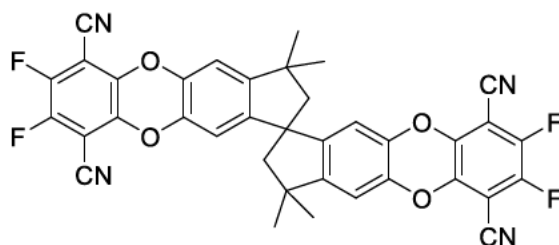
2,3,8,9-Tetrahydroxy-6H,12H-5,11-methanodibenzole[1,5]-diazocine (2)

(Based on literature procedure²⁴⁴)



2,3,8,9-Tetramethoxy-6H,12H-5,11-methanodibenzole[1,5]-diazocine (17.32 g, 50.58 mmol) was dissolved in DCM (250.0 ml) under a nitrogen atmosphere at 0 °C. BBr₃ (24 ml, 5 molar equivalents) was added dropwise with stirring. After addition of BBr₃, the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched with water (100.0 mL) and DCM was removed under a vigorous flow of nitrogen then the solid was collected by suction filtration and dried under vacuum for 12 h at 30 °C to give the white solid (2.78g, 20%). Mp: 134–136 °C; ν_{max} (Cm⁻¹): 3128, 1606, 1517, 1448, 1384, 1273, ¹H NMR (500 MHz, DMSO-d₆) δ 9.80 (s, 4H, OH), 6.82 (s, 2H, ArH), 6.51 (s, 2H, ArH), 4.98 (s, 2H, NCH₂), 4.70 (s, 2H, NCH₂), 4.20 (s, 2H, NCH₂N); ¹³C NMR (126 MHz, DMSO-d₆) δ 147.6, 146.8, 139.7, 120.1, 111.6, 107.9, 667.3, 57.2.

TFTTSBI (3)

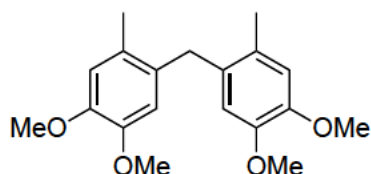


3,3,3',3'-Tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol (4.00 g, 11.75 mmol), tetrafluorophthalonitrile (4.70 g, 23.50 mmol) was dissolved in dimethylacetamide (60 mL). Potassium carbonate (6.50 g, 47.00 mmol) was then added to the reaction mixture and stirred vigorously at 80 °C for 15 min. Reaction mixture was allowed to cool room temperature and product was precipitated onto methanol (150 mL). The bright yellow powder was dissolved in dichloromethane (50 mL) and washed with water to remove the remaining DMAc (6.83 g, 88%). Mp: >300 °C, ν_{max} (cm⁻¹): 2862, 224, 1469, 1408, 1311, 1006, ¹H NMR (500 MHz, CDCl₃) δ 6.88 (s, 2H), 6.46 (s, 2H), 2.38 (d, *J* = 13.2 Hz, 2H), 2.18 (d, *J* = 13.3 Hz, 2H), 1.39 (s, 6H), 1.33 (s, 6H), ¹³C NMR (126 MHz, CDCl₃) δ 150.5, 147.5,

144.5, 141.2, 141.2, 139.0, 138.8, 112.4, 110.8, 107.7, 107.7, 107.7, 58.7, 57.2, 43.7, 31.3, 29.8.

Bis-(4,5-dimethoxy-2-methyl-phenyl)-methane (6)

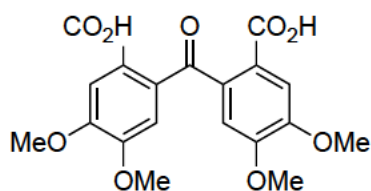
(Based on literature procedure²⁵¹)



Formaldehyde (14.43 g, 480.57 mmol) was added slowly to an ice-cold mixture of 3,4-methoxytoluene (18.27 g, 120.05 mmol) in glacial AcOH (60.00 ml) and concentrated sulphuric acid (6.00 ml) under stirring then allowed to stand for 2 h. The white solid was filtered and washed with copious amount of water and recrystallised from MeOH, yielding (16.03g, 89%). Mp: 121–123°C (literature²⁵¹ 121 – 122 °C); ν_{max} (cm⁻¹): 2964, 2034, 1971, 1604, 1516, 1438, 1444, 1330, 1201, 1089; ¹H NMR (500 MHz, CDCl₃) δ 7.80 (s, 2H, ArH), 7.00 (s, 2H, ArH), 4.43 (s, 6H, OMe), 4.34 (s, 2H, CH₂), 4.27 (s, 6H, OMe), 2.79 (s, 6H, ArCH₃). ¹³C NMR (126 MHz, CDCl₃) δ 147.3, 130.9, 128.8, 114.0, 113.2, 56.4, 36.2, 19.4, TOF-HRMS (EI, m/z): calculated C₁₉H₂₄O₄ 316.1658 found: 342.1566 [M⁺].

2,2'-Dicarboxy-4,5,4',5'-tetramethoxy-benzophenone (7)

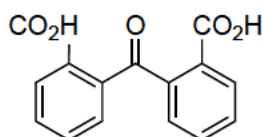
(Based on literature procedure²⁵²)



Bis-(4,5-dimethoxy-2-methyl-phenyl)-methane (16.00 g, 50.57 mmol) was added to 50/50 v/v% of Pyridine and water (500 ml) and 30 eq. of KMnO₄ (239.74 g, 1509.03 mmol) was added to the reaction mixture in two parts. The first half of KMnO₄ was added to the reaction very slowly and the mixture was refluxed for 12 h: the dark purple solution became black after 12 h. The remaining half of the KMnO₄ was added, and the mixture was refluxed for further 24 h. The reaction mixture was filtered hot and manganese

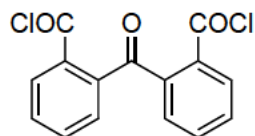
dioxide was washed with hot deionised water. The filtrate was cooled to room temperature and pyridine/water mixture was removed under reduced pressure. The solid obtained was dissolved in deionised water and neutralised with concentrated hydrochloric acid to form a white precipitate which was collected by vacuum filtration and washed with water and MeOH to give (9.63 g, 60%). Mp: 247 – 258 °C, ν_{max} (cm⁻¹): 1681, 1571, 1521, 1425, 1350, 1271, 1174, 1099, ¹H NMR (500 MHz, DMSO-d₆) δ 12.86 (s, 2H, RCOOH), 7.25 (s, 2H, ArH), 6.98 (s, 2H, ArH), 3.89 (s, 6H, OMe), 3.76 (s, 6H, OMe). ¹³C NMR (126 MHz, DMSO-d₆) 194.7, 168.3, 150.2, 149.7, 132.7, 126.4, 113.0, 111.9, 56.3, TOF-HRMS (EI, m/z): calculated C₁₉H₁₈O₉ 390.0931 found: 390.0945 [M⁺].

2,2'-Dicarboxy-benzophenone (4)



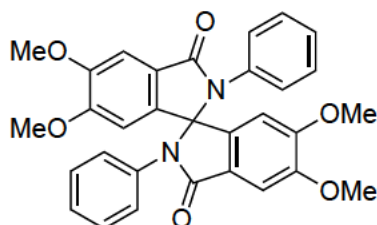
5-Dibenzosuberone (10.00 g, 48.49 mmol) was added to 50/50 v/v% of Pyridine and water (500 mL) and 20 eq. of KMnO₄ (153.25 g, 969.74 mmol) was added to the reaction mixture in two parts. The first half of KMnO₄ was added to the reaction very slowly and the mixture was refluxed for 12 h: the dark purple solution became black after 12h. The remaining half of the KMnO₄ was added, and the mixture was refluxed for a further 24 h. The reaction mixture was filtered hot and manganese dioxide was washed with hot deionised water. The Filtrate was cooled to room temperature and the pyridine/water mixture was removed by vacuum filtration. The solid obtained was dissolved in deionised water and neutralised with concentrated hydrochloric acid to form a white precipitate which was collected by vacuum filtration and washed with water and MeOH to give **4** as white powder (6.35 g, 64%). Mp: 185 – 190 °C (lit²⁵³ 193 - 197 °C); ν_{max} (cm⁻¹): 1672, 1577, 1450, 1421, 1411, 1292, 1138, 935, ¹H NMR (500 MHz, CDCl₃) δ 12.60 (d, 2H, ArH), 12.47 (d, 2H, ArH), 12.38 (d, 2H, ArH), 12.21 (d, 2H, ArH), 8.71 (s, 2H, RCOOH). ¹³C NMR (126 MHz, CDCl₃) δ 196.6, 168.6, 138.6, 132.9, 131.4, 130.9, 129.5, 129.0, TOF-HRMS (EI, m/z): calculated C₁₅H₁₀O₅ 270.0518 found: 270.0522 [M⁺].

2,2'-Dichlorocarboxy-benzophenone (5)



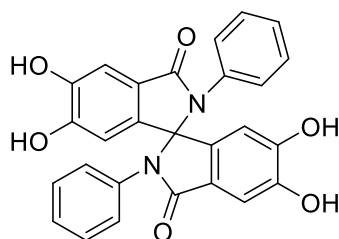
A mixture of 2,2'-Dicarboxy-benzophenone (**4**) (3.00 g, 11.10 mmol) and DCM (200.00 mL) was degassed for 15 minutes under reflux with nitrogen flow. The reaction flask was cooled to room temperature and transferred to ice bath allowing the internal temperature to reach 0 °C before thionyl chloride (3.69 g, 33.30 mmol) was added dropwise, producing a white precipitate. Once all thionyl chloride had been added to the reaction mixture, it was refluxed for 72 h, after which the white precipitate had dissolved back into the solvent to form a transparent liquid with a hint of yellow. The stopper from the second neck of the round bottom flask was loosened to allow evaporation of DCM and excess SOCl₂ without effecting the nitrogen atmosphere. Upon complete removal of DCM and excess SOCl₂, the white powder remained. Petroleum ether (60 - 80 °C) was added to the product under stirring to removed HCl residues. The final product **5** was filtered under a nitrogen atmosphere (2.80 g, 82%). Mp: 78 – 81 °C, ν_{max} (cm⁻¹): 1780, 1606, 1463, 1340, 1282, 1244, 1080, 991, 690, ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, 2H, ArH), 8.04 (d, 2H, ArH), 7.74 (t, 2H, ArH), 7.73 (t, 2H, ArH). ¹³C NMR (126 MHz, CDCl₃) δ 217.1, 166.9, 144.6, 135.9, 132.5, 126.7, 123.5.

2,2'-Bis(3,4-dimethoxyphenyl)-1,1'-spirobi[isoindole]-3,3'(2H,2'H)-dione (10)



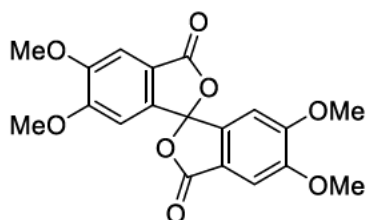
2,2'-Dicarboxy-4,5,4',5'-tetramethoxy-benzophenone (6.00 g, 0.12 mmol), aniline (14.04 mL, 153.70 mmol), and aniline hydrochloride (5.98 g, 23.06 mmol) were stirred at 158 °C for 5 h. The dark purple solution was cooled to room temperature and quenched onto a mixture of ice (14.00 g) and concentrated HCl (12.00 g) under constant stirring. The light purple precipitate that formed was filtered and washed with copious amount of water and recrystallised from methanol (5.73 g, 70%). Mp: 160 – 164 °C, ν_{max} (cm⁻¹): 1697, 1598, 1494, 1371, 1310, 1213, 1122, 1004, ¹H NMR (500 MHz, CDCl₃) δ 7.40 (s, 1H, ArH), 7.36 (s, 1H, ArH), 6.47 (s, 1H, R-CONH-R), 3.99 (d, 6H, OCH₃), 3.82 (d, 6H, OCH₃), 3.39 (d, 2H, CH₂), 3.00 – 2.83 (m, 2H, CH₂), 1.47 – 1.15 (m, 2H, CH₂), 0.83 (t, 3H, CH₃). ¹³C NMR (126 MHz, CDCl₃) δ 168.3, 168.2, 156.0, 153.8, 152.2, 151.8, 139.9, 135.4, 124.0, 119.5, 106.3, 105.6, 104.5, 103.8, 97.5, 56.8, 56.6, 39.6, 31.3, 20.4, 13.8.

5,5',6,6'-Tetrahydroxy-2,2'-diphenyl-1,1'-spirobi[isoindole]-3,3'(2H,2'H)-dione (11)



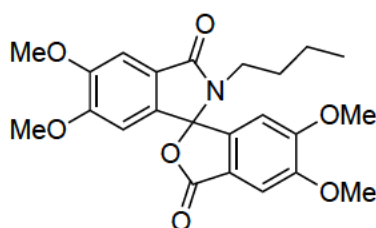
2,2'-Bis(3,4-dimethoxyphenyl)-1,1'-spirobi[isoindole]-3,3'(2H,2'H)-dione (**10**) (4.00 g, 4.65 mmol) was dissolved in DCM (40.00 mL) under nitrogen atmosphere at 0 °C. Boron tribromide (4.43 mL, 6 molar equivalents) was added slowly, and the reaction was stirred at room temperature for 12 h. The reaction was quenched with water (50.00 mL), DCM was evaporated under a vigorous nitrogen flow. The solid precipitate was collected by vacuum filtration and dried under vacuum for 12 h at 30 °C (1.86 g, 52%). Mp: 130 – 132 °C, ν_{max} (cm⁻¹): 3037, 1651, 1479, 1305, 1124, ¹H NMR (500 MHz, DMSO-d₆) δ 9.97 (s, 2H, OH), 9.82 (s, 2H, OH), 7.30 – 7.21 (m, 4H, ArH), 7.19 – 7.10 (m, 4H, ArH), 6.95 – 6.89 (m, 4H, ArH), 6.47 (s, 2H, ArH), ¹³C NMR (126 MHz, DMSO-d₆) δ 167.2, 151.7, 148.1, 136.2, 136.1, 129.2, 126.8, 125.3, 122.2, 109.6, 108.6, 84.6.

5,5',6,6'-Tetramethoxy-3*H*,3'*H*-1,1'-spirobi[[2]benzofuran]-3,3'-dione (8)



2,2'-Dicarboxy-4,5,4',5'-tetramethoxy-benzophenone (**7**) (3.00 g, 7.68 mmol) was dissolved in a mixture of NMP (200 ml) and quinoline (10 ml) and allowed to reflux for 72 h. The reaction was quenched with water, resulting in a white precipitation forming which was collected under vacuum filtration and washed repeatedly with water and methanol and recrystallised from hot methanol (1.20 g, 42%). Mp: 127 – 129 °C, ν_{max} (cm⁻¹): 1759, 1600, 1504, 1367, 1309, 1228, ¹H NMR (500 MHz, CDCl₃) δ 7.37 (s, 1H, ArH), 6.61 (s, 1H, ArH), 4.00 (s, 3H, CH₃), 3.88 (s, 3H, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 167.4, 156.1, 152.8, 139.0, 119.1, 106.9, 104.7, 56.8. TOF-HRMS (EI, m/z): calculated C₁₉H₁₆O₈ 372.0838 found: 372.0839 [M⁺].

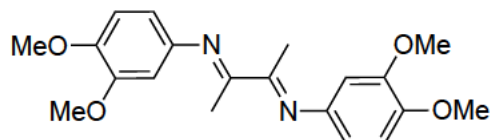
2'-Butyl-5,5',6,6'-tetramethoxy-3*H*-spiro[[2]benzofuran-1,1'-isoindole]-3,3'(2'*H*)-dione (9)



2,2'-Dicarboxy-4,5,4',5'-tetramethoxybenzophenone (**7**) (3.00 g, 7.69 mmol) and *n*-butylaniline (1.12 g, 15.37 mmol) were added to DMF (150 mL) and reaction was refluxed for 72 h. The light orange mixture was quenched with water and the crude product was collected by vacuum filtration and washed with methanol (2.87 g, 87%). Mp: 130 – 132 °C, ν_{max} (cm⁻¹): 2935, 1755, 1707, 1602, 1367, 1301, ¹H NMR (500 MHz, CDCl₃) δ 7.40 (s, 1H, ArH), 7.36 (s, 1H, ArH), 6.47 (s, 1H, R-CONH-R), 3.99 (d, 6H, OCH₃), 3.82 (d, 6H, OCH₃),

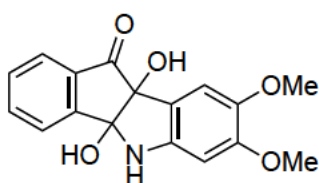
3.39 (d, 2H, CH₂), 3.00 – 2.83 (m, 2H, CH₂), 1.47 – 1.15 (m, 2H, CH₂), 0.83 (t, 3H, CH₃). ¹³C NMR (126 MHz, CDCl₃) δ 168.3, 168.2, 156.0, 153.8, 152.2, 151.8, 139.9, 135.4, 124.0, 119.5, 106.3, 105.6, 104.5, 103.8, 97.5, 56.8, 56.6, 39.6, 31.3, 20.4, 13.8. TOF-HRMS (EI, m/z): calculated C₁₉H₁₆O₈ 427.1612 found: 427.1613 [M⁺].

(2*E*,3*E*)-*N*²,*N*³-bis(3,4-dimethoxyphenyl)butane-2,3-diimine (14)



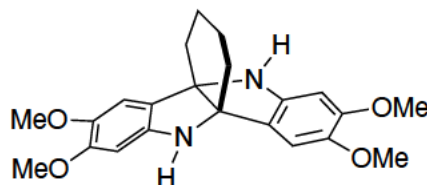
3,4-Dimethoxyaniline (7.12 g, 46.46 mmol), 2,3-butanedione (2.00 g, 86.09 mmol) and formic acid (0.26 mL, 6.97 mmol), along with methanol (80 mL), were vigorously stirred at room temperature for 24 h. The reaction mixture was cooled to -20 °C for 2 days inside a freezer. The precipitate was collected by vacuum filtration and washed with methanol (3 x 10 mL, -20 °C) followed by pentane (3 x 10 mL), and air dried at room temperature overnight. The crude solid was recrystallised from boiling ethanol (100 mL), left at room temperature overnight, then cooled to -20 °C for 1 day. The crystals were collected by filtration, washed with ethanol (5 x 10 mL, -20 °C) followed by pentane (3 x 10 mL), and air dried at room temperature (7.73 g, 93%). Mp: 146 – 148 °C, ν_{max} (cm⁻¹): 2956, 1635, 1506, 1440, 1225, 1130, 1022, ¹H NMR (500 MHz, DMSO-*d*₆) δ 6.96 (d, 2H, ArH), 6.48 (d, 2H, ArH), 6.35 (d, 2H, ArH), 3.75 (s, 12H, OCH₃), 2.12 (s, 6H, CH₃), ¹³C NMR (126 MHz, DMSO-*d*₆) δ 168.2, 149.6, 145.8, 144.5, 112.8, 110.8, 104.8, 56.2, 56.0, 15.7, TOF-HRMS (EI, m/z): calculated C₂₀H₂₄N₂O₄ 356.17306 found: 356.17154 [M⁺].

4*b*,9*b*-Dihydroxy-7,8-dimethoxy-5,9*b*-dihydroindeno[1,2-*b*]indol-10(4*bH*)-one (13)



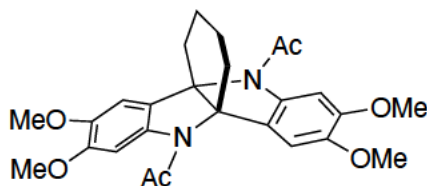
3,4-dimethoxyaniline (8.77 g, 44.91 mmol), ninhydrin (2.00 g, 11.23 mmol) and formic acid (0.13 mL, 3.37 mmol) were vigorously stirred in methanol (40 mL) at room temperature for 24 h. The reaction mixture was cooled to -20 °C for 2 days. The precipitate was collected by vacuum filtration and washed with methanol (3 x 10 mL, -20 °C) and air dried at room temperature overnight. The crude solid was recrystallised from boiling ethanol (100 mL), left at room temperature overnight, then cooled to -20 °C for 1 day. The crystals were collected by filtration, washed with ethanol (5 x 10 mL, -20 °C) and air dried at room temperature to give light purple crystals (4.73 g, 81%). ¹H NMR (500 MHz, DMSO) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.81 (td, *J* = 7.5, 1.3 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.44 (m, 1H), 7.02 (s, 1H), 6.81 (s, 1H), 6.12 (s, 1H), 6.00 (d, *J* = 23.2 Hz, 2H), 3.63 (d, *J* = 9.1 Hz, 6H). ¹³C NMR (126 MHz, DMSO) δ 200.68, 152.53, 151.99, 142.68, 141.77, 135.83, 133.96, 129.35, 124.99, 122.38, 114.95, 110.15, 94.02, 92.50, 83.94,

2,3,7,8-tetramethoxy-5*H*,10*H*-4*b*,9*b*-butanoindolo[3,2-*b*]indole (12)



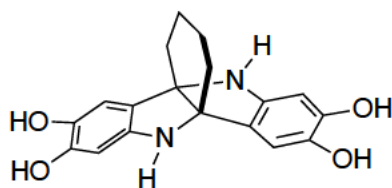
3,4-Dimethoxyaniline (5.46 g, 35.62 mmol) and 1,2-cyclohexanedione (2.00 g, 17.84 mmol) was reacted with formic acid (0.2 mL, 5.35 mmol) along with methanol (40 mL) under vigorous stirring at room temperature for 24 h. The reaction mixture was cooled to -20 °C for 2 days. The precipitate was collected by vacuum filtration and washed with methanol (3 x 10 mL, -20 °C) and air dried at room temperature overnight. The crude solid was recrystallised from boiling ethanol (100 mL), left at room temperature overnight, then cooled to -20 °C for 1 day, The crystals were collected by filtration (6.02 g, 89%). Mp: 142 – 145 °C, ν_{max} (cm⁻¹): 3319, 1682, 1494, 1312, 1139, 1105, ¹H NMR (500 MHz, DMSO-*d*₆) δ 6.88 (s, 2H, Ar), 6.16 (s, 2H, ArH), 5.58 (s, 2H, NH), 3.63 (d, 12H, OCH₃), 1.95 (dd, 2H, CH₂), 1.50 – 1.28 (m, 6H, CH₂), ¹³C NMR (126 MHz, DMSO-*d*₆) δ 149.36, 144.53, 141.42, 126.93, 109.21, 95.48, 72.20, 56.87, 55.48, 33.19, 19.38, TOF-HRMS (EI, *m/z*): calculated C₂₆H₃₀N₂O₆ 382.18871 found: 382.18842 [M⁺].

1,1'-[(4*bR*,9*bR*)-2,3,7,8-tetramethoxy-5*H*,10*H*-4*b*,9*b*-butanoindolo[3,2-*b*]indole-5,10-diyl]di(ethan-1-one) (15)



Anhydrous sodium acetate (8.78 g, 104.59 mmol) was added to a stirring solution of (4*bR*,9*bR*)-2,3,7,8-tetramethoxy-5*H*,10*H*-4*b*,9*b*-butanoindolo[3,2-*b*]indole (**12**) (2.00 g, 5.23 mmol) in acetic anhydride (50 mL). Reaction mixture was allowed to stir at room temperature for 8 hours. The crude product was filtered and washed with water (1.87 g, 77%). Mp: 143 – 146 °C, ν_{max} (cm⁻¹): 1682, 1467, 1325, 1211, 1028, ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.40 (s, 2H), 6.80 (s, 2H), 3.78 (s, 12H), 2.17 (d, *J* = 84.6 Hz, 6H), 1.91 (s, 3H), 1.46 (s, 3H), 0.96 (t, *J* = 10.4 Hz, 2H), ¹³C NMR (126 MHz, DMSO-*d*₆) δ 167.72, 150.55, 145.12, 137.67, 121.29, 113.94, 101.88, 78.83, 57.11, 56.50, 29.35, 25.67, 20.28.

1,1'-[(4*bR*,9*bR*)-2,3,7,8-tetrahydroxy-5*H*,10*H*-4*b*,9*b*-butanoindolo[3,2-*b*]indole-5,10-diyl]di(ethan-1-one) (16)

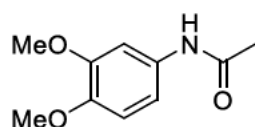


1,1'-[(4*bR*,9*bR*)-2,3,7,8-Tetramethoxy-5*H*,10*H*-4*b*,9*b*-butanoindolo[3,2-*b*]indole-5,10-diyl]di(ethan-1-one) (**15**) (2.00 g, 4.29 mmol) was dissolved in DCM (30.00 mL) under a nitrogen atmosphere at 0 °C. BBr₃ (2.48 mL, 6 molar equivalents) was added slowly, and the reaction was stirred at room temperature for 12 h. The reaction was quenched with water (50 ml) and the solid was collected by suction filtration and dried under nitrogen flow (1.18 g 67%). Mp: 130 – 132 °C (dec), ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.90 (d, *J* = 106.3 Hz, 4H), 7.75 – 6.44 (m, 4H), 2.79 (s, 2H), 2.29 – 1.80 (m, 6H), 1.49 (d, *J* = 59.7 Hz,

4H), ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.83, 146.45, 140.90, 116.08, 103.11, 77.71, 29.59, 25.83, 20.04.

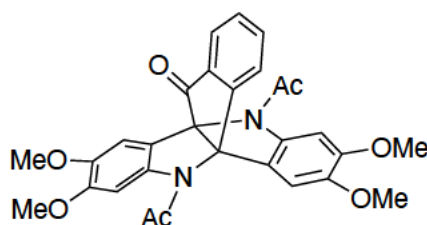
***N*-acetyl-3,4-dimethoxyaniline (17)**

(Based on literature reaction²⁵⁴)



To a suspension of 3,4-dimethoxyaniline (50.00 g, 326.41 mmol) in water (420 mL) were alternately added a one-fifth portion of a solution (100 mL) of sodium hydroxide (17.00 g, 425.03 mmol) in water and a one-fifth portion of acetic anhydride (40.09 g, 424.14 mmol) at less than 65 °C with stirring. After stirring for 20 min at 55–60 °C, the reaction mixture was cooled to about 5 °C and stirred for 1 h to precipitate crystals. The resulting crystals were collected by filtration, washed with water (200 mL) and then dried at 50–60 °C for 7 h to give dark purple fine powder (43.63 g, 95%). Mp: 127 – 128 °C (lit²⁵⁵ 126 – 128 °C), ν_{max} (cm^{-1}): 3246, 1651, 1369, 1234, 1022, ^1H NMR (500 MHz, DMSO-d_6) δ 9.76 (s, 1H), 7.28 (d, J = 2.5 Hz, 1H), 7.07 (dd, J = 8.7, 2.4 Hz, 1H), 6.86 (d, J = 8.7 Hz, 1H), 3.71 (d, J = 5.2 Hz, 6H), 2.00 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.25, 148.99, 145.13, 133.50, 112.57, 111.41, 111.31, 104.81, 104.71, 56.19, 55.80, 24.34.

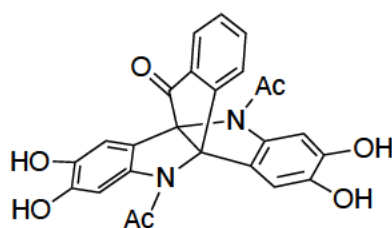
1,1'-[(4*bR*,9*bR*)-2,3,7,8-Tetramethoxy-5*H*,10*H*-4*b*,9*b*-2*H*-inden-2-one[3,2-*b*]indole-5,10-diyl]di(ethan-1-one) (18)



N-Acetyl-3,4-dimethoxyaniline (8.77 g, 44.91 mmol), Ninhydrin (2.00 g, 11.23 mmol) and formic acid (0.13 mL, 3.37 mmol) were vigorously stirred in methanol (40 mL) at room

temperature for 24 h. The reaction mixture was cooled to -20 °C for 2 days. The precipitate was collected by vacuum filtration and washed with methanol (3 x 10 mL, -20 °C) and air dried at room temperature overnight. The crude solid was recrystallised from boiling ethanol (100 mL), left at room temperature overnight, then cooled to -20 °C for 1 day. The crystals were collected by filtration, washed with ethanol (5 x 10 mL, -20 °C) and air dried at room temperature to give light purple crystals (4.63 g, 80%). Mp: 158 – 159 °C, ν_{max} (cm⁻¹): 3257, 1652, 1608, 1232, 1012, ¹H NMR (500 MHz, DMSO-d₆) δ 7.91 (dd, J = 6.2, 1.5 Hz, 1H), 7.54 (td, J = 6.3, 1.5 Hz, 1H), 7.44 (td, J = 6.8, 1.5 Hz, 1H), 7.40 (dd, J = 7.0, 1.5 Hz, 1H), 7.11 (s, 2H), 6.63 (d, J = 3.4 Hz, 2H), 3.87 (d, J = 20.7 Hz, 12H), 2.31 (s, 6H). ¹³C NMR (126 MHz, DMSO-d₆) δ , 190.36, 170.02, 169.89, 151.87, 145.52, 144.46, 136.13, 135.05, 134.00, 133.35, 130.70, 127.83, 126.51, 125.97, 125.32, 108.63, 108.23, 101.12, 99.90, 89.57, 81.75, 56.07, 25.62, TOF-HRMS (EI, m/z): calculated C₂₉H₂₆N₂O₇ 514.1735 found: 514.1736 [M⁺].

1,1'-[(2,3,7,8-tetrahydroxy-5*H*,10*H*-4*b*,9*b*-2*H*-inden-2-one[3,2-*b*]indole-5,10-diyl)di(ethan-1-one) (19)

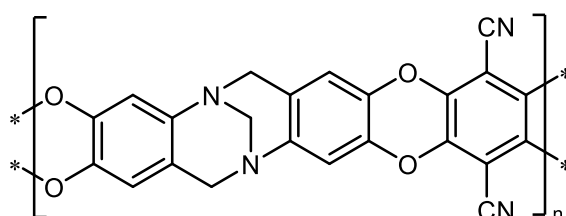


1,1'-[(4*bR*,9*bR*)-2,3,7,8-Tetramethoxy-5*H*,10*H*-4*b*,9*b*-2*H*-inden-2-one[3,2-*b*]indole-5,10-diyl]di(ethan-1-one) (**18**) (4.00 g, 7.77 mmol) was dissolved in DCM (30.00 mL) under a nitrogen atmosphere at 0 °C. Boron tribromide (4.43 mL, 6 molar equivalents) was added slowly, and the reaction was stirred at room temperature for 12 h. The reaction was quenched with water (50.00 mL) and the solid was collected by suction filtration and dried under vacuum for 12 h at 30 °C to give white powder (1.27 g, 35%). Mp: 167 – 169 °C, ν_{max} (cm⁻¹): 3169, 1649, 1685, 1201, 1026, ¹H NMR (500 MHz, DMSO-d₆) δ 8.18 (d, J = 6.0 Hz, 2H), 7.91 (dd, J = 6.3, 1.5 Hz, 1H), 7.89 (s, 2H), 7.55 (td, J = 6.3, 1.5 Hz, 1H), 7.47 – 7.40 (m, 2H), 6.86 (s, 2H), 6.47 (d, J = 6.5 Hz, 2H), 2.31 (s, 6H). ¹³C NMR (126 MHz, DMSO-

d₆) δ 194.41, 170.10, 169.85, 146.40, 146.38, 144.42, 140.88, 140.59, 134.12, 134.08, 133.39, 133.22, 130.77, 126.54, 125.42, 123.86, 121.54, 111.92, 111.80, 104.29, 102.82, 91.74, 89.48, 25.81, 25.78, TOF-HRMS (EI, m/z): calculated $C_{25}H_{18}N_2O_7$ 458.11 found: 453.08 [M^+] suggesting the catechol sample submitted for FT-IR has undergone oxidation to form its quinone counterpart, as the sample was submitted under ambient conditions.

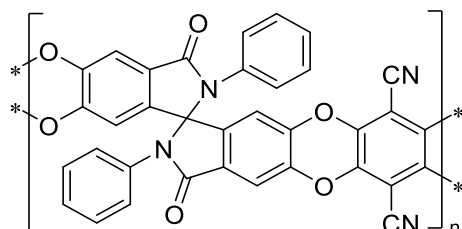
Polymer synthesis

PIM_TB



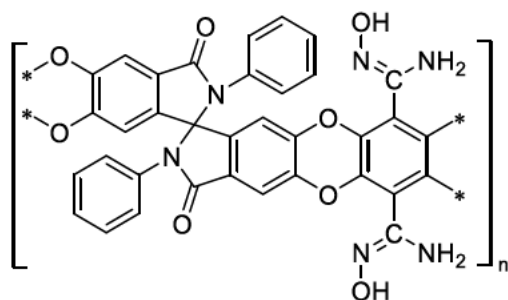
Tetramethoxy-TB (2.00 g, 6.98 mmol) and tetrafluorophthalonitrile (1.40 g, 6.98 mmol) was added to DMAc (42.5 – 60 ml) along with K_2CO_3 (7.72 g, 55.88 mmol) the reaction mixture was heated at 60 °C 72 hours. The yellow powder was collected by vacuum filtration (2.37 g, 83%). ν_{max} (cm^{-1}): 2966, 2241, 1446, 1259, 1207, 1147, MAS ^{13}C NMR (76 MHz) δ 145.33, 137.90, 134.52, 125.41, 113.40, 94.23, 65.93, 57.41, 35.67, N_2 adsorption (77 K) SA_{BET} = 42.06 $m^2 g^{-1}$, Total pore volume = 0.15 $cm^3 g^{-1}$ at (P/P_0 = 0.98), TGA: thermal degradation occurs at 450 °C.

SBL-PIM



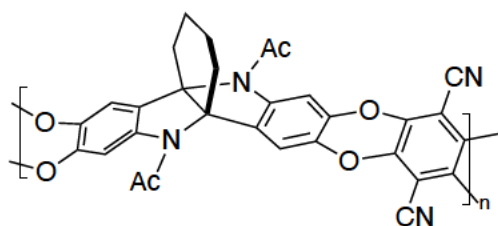
5,5',6,6'-Tetrahydroxy-2,2'-diphenyl-1,1'-spirobi[isindole]-3,3'-(2*H*,2'*H*)-dione **(11)** (1.40000 g, 3.00 mmol), and tetrafluoroterephthalonitrile (0.60058 g, 3.00 mmol) were added to DMF (25.00 – 40.00 ml) along with excess amount of potassium carbonate (3.31858 g, 8 molar eq). The reaction mixture was heated at 65°C under nitrogen atmosphere. The dark yellow powder was collected by filtration (1.20 g, 69%). ν_{max} (cm⁻¹): 2360, 1597, 1492, 1446, 1269, ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.31 (s, 1H), 7.52 (s, 3H), 7.42 – 7.17 (m, 5H), 7.12 (s, 4H), ¹³C NMR (126 MHz, CDCl₃) δ 206.95, 124.84, 77.22, 50.89, 30.92, 29.72, N₂ adsorption (77 K) S_{ABET} = 35.26 m² g⁻¹, Total pore volume = 0.05 cm³ g⁻¹ at (P/P₀ = 0.48), TGA: thermal degradation occurs at 500 °C.

SBL-AO-PIM



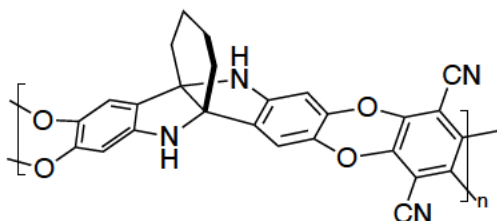
Hydroxylamine hydrochloride (3.00 g, 90.93 mmol) was added to the mixture of DMF and **SBL-PIM** (1.00 g, 1.07 mmol). The reaction mixture was refluxed for 24 h at 80 °C then the resulting yellow powder was filtered, washed with water, methanol and acetone (1.09 g, 98%). ν_{max} (cm⁻¹): 3365, 1597, 1492, 1446, 1294, ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.93 (s, 2H), 7.99 (d, *J* = 41.6 Hz, 2H), 7.86 – 6.27 (m, 14H), N₂ adsorption (77 K) S_{ABET} = 64.89 m² g⁻¹, Total pore volume = 0.16 cm³ g⁻¹ at (P/P₀ = 0.97), TGA: thermal degradation occurs at 500 °C.

BIDCH-Ac-PIM



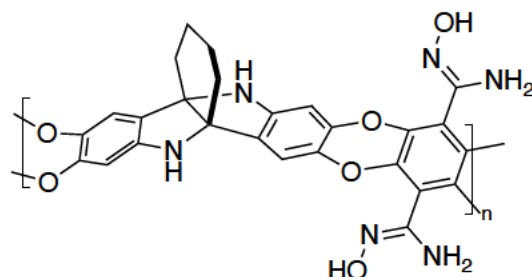
1,1'-[(4*bR*,9*bR*)-2,3,7,8-Tetrahydroxy-5*H*,10*H*-4*b*,9*b*-butanoindolo[3,2-*b*]indole-5,10-diyl]di(ethan-1-one) (**16**) (1.40000 g, 3.41 mmol), and tetrafluorophthalonitrile (0.68255 g, 3.41 mmol) were added to DMF (25.00 – 40.00 ml) along with an excess of potassium carbonate (3.77153 g, 8 molar eq) and stirred at 65°C for 72 hours. The final product was obtained by vacuum filtration to give a yellow powder (1.49 g, 82%). ν_{max} (cm⁻¹): 1651, 1444, 1375, 1267, 1195, ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.64 (s, 2H), 7.16 (s, 2H), 3.13 (d, *J* = 37.3 Hz, 1H), 2.64 (s, 4H), 2.27 (s, 4H), 1.45 (d, *J* = 63.5 Hz, 3H), 0.96 (s, 3H), MAS ¹³C NMR (76 MHz) δ 167.97, 139.79, 134.55, 125.55, 116.58, 104.90, 93.89, 77.32, 24.99, 20.23, 15.55, N₂ adsorption (77 K) *S*_{BET} = 415 m² g⁻¹, Total pore volume = 0.24 cm³ g⁻¹ at (*P*/*P*₀ = 0.98), TGA: thermal degradation occurs at 400 °C.

BIDCH-PIM



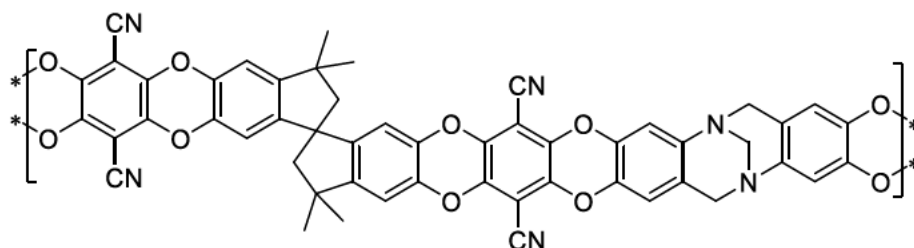
An excess amount of conc. HCl (10.00 mL, 272.47 mmol) and **BIDCH-Ac-PIM** (2.00 g, 3.77 mmol) was refluxed in EtOH (30.00 mL) for 2 hrs. The deprotected polymer was recovered by vacuum filtration and washed with copious amount of water to give a yellow powder (1.35 g, 80%). ν_{max} (cm⁻¹): 1651, 1444, 1375, 1267, 1195, ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.64 (s, 2H), 7.16 (s, 2H), 3.13 (d, *J* = 37.3 Hz, 1H), 2.64 (s, 4H), 2.27 (s, 4H), 1.45 (d, *J* = 63.5 Hz, 3H), 0.96 (s, 3H), MAS ¹³C NMR (76 MHz) δ 167.97, 139.79, 134.55, 125.55, 116.58, 104.90, 93.89, 77.32, 24.99, 20.23, 15.55, N₂ adsorption (77 K) *S*_{BET} = 24 m² g⁻¹, Total pore volume = 0.24 cm³ g⁻¹ at (*P*/*P*₀ = 0.98), TGA: thermal degradation occurs at 400 °C.

BIDCH-AO-PIM



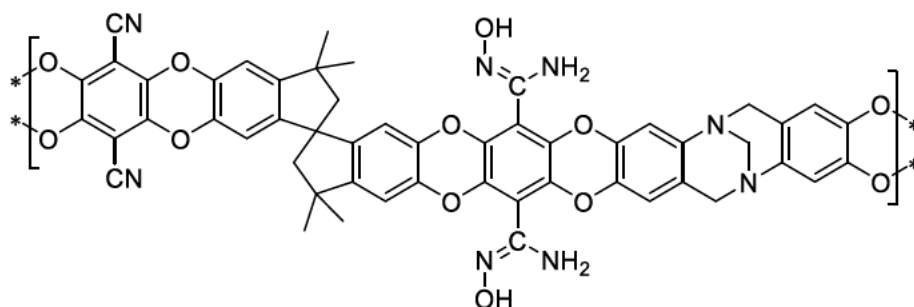
Hydroxylamine hydrochloride (3.00 g, 90.93 mmol) was added to a mixture of DMF and **BIDCH-PIM** (1.00 g, 2.24 mmol). The mixture was refluxed for 24 h at 80 °C. The resulting yellow powder obtained by filtration was washed with water and methanol (0.98 g, 86%). ν_{max} (cm⁻¹): 3369, 2995, 2781, 1647, 1436, 1261, 1195, ¹H NMR (500 MHz, DMSO-d₆) δ 8.53 (s, 4H), 8.00 (s, 1H), 7.78 (s, 1H), 7.56 (s, 1H), 7.08 (d, J = 73.1 Hz, 1H), 2.86 (s, 2H), 2.73 (d, J = 15.7 Hz, 2H), 2.46 (p, J = 1.8 Hz, 4H), N₂ adsorption (77 K) S_{BET} = 5 m² g⁻¹, Total pore volume = 0.19 cm³ g⁻¹ at (P/P₀ = 0.97), TGA: thermal degradation occurs at 450 °C.

TB_PIM-1



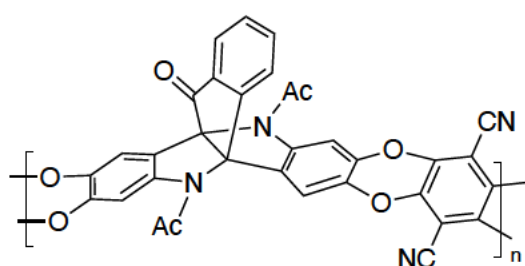
TB catechol (2.0000 g, 6.99 mmol), and **TFTTSBI** (4.6148g, 3.41 mmol) were added to DMF (82.6 – 132.3 mL) along with excess amount of potassium carbonate (7.7241 g, 8 molar eq) then stirred at 70 °C under nitrogen atmosphere. The yellow powder was obtained by filtration (4.37 g, 70%). ν_{max} (cm⁻¹): 2237, 1670, 1444, 1261, 1033, MAS ¹³C NMR (76 MHz) δ 146.97, 138.82, 124.72, 111.59, 94.11, 66.43, 57.58, 42.91, 29.83, N₂ adsorption (77 K) S_{BET} = 550 m² g⁻¹, Total pore volume = 0.38 cm³ g⁻¹ at (P/P₀ = 0.97), TGA: thermal degradation occurs at 450 °C.

TB_AO_PIM-1



Hydroxylamine hydrochloride (3.00 g, 90.93 mmol) was added to a mixture of DMF and **TB_PIM-1** (1.00 g, 1.11 mmol). The mixture was refluxed for 24 h at 80 °C, resulting in a yellow powder that was obtained by filtration and washed with water and methanol (0.89 g, 83%). ν_{max} (cm⁻¹): 3609, 2949, 873, MAS ¹³C NMR (76 MHz) δ 146.83, 138.79, 124.51, 111.51, 93.85, 66.39, 57.50, 42.83, 29.95, N₂ adsorption (77 K) S_{BET} = 451 m² g⁻¹, Total pore volume = 0.32 cm³ g⁻¹ at (P/P_o = 0.97), TGA: thermal degradation occurs at 490 °C.

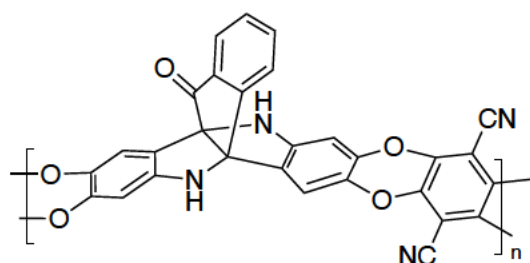
BIDNH-Ac-PIM



1,1'-[(4*bR*,9*bR*)-2,3,7,8-Tetrahydroxy-5*H*,10*H*-4*b*,9*b*-2*H*-inden-2-one[3,2-*b*]indole-5,10-diyl]di(ethan-1-one) (**19**) (1.7942 g, 3.91 mmol) and tetrafluoroterephthalonitrile (0.7831 g, 3.91 mmol) were added to DMF (32.2 – 51.5 mL) along with an excess of potassium carbonate (4.3211 g, 8 molar eq). The reaction mixture was stirred at 70 °C under nitrogen

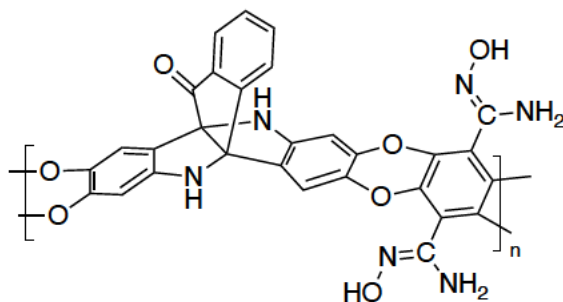
atmosphere. The yellow powder formed was collected by filtration (1.03 g, 45%). ν_{max} (cm^{-1}): 3192, 2922, 1660, 1483, 1319, 1257, 1149, MAS ^{13}C NMR (76 MHz, CDCl_3) δ 170.25, 137.22, 133.56, 118.00, 106.04, 94.27, 24.28, ^1H NMR (500 MHz, DMSO-d_6) δ 7.96 (s, 1H), 7.52 (dd, J = 26.2, 2.3 Hz, 2H), 7.22 (ddd, J = 8.9, 2.4, 1.2 Hz, 1H), 7.14 – 7.08 (m, 1H), 2.91 (s, 3H), 2.75 (s, 3H), N_2 adsorption (77 K) SA_{BET} = $10 \text{ m}^2 \text{ g}^{-1}$, Total pore volume = $0.041 \text{ cm}^3 \text{ g}^{-1}$ at (P/P_0 = 0.97), TGA: approximate 40% weight loss at 350 °C followed by thermal degradation occurs at 450 °C.

BIDNH-PIM



An excess amount of Conc HCl (10.00 mL, 272.47 mmol) and 1,1'-[(2,3,7,8-tetrahydroxy-5*H*,10*H*-4*b*,9*b*-2*H*-inden-2-one[3,2-*b*]indole-5,10-diyl]di(ethan-1-one) (**19**) (2.00 g, 3.46 mmol) was refluxed in EtOH (30.00 mL) for 2 h. The resulting yellow powder was collected under vacuum filtration and washed with water (1.53 g, 89%). ν_{max} (cm^{-1}): 3298, 2916, 1668, 1454, 1367, 1263, ^1H NMR (500 MHz, DMSO-d_6) δ 10.12 (d, J = 26.9 Hz, 2H), 7.58 – 7.45 (m, 2H), 7.19 – 7.03 (m, 4H), 6.42 – 6.25 (m, 2H), N_2 adsorption (77 K) SA_{BET} = $6 \text{ m}^2 \text{ g}^{-1}$, Total pore volume = $0.02 \text{ cm}^3 \text{ g}^{-1}$ at (P/P_0 = 0.97), TGA: approximate 40% weight loss at 290 °C followed by further ~ 37% weight loss at 450 °C and thermal degradation at 600 °C.

BIDNH-AO-PIM



Hydroxylamine hydrochloride (3.00 g, 90.93 mmol) was added to the mixture of DMF and **BIDNH-PIM** (1.00 g, 2.02 mmol). The mixture was refluxed for 24 h at 80 °C then the yellow powder obtained by filtration and was washed with water and methanol (0.93 g, 83%). ν_{max} (cm⁻¹): 3304, 1654, 1458, 1367, 1246, ¹H NMR (500 MHz, DMSO-d₆) δ 10.07 (d, J = 3.4 Hz, 1H), 10.00 (d, J = 6.1 Hz, 1H), 8.27 (d, J = 1.9 Hz, 1H), 8.22 – 8.17 (m, 1H), 8.15 – 8.08 (m, 1H), 7.96 (dd, J = 11.3, 2.5 Hz, 1H), 7.59 – 7.37 (m, 2H), 7.19 – 6.89 (m, 4H), 2.06 – 2.02 (m, 5H), N₂ adsorption (77 K) SA_{BET} = 1 m² g⁻¹, Total pore volume = 0.00035 cm³ g⁻¹ at (P/P_o = 0.45), TGA: approximate 45% weight loss at 300 °C followed by thermal degradation at 500 °C.

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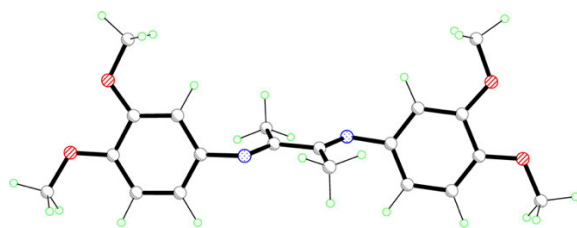
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Appendix

Crystal Data and Experimental

Crystal Data and Experimental

$R_1=1.66\%$



Experimental. Single orange block-shaped crystals of **NM24015** recrystallised from methanol by slow evaporation. A suitable crystal with dimensions $0.14 \times 0.07 \times 0.02 \text{ mm}^3$ was selected and mounted on a mitegen tip NVH oil on a Bruker D8 VENTURE diffractometer. The crystal was kept at a steady $T = 100.00 \text{ K}$ during data collection. The structure was solved with the ShelXS (Sheldrick, 2008) solution program using direct methods and by using Olex2 1.5-beta (Dolomanov et al., 2009) as the graphical interface. The model was refined with olex2.refine 1.5-beta (Bourhis et al., 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$, $M_r = 356.425$, orthorhombic, $Pna2_1$ (No. 33), $a = 18.5907(8) \text{ \AA}$, $b = 17.8710(7) \text{ \AA}$, $c = 5.4572(2) \text{ \AA}$, $a = b = c = 90^\circ$, $V = 1813.07(12) \text{ \AA}^3$, $T = 100.00 \text{ K}$, $Z = 4$, $Z' = 1$, $m(\text{Mo K}\alpha) = 0.091$, 117536 reflections measured, 6037 unique ($R_{\text{int}} = 0.0546$) which were used in all calculations. The final wR_2 was 0.0201 (all data) and R_1 was 0.0166 ($I \geq 2 \sigma(I)$).

Compound	NM24015
Formula	$\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$
$D_{\text{calc.}} / \text{g cm}^{-3}$	1.306
m / mm^{-1}	0.091
Formula Weight	356.425
Colour	orange
Shape	block-shaped
Size/ mm^3	$0.14 \times 0.07 \times 0.02$
T / K	100.00
Crystal System	orthorhombic
Flack Parameter	0.13(16)
Hooft Parameter	0.13(16)
Space Group	$Pna2_1$
$a / \text{\AA}$	18.5907(8)
$b / \text{\AA}$	17.8710(7)
$c / \text{\AA}$	5.4572(2)
$a / ^\circ$	90
$b / ^\circ$	90
$g / ^\circ$	90
$V / \text{\AA}^3$	1813.07(12)
Z	4
Z'	1
Wavelength/ $\text{\AA}$	0.71073
Radiation type	Mo K_α
$Q_{\text{min}} / ^\circ$	2.19
$Q_{\text{max}} / ^\circ$	31.55
Measured Refl's.	117536
Indep't Refl's	6037
Refl's $I \geq 2 \sigma(I)$	5590
R_{int}	0.0546
Parameters	451
Restraints	1
Largest Peak	0.1076
Deepest Hole	-0.1123
GooF	1.1214
wR_2 (all data)	0.0201
wR_2	0.0190
R_1 (all data)	0.0219
R_1	0.0166

Structure Quality Indicators

Reflections:	d min (MoK α) 2 Θ =63.1°	0.68	I/ σ (I)	52.2	R _{int} m=20.09	5.46%	Full 50.5°	99.9		
Refinement:	Shift	-0.000	Max Peak	0.1	Min Peak	-0.1	GooF	1.121	Hooft	.13(16)

An orange block-shaped crystal with dimensions $0.14 \times 0.07 \times 0.02$ mm³ was mounted on a mitegen tip NVH oil. Data were collected using a Bruker D8 VENTURE diffractometer equipped with an Oxford Cryosystems Cryostream 800 low-temperature device operating at $T = 100.00$ K.

Data were measured using f and w scans with Mo K α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program APEX5. The maximum resolution that was achieved was $Q = 31.55^\circ$ (0.68 Å).

The unit cell was refined using SAINT V8.40B (? , 2016) on 9741 reflections, 8% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using SAINT V8.40B (? , 2016). The final completeness is 99.95 % out to 31.55° in Q . SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. $wR_2(\text{int})$ was 0.1227 before and 0.0555 after correction. The Ratio of minimum to maximum transmission is 0.9599. The $I/2$ correction factor is Not present. The absorption coefficient m of this material is 0.091 mm⁻¹ at this wavelength ($\lambda = 0.71073$ Å) and the minimum and maximum transmissions are 0.716 and 0.746.

The structure was solved and the space group $Pna2_1$ (# 33) determined by the ShelXS (Sheldrick, 2008) structure solution program using direct methods and refined by full matrix least squares minimisation on F^2 using version of olex2.refine 1.5-beta (Bourhis et al., 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_olex2_refine_details: Refinement using NoSpherA2, an implementation of Non-SPHERical Atom-form-factors in Olex2. Please cite: F. Kleemiss et al. Chem. Sci. DOI 10.1039/D0SC05526C - 2021 NoSpherA2 implementation of HAR makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED) - not from spherical-atom form factors. The ED is calculated from a gaussian basis set single determinant SCF wavefunction - either Hartree-Fock or DFT using selected functionals - for a fragment of the crystal. This fragment can be embedded in an electrostatic crystal field by employing cluster charges or modelled using implicit solvation models, depending on the software used. The following options were used: SOFTWARE: ORCA 5.0 PARTITIONING: NoSpherA2 INT ACCURACY: Normal METHOD: R2SCAN BASIS SET: cc-pVTZ CHARGE: 0 MULTIPLICITY: 1 DATE: 2024-03-10_13-42-41

_exptl_absorpt_process_details: SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. $wR_2(\text{int})$ was 0.1227 before and 0.0555 after correction. The Ratio of minimum to maximum transmission is 0.9599. The $I/2$ correction factor is Not present.

There is a single formula unit in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1. The moiety formula is C₂₀ H₂₄ N₂ O₄.

The Flack parameter was refined to 0.13(16). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.13(16). This structure is in chiral space group, but there are no chiral atoms. Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be

inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

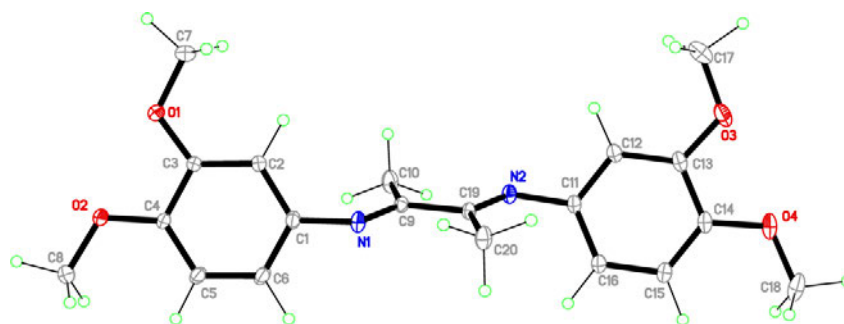
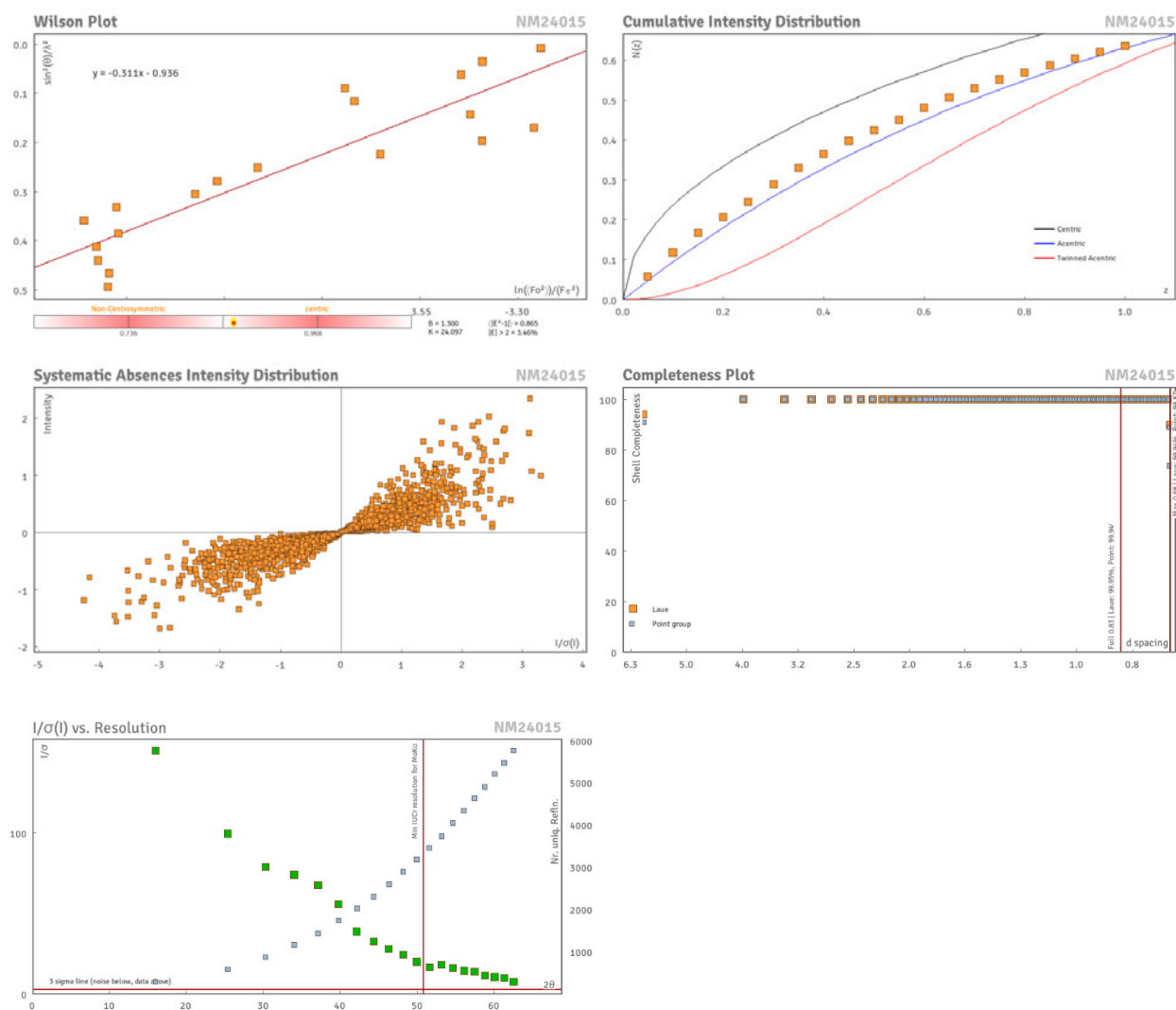


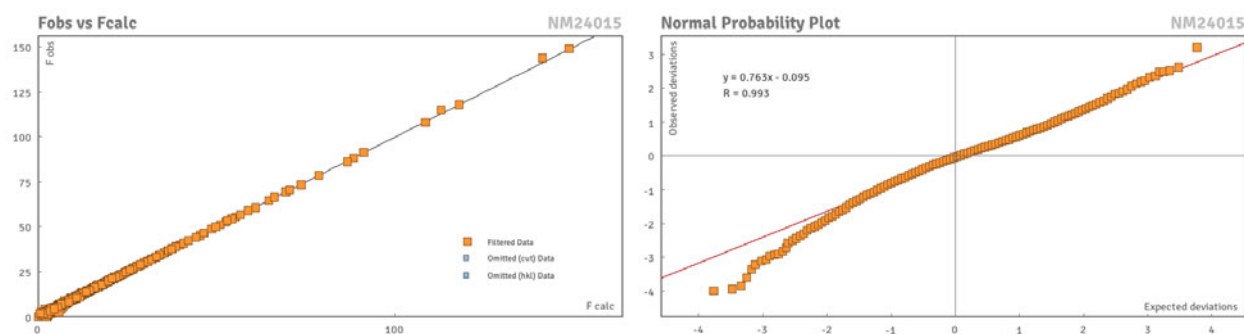
Figure 9 The molecular structure of NM24015. Displacement ellipsoids are at the 50% probability level.

_refine_special_details: NoSpherA2 refinement

Data Plots: Diffraction Data



Data Plots: Refinement and Data



Reflection Statistics

Total reflections (after filtering)	121287	Unique reflections	6037
Completeness	0.999	Mean I/s	39.52
hkl _{max} collected	(27, 26, 8)	hkl _{min} collected	(-27, -26, -8)
hkl _{max} used	(27, 26, 8)	hkl _{min} used	(0, 0, -8)
Lim d _{max} collected	100.0	Lim d _{min} collected	0.36
d _{max} used	9.3	d _{min} used	0.68
Friedel pairs	11951	Friedel pairs merged	0
Inconsistent equivalents	1	R _{int}	0.0546
R _{sigma}	0.0192	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(861, 1922, 2793, 4105, 4619, 3850, 2850, 1924, 844, 233, 28, 1)	Maximum multiplicity	39
Removed systematic absences	3751	Filtered off (Shel/OMIT)	0

Table 3: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **NM24015**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
O1	8121.57(16)	11582.80(15)	-1141.7(6)	23.12(7)
O2	7713.79(16)	12626.50(15)	1854.9(6)	22.15(7)
O3	4709.90(16)	5889.11(15)	-1705.7(5)	21.94(7)
O4	3785.19(16)	5802.10(15)	1841.8(6)	21.07(7)
N1	6462.62(17)	9805.37(16)	2647.3(6)	14.02(7)
N2	5268.48(17)	8468.83(17)	351.2(6)	12.90(7)
C1	6734.4(2)	10538.7(2)	2296.7(7)	13.32(8)
C2	7267.9(2)	10686.0(2)	544.4(8)	15.13(8)
C3	7587.3(2)	11389.7(2)	429.3(7)	14.93(8)
C4	7364.5(2)	11957.9(2)	2054.8(8)	15.35(8)
C5	6823.5(2)	11811.4(2)	3724.7(8)	19.64(9)
C6	6513.0(2)	11101.0(2)	3870.1(9)	18.81(9)
C7	8355.7(3)	11030.0(3)	-2829.9(10)	26.32(11)
C8	7608.0(3)	13146.0(3)	3788.2(10)	24.55(10)
C9	6000.6(2)	9521.9(2)	1180.5(7)	11.02(8)
C10	5692.0(3)	9906.0(2)	-1024.1(9)	18.52(9)
C11	4934.9(2)	7779.5(2)	928.8(7)	12.14(8)
C12	5020.2(2)	7174.9(2)	-687.0(8)	14.12(8)
C13	4645.7(2)	6512.5(2)	-295.0(7)	14.93(8)
C14	4152.6(2)	6459.7(2)	1668.6(8)	15.14(8)
C15	4075.1(2)	7059.1(2)	3264.6(8)	15.22(8)

Atom	x	y	z	U_{eq}
C16	4472.9(2)	7715.6(2)	2920.7(8)	13.94(8)
C17	5277.4(3)	5872.6(3)	-3471.8(9)	22.6(1)
C18	3299.0(3)	5732.2(3)	3843.0(10)	25.2(1)
C19	5733.78(19)	8752.2(2)	1811.3(8)	11.00(7)
C20	6028.5(3)	8381.3(2)	4060.5(8)	16.64(8)

Table 4: Anisotropic Displacement Parameters ($\times 10^4$) for **NM24015**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	27.37(16)	19.82(15)	22.18(16)	-11.21(12)	14.00(14)	-7.76(14)
O2	26.88(16)	15.58(13)	23.98(17)	-10.69(12)	13.34(15)	-6.48(13)
O3	30.82(17)	11.81(14)	23.18(18)	-1.35(12)	-2.88(14)	-3.56(12)
O4	22.68(15)	12.34(13)	28.19(18)	-6.21(11)	-4.44(14)	3.07(13)
N1	13.85(16)	11.28(14)	16.93(18)	-3.07(12)	-2.73(14)	2.52(13)
N2	14.70(16)	10.52(15)	13.47(17)	-2.36(12)	-2.80(14)	2.07(13)
C1	12.58(18)	10.75(17)	16.6(2)	-2.33(14)	0.72(16)	0.53(15)
C2	17.2(2)	12.81(19)	15.3(2)	-4.30(15)	3.21(17)	-2.57(16)
H2	44(3)	25(3)	37(4)	-9(3)	19(3)	-13(3)
C3	16.1(2)	13.72(19)	15.0(2)	-5.22(15)	4.87(17)	-3.23(17)
C4	16.25(19)	12.35(17)	17.4(2)	-4.93(14)	6.38(17)	-2.64(17)
C5	20.7(2)	12.1(2)	26.0(3)	-3.73(16)	12.81(19)	-2.04(19)
H5	57(4)	24(3)	56(4)	-8(3)	37(3)	-14(3)
C6	18.2(2)	11.93(18)	26.3(2)	-2.74(15)	10.7(2)	-0.24(19)
H6	47(4)	27(3)	49(4)	-6(3)	33(3)	-5(3)
C7	29.1(3)	26.5(3)	23.3(3)	-8.0(2)	13.2(2)	-10.1(2)
H7a	47(4)	44(4)	40(4)	-8(3)	8(3)	-13(3)
H7b	59(4)	59(4)	56(5)	-22(3)	46(4)	-18(3)
H7c	43(4)	41(3)	45(4)	0(3)	0(3)	-15(3)
C8	29.2(3)	18.2(2)	26.3(3)	-9.8(2)	11.1(2)	-8.6(2)
H8a	52(4)	37(3)	53(4)	-25(3)	16(4)	-17(3)
H8b	61(4)	52(4)	28(4)	-15(3)	4(3)	-2(3)
H8c	44(4)	37(3)	58(4)	0(3)	17(4)	-12(3)
C9	11.51(17)	9.04(17)	12.51(19)	-0.31(14)	0.12(15)	0.99(14)
C10	24.9(2)	13.0(2)	17.7(2)	-3.69(17)	-6.0(2)	5.08(18)
H10a	71(5)	58(4)	27(4)	3(3)	-1(4)	11(3)
H10b	75(4)	19(3)	45(4)	-8(3)	-26(4)	8(3)
H10c	33(4)	61(4)	62(5)	-20(3)	-29(4)	31(4)
C11	13.55(19)	9.69(17)	13.2(2)	-1.81(14)	-2.35(16)	1.21(14)
C12	16.5(2)	10.89(18)	15.0(2)	-1.08(14)	-1.81(17)	0.26(15)
H12	37(3)	32(3)	29(3)	-3(2)	8(3)	-2(3)
C13	18.1(2)	9.85(18)	16.9(2)	-0.90(15)	-4.18(17)	0.04(15)
C14	16.03(19)	10.34(17)	19.1(2)	-2.44(13)	-4.15(17)	2.57(17)
C15	15.6(2)	12.11(19)	17.9(2)	-2.36(15)	-0.62(17)	2.39(16)
H15	37(3)	31(3)	34(4)	-3(2)	15(3)	-1(3)
C16	15.41(19)	10.78(18)	15.6(2)	-1.80(15)	-0.64(16)	0.81(16)
H16	44(3)	20(3)	30(3)	-4(2)	9(3)	-5(3)
C17	28.6(3)	18.6(2)	20.6(3)	6.70(19)	-5.9(2)	-5.6(2)
H17a	74(4)	31(3)	49(4)	7(3)	6(3)	-20(3)
H17b	40(4)	47(4)	35(4)	15(3)	0(3)	12(3)
H17c	37(4)	62(4)	37(4)	9(3)	-15(3)	-7(3)
C18	24.8(3)	21.9(2)	28.9(3)	-11.1(2)	-4.9(2)	9.4(2)
H18a	37(3)	44(3)	62(4)	-2(3)	4(4)	10(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H18b	46(4)	44(4)	34(4)	-10(3)	-11(3)	10(3)
H18c	61(4)	46(4)	52(4)	-35(3)	-2(3)	13(4)
C19	11.42(17)	9.02(16)	12.56(18)	-0.50(13)	-0.74(16)	1.45(15)
C20	19.2(2)	12.9(2)	17.8(2)	-2.71(16)	-6.25(19)	4.84(18)
H20a	50(4)	51(4)	26(3)	9(3)	-5(3)	-1(3)
H20b	54(4)	22(3)	46(4)	3(3)	-16(3)	12(3)
H20c	27(3)	56(4)	55(4)	-13(3)	-20(3)	23(4)

Table 5: Bond Lengths in Å for **NM24015**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C3	1.3568(5)	C2	C3	1.3921(5)
O1	C7	1.4192(5)	C3	C4	1.4104(5)
O2	C4	1.3643(4)	C4	C5	1.3822(5)
O2	C8	1.4190(5)	C5	C6	1.3969(5)
O3	C13	1.3594(5)	C9	C10	1.4993(6)
O3	C17	1.4292(5)	C9	C19	1.5022(5)
O4	C14	1.3625(4)	C11	C12	1.4036(5)
O4	C18	1.4231(6)	C11	C16	1.3901(5)
N1	C1	1.4175(4)	C12	C13	1.3900(5)
N1	C9	1.2787(5)	C13	C14	1.4134(6)
N2	C11	1.4147(5)	C14	C15	1.3881(6)
N2	C19	1.2804(5)	C15	C16	1.3996(5)
C1	C2	1.4028(6)	C19	C20	1.4987(6)
C1	C6	1.3843(5)			

Table 6: Bond Angles in ° for **NM24015**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O1	C3	117.24(3)	C10	C9	N1	125.30(3)
C8	O2	C4	116.59(3)	C19	C9	N1	116.18(3)
C17	O3	C13	117.62(3)	C19	C9	C10	118.48(3)
C18	O4	C14	116.57(3)	C12	C11	N2	118.74(3)
C9	N1	C1	121.42(3)	C16	C11	N2	121.10(3)
C19	N2	C11	120.13(3)	C16	C11	C12	119.86(3)
C2	C1	N1	121.17(3)	C13	C12	C11	120.16(4)
C6	C1	N1	118.78(4)	C12	C13	O3	124.53(4)
C6	C1	C2	119.79(4)	C14	C13	O3	115.57(3)
C3	C2	C1	120.12(4)	C14	C13	C12	119.89(4)
C2	C3	O1	124.78(4)	C13	C14	O4	115.80(3)
C4	C3	O1	115.43(3)	C15	C14	O4	124.76(4)
C4	C3	C2	119.78(4)	C15	C14	C13	119.44(3)
C3	C4	O2	116.13(3)	C16	C15	C14	120.53(4)
C5	C4	O2	124.40(3)	C15	C16	C11	120.01(4)
C5	C4	C3	119.47(3)	C9	C19	N2	116.27(3)
C6	C5	C4	120.68(4)	C20	C19	N2	125.57(3)
C5	C6	C1	120.11(4)	C20	C19	C9	118.16(3)

Table 7: Torsion Angles in ° for **NM24015**.

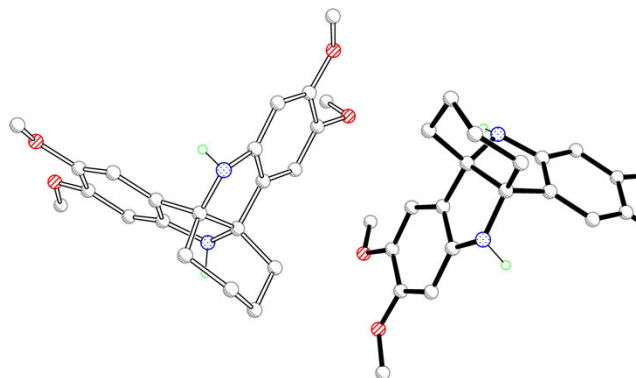
Atom	Atom	Atom	Atom	Angle/°
O1	C3	C2	C1	177.92(4)
O1	C3	C4	O2	-0.26(4)
O1	C3	C4	C5	-179.90(4)
O2	C4	C3	C2	178.76(3)
O2	C4	C5	C6	-177.49(4)
O3	C13	C12	C11	-177.74(4)
O3	C13	C14	O4	-2.38(4)
O3	C13	C14	C15	177.32(3)
O4	C14	C13	C12	176.98(3)
O4	C14	C15	C16	-179.41(4)
N1	C1	C2	C3	-172.38(4)
N1	C1	C6	C5	173.74(4)
N1	C9	C19	N2	179.67(3)
N1	C9	C19	C20	-0.41(4)
N2	C11	C12	C13	-173.97(3)
N2	C11	C16	C15	171.40(4)
N2	C19	C9	C10	1.90(4)
C1	C2	C3	C4	-1.01(5)
C1	C6	C5	C4	-1.46(5)
C2	C3	C4	C5	-0.87(5)
C3	C4	C5	C6	2.11(5)
C11	C12	C13	C14	2.96(4)
C11	C16	C15	C14	1.85(5)
C12	C13	C14	C15	-3.32(5)
C13	C14	C15	C16	0.92(4)

Atom	x	y	z	U_{eq}
H2	7438(2)	10242(2)	-662(10)	35.4(14)
H5	6641(3)	12240(2)	4970(11)	45.6(17)
H6	6100(3)	10986(3)	5216(10)	41.3(16)
H7a	7922(3)	10865(3)	-4062(10)	43.7(16)
H7b	8784(3)	11292(3)	-3883(11)	58(2)
H7c	8558(3)	10535(3)	-1888(10)	42.8(16)
H8a	7976(3)	13605(3)	3411(11)	47.2(17)
H8b	7730(3)	12889(3)	5565(11)	47.2(16)
H8c	7060(3)	13351(3)	3818(11)	46.3(15)
H10a	5995(3)	9759(3)	-2635(11)	51.9(17)
H10b	5724(3)	10514(3)	-814(10)	46.1(17)
H10c	5140(3)	9729(3)	-1317(11)	52.2(19)
H12	5379(2)	7238(2)	-2222(10)	32.3(14)
H15	3707(3)	7027(3)	4798(9)	33.9(14)
H16	4403(2)	8179(2)	4173(9)	31.2(13)

Atom	x	y	z	U_{eq}	
H17a	5259(3)	5324(3)	-4264(10)	51.1(17)	
H17b	5201(3)	6298(3)	-4853(10)	40.8(15)	
H17c	5798(3)	5970(3)	-2599(10)	45.4(16)	
H18a	2888(3)	6168(3)	3779(12)	47.8(16)	Table 8: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement
H18b	3583(3)	5760(3)	5584(11)	41.1(15)	
H18c	3049(3)	5189(3)	3637(11)	53.1(17)	
H20a	5725(3)	8542(3)	5679(11)	42.2(15)	
H20b	6008(3)	7779(2)	3885(10)	40.7(15)	
H20c	6582(3)	8567(3)	4377(11)	45.8(17)	

Parameters ($\text{\AA}^2 \times 10^3$) for **NM24015**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

$R_1=5.50\%$



Experimental. Single colourless prism-shaped crystals of **NM24014** recrystallised from methanol by slow evaporation. A suitable crystal with dimensions $0.51 \times 0.17 \times 0.09 \text{ mm}^3$ was selected and mounted on a MITIGEN holder in perfluoroether oil on a Bruker D8 VENTURE diffractometer. The crystal was kept at a steady $T = 100.00 \text{ K}$ during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Olex2 1.5-beta (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4$, $M_r = 382.45$, monoclinic, $P2_1$ (No. 4), $a = 12.0413(11) \text{ \AA}$, $b = 7.4153(7) \text{ \AA}$, $c = 21.418(2) \text{ \AA}$, $\beta = 102.051(4)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 1870.3(3) \text{ \AA}^3$, $T = 100.00 \text{ K}$, $Z = 4$, $Z' = 2$, $m(\text{MoK}\alpha) = 0.094$, 88040 reflections measured, 16045 unique ($R_{\text{int}} = 0.0716$) which were used in all calculations. The final wR_2 was 0.1156 (all data) and R_1 was 0.0550 ($I \geq 2 \sigma(I)$).

Compound	NM24014
Formula	$\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4$
$D_{\text{calc.}}/\text{g cm}^{-3}$	1.358
m/mm^{-1}	0.094
Formula Weight	382.45
Colour	colourless
Shape	prism-shaped
Size/ mm^3	$0.51 \times 0.17 \times 0.09$
T/K	100.00
Crystal System	monoclinic
Flack Parameter	0.2(3)
Hooft Parameter	0.3(3)
Space Group	$P2_1$
$a/\text{\AA}$	12.0413(11)
$b/\text{\AA}$	7.4153(7)
$c/\text{\AA}$	21.418(2)
$\alpha/^\circ$	90
$\beta/^\circ$	102.051(4)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	1870.3(3)
Z	4
Z'	2
Wavelength/ $\text{\AA}$	0.71073
Radiation type	$\text{MoK}\alpha$
$Q_{\text{min}}/^\circ$	2.154
$Q_{\text{max}}/^\circ$	34.987
Measured Refl's.	88040
Indep't Refl's	16045
Refl's $I \geq 2 \sigma(I)$	13042
R_{int}	0.0716
Parameters	529
Restraints	1
Largest Peak	0.410
Deepest Hole	-0.317
GooF	1.081
wR_2 (all data)	0.1156
wR_2	0.1044
R_1 (all data)	0.0741
R_1	0.0550

Structure Quality Indicators

Reflections:	d min (MoK α) 2 Θ =70.0°	0.62	I/ σ (I)	14.7	R _{int} m=5.49	7.16%	Full 50.5° 99% to 70.0°	99.9		
Refinement:	Shift	0.000	Max Peak	0.4	Min Peak	-0.3	Goof	1.081	Hoof	.3(3)

A colourless prism-shaped crystal with dimensions $0.51 \times 0.17 \times 0.09$ mm³ was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using a Bruker D8 VENTURE diffractometer equipped with an Oxford Cryosystems Cryostream 800 low-temperature device operating at $T = 100.00$ K.

Data were measured using f and w scans with MoK α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program APEX5. The maximum resolution that was achieved was $Q = 34.987^\circ$ (0.62 Å).

The unit cell was refined using SAINT V8.40B (, 2016) on 9958 reflections, 11% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using SAINT V8.40B (, 2016). The final completeness is 99.90 % out to 34.987° in Q . SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. $wR_2(\text{int})$ was 0.1342 before and 0.0695 after correction. The Ratio of minimum to maximum transmission is 0.9517. The $I/2$ correction factor is Not present. The absorption coefficient m of this material is 0.094 mm⁻¹ at this wavelength ($\lambda = 0.71073$ Å) and the minimum and maximum transmissions are 0.710 and 0.746.

The structure was solved and the space group $P2_1$ (# 4) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

_refine_special_details: N-bound H atoms located in a difference map and freely refined.

_exptl_absorpt_process_details: SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. $wR_2(\text{int})$ was 0.1342 before and 0.0695 after correction. The Ratio of minimum to maximum transmission is 0.9517. The $I/2$ correction factor is Not present.

The value of Z' is 2. This means that there are two independent molecules in the asymmetric unit. The moiety formula is C₂₂ H₂₆ N₂ O₄.

The Flack parameter was refined to 0.2(3). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.3(3). The chiral atoms in this structure are: C7(S), C12(S), C57(S), C62(S). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

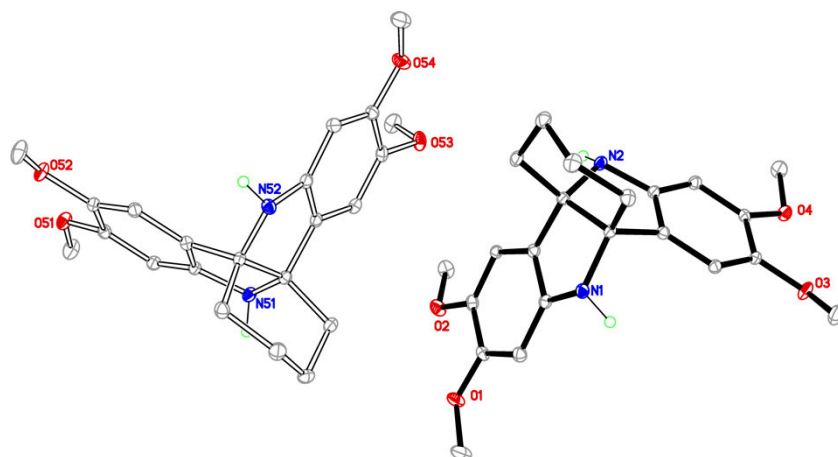
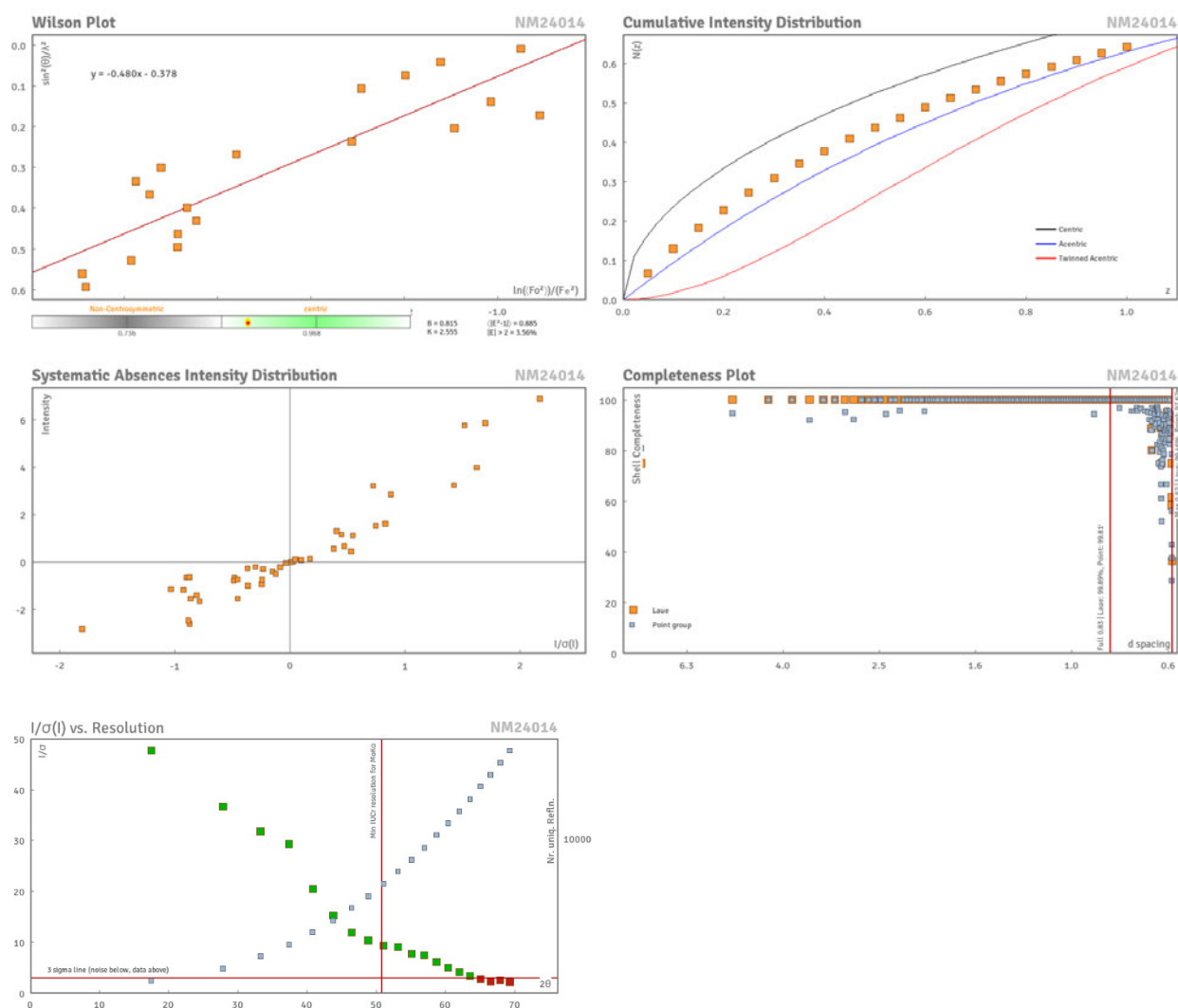
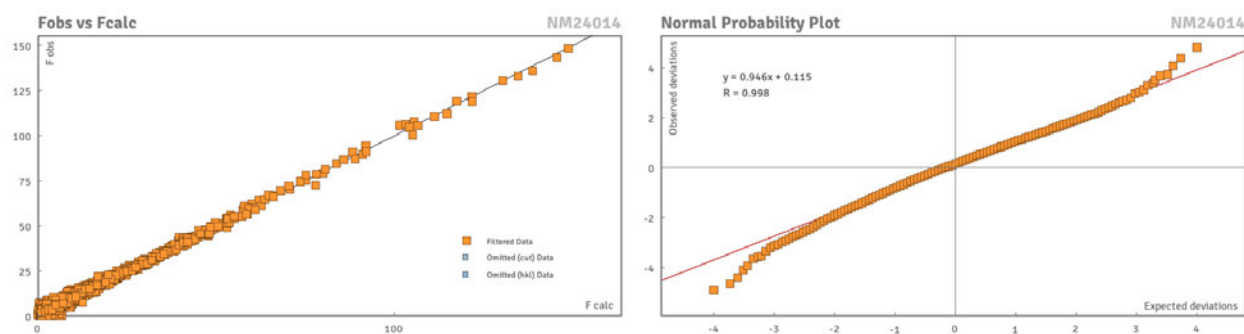


Figure 10 The asymmetric unit of NM24014. Displacement ellipsoids are at the 50% probability level and C-bound H atoms are not shown.

Data Plots: Diffraction Data



Data Plots: Refinement and Data



Reflection Statistics

Total reflections (after filtering)	88087	Unique reflections	16045
Completeness	0.976	Mean I/s	13.46
hkl _{max} collected	(18, 11, 34)	hkl _{min} collected	(-19, -11, -34)
hkl _{max} used	(18, 11, 34)	hkl _{min} used	(-19, -11, 0)
Lim d _{max} collected	100.0	Lim d _{min} collected	0.36
d _{max} used	9.46	d _{min} used	0.62
Friedel pairs	11969	Friedel pairs merged	0
Inconsistent equivalents	3	R _{int}	0.0716
R _{sigma}	0.0681	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(6837, 5405, 4319, 4505, 3485, 2144, 812, 373, 54, 2)	Maximum multiplicity	17
Removed systematic absences	47	Filtered off (Shel/OMIT)	0

Table 9: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **NM24014**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
O1	4361.6(11)	4452(2)	9396.8(7)	14.7(3)
O2	4548.9(11)	2070.0(19)	8539.6(7)	15.1(3)
O3	11573.7(11)	5801.4(19)	10195.8(6)	13.8(3)
O4	11897.4(11)	2963.4(19)	9567.1(6)	12.7(3)
N1	7410.2(12)	8003(2)	8761.7(7)	10.0(3)
N2	8591.3(13)	4665(2)	7882.9(7)	10.3(3)
C1	6694.6(14)	6516(2)	8775.7(8)	9.6(3)
C2	5892.4(15)	6314(2)	9157.0(9)	11.4(3)
C3	5188.2(14)	4806(2)	9059.8(9)	11.0(3)
C4	5285.6(15)	3510(2)	8591.8(9)	11.1(3)
C5	6082.4(14)	3748(2)	8209.6(8)	9.5(3)
C6	6796.1(14)	5253(2)	8312.9(8)	9.5(3)
C7	7653.2(14)	5927(2)	7934.5(8)	9.2(3)
C8	7040.5(15)	6556(3)	7268.9(8)	11.9(3)
C9	7715.0(15)	7989(3)	6992.9(8)	13.9(3)
C10	7935.5(16)	9614(3)	7443.3(9)	14.4(3)
C11	8705.8(15)	9067(3)	8075.9(9)	12.3(3)
C12	8268.1(14)	7437(2)	8400.1(8)	8.7(3)
C13	9255.6(14)	6371(2)	8782.7(8)	9.0(3)
C14	9981.2(14)	6788(2)	9360.1(8)	9.9(3)
C15	10853.2(14)	5597(2)	9609.8(8)	9.5(3)

Atom	x	y	z	U_{eq}
C16	11022.8(14)	4029(2)	9268.9(8)	9.8(3)
C17	10303.8(14)	3619(2)	8684.3(8)	10.6(3)
C18	9409.8(14)	4805(2)	8457.3(8)	9.5(3)
C19	4167.9(17)	5808(3)	9833.3(10)	19.1(4)
C20	4924.0(16)	445(3)	8295.5(10)	16.1(4)
C21	11813.8(16)	7613(3)	10405.2(10)	17.2(4)
C22	12191.5(16)	1476(3)	9210.0(10)	16.4(4)
O51	-2056.3(11)	2779.7(19)	5418.5(6)	13.9(3)
O52	-1711.7(11)	5606.2(19)	4797.2(6)	13.7(3)
O53	5304.4(11)	2033.0(19)	6742.4(7)	15.3(3)
O54	5523.0(12)	4294(2)	5799.1(7)	17.5(3)
N51	1158.4(13)	4495(2)	7158.5(7)	11.2(3)
N52	2384.6(12)	7875(2)	6310.2(7)	10.5(3)
C51	337.0(14)	4720(2)	6581.2(8)	9.9(3)
C52	-540.9(15)	3519(3)	6336.1(8)	11.0(3)
C53	-1208.6(15)	3882(2)	5733.8(9)	10.9(3)
C54	-1011.2(14)	5434(3)	5390.6(8)	10.6(3)
C55	-143.8(14)	6624(3)	5648.4(9)	11.0(3)
C56	526.4(14)	6246(2)	6248.8(8)	10.4(3)
C57	1484.8(14)	7351(2)	6647.4(8)	9.6(3)
C58	1016.5(15)	8988(3)	6945.1(9)	12.5(3)
C59	1772.6(16)	9588(3)	7576.7(9)	15.1(3)
C60	1975.0(16)	8023(3)	8053.8(9)	14.6(3)
C61	2629.1(15)	6515(3)	7804.7(8)	12.5(3)
C62	2056.8(14)	5853(2)	7133.8(8)	9.5(3)
C63	2960.9(14)	5161(2)	6793.8(8)	10.4(3)
C64	3692.1(15)	3703(2)	6938.5(8)	11.1(3)
C65	4542.9(15)	3449(3)	6596.9(9)	12.0(3)
C66	4663.9(15)	4667(3)	6111.3(9)	12.4(3)
C67	3949.2(15)	6167(3)	5975.2(9)	12.2(3)
C68	3110.0(14)	6395(2)	6330.2(8)	10.4(3)
C69	-2353.9(17)	1276(3)	5766.8(10)	18.1(4)
C70	-1715.6(17)	7323(3)	4495.2(10)	19.4(4)
C71	4860.3(17)	373(3)	6462.5(10)	18.8(4)
C72	5790.3(17)	5677(3)	5388.6(10)	22.0(4)

Table 10: Anisotropic Displacement Parameters ($\times 10^4$) for **NM24014**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	13.8(6)	14.7(6)	18.2(6)	-2.5(5)	9.2(5)	-2.3(5)
O2	12.6(6)	12.2(6)	21.7(7)	-3.7(5)	6.3(5)	-4.7(5)
O3	15.5(6)	12.6(6)	10.5(6)	-2.4(5)	-3.5(5)	1.3(5)
O4	11.3(5)	12.6(6)	12.8(6)	-2.1(5)	-0.6(4)	4.9(5)
N1	9.0(6)	10.1(7)	10.6(6)	-1.6(5)	1.4(5)	-1.1(5)
N2	10.1(6)	10.8(7)	9.3(6)	-3.1(6)	0.4(5)	0.5(6)
C1	9.6(7)	9.4(7)	9.3(7)	1.1(6)	0.5(6)	0.2(6)
C2	11.0(7)	10.4(8)	12.8(8)	-0.6(6)	2.3(6)	1.2(6)
C3	8.5(7)	11.1(8)	13.4(8)	1.9(6)	2.7(6)	1.0(6)
C4	9.5(7)	9.5(7)	13.8(8)	0.6(6)	0.9(6)	-0.9(6)
C5	9.0(7)	9.2(7)	9.7(7)	-0.7(6)	0.8(6)	0.6(6)
C6	9.2(7)	9.7(7)	9.2(7)	1.1(6)	1.2(5)	0.6(6)
C7	9.5(7)	9.9(7)	8.0(7)	-0.4(6)	1.1(5)	-0.4(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C8	10.8(7)	14.4(8)	9.3(7)	1.1(6)	-0.6(6)	-0.5(7)
C9	13.5(7)	17.3(9)	10.0(7)	3.2(7)	0.5(6)	-2.0(7)
C10	16.2(8)	12.5(8)	13.9(8)	3.9(7)	1.8(6)	-0.6(7)
C11	11.4(7)	12.0(8)	12.9(8)	2.0(6)	1.5(6)	-1.1(6)
C12	9.2(7)	8.8(7)	7.8(7)	-0.4(6)	1.1(5)	-0.5(6)
C13	8.7(7)	9.1(7)	9.2(7)	0.8(6)	1.7(5)	0.9(6)
C14	9.8(7)	9.7(8)	10.1(7)	-1.5(6)	1.9(6)	-0.2(6)
C15	8.3(6)	11.7(8)	7.8(7)	-0.1(6)	0.3(5)	0.4(6)
C16	8.0(7)	10.8(8)	10.8(7)	-0.1(6)	2.1(6)	0.7(6)
C17	10.8(7)	10.3(8)	10.3(7)	-1.8(6)	1.6(6)	0.6(6)
C18	9.4(7)	11.0(8)	7.8(7)	-0.4(6)	1.4(5)	-1.7(6)
C19	19.4(9)	19.6(9)	22.0(9)	-4.7(8)	12.6(7)	-2.0(8)
C20	15.7(8)	9.6(8)	22.7(9)	-1.1(7)	3.3(7)	-0.6(7)
C21	13.8(8)	17.0(9)	18.4(9)	-7.0(7)	-2.1(7)	0.7(7)
C22	15.1(8)	13.9(9)	19.1(9)	-3.7(7)	1.2(7)	6.5(7)
O51	14.0(6)	13.4(6)	12.7(6)	1.2(5)	-0.7(5)	-5.8(5)
O52	14.3(6)	13.9(6)	10.4(6)	2.7(5)	-2.8(5)	-3.1(5)
O53	11.3(6)	11.9(6)	20.4(7)	-2.5(5)	-1.4(5)	3.7(5)
O54	14.8(6)	20.3(7)	19.6(7)	-1.7(6)	8.4(5)	3.6(6)
N51	11.2(6)	13.2(7)	8.8(6)	1.1(6)	1.0(5)	-3.4(6)
N52	9.4(6)	10.4(7)	11.8(7)	1.5(6)	2.6(5)	1.0(6)
C51	10.0(7)	10.7(8)	8.8(7)	0.5(6)	1.4(6)	1.1(6)
C52	11.2(7)	11.2(8)	10.8(7)	1.3(6)	2.7(6)	-1.7(6)
C53	9.5(7)	10.9(8)	12.3(7)	0.0(6)	2.4(6)	-1.6(6)
C54	9.2(7)	12.7(8)	9.5(7)	0.7(6)	1.0(6)	0.6(6)
C55	10.5(7)	11.8(8)	10.9(7)	1.6(6)	2.6(6)	0.1(6)
C56	8.9(7)	11.6(8)	10.7(7)	0.1(6)	1.6(6)	0.4(6)
C57	8.8(7)	10.3(8)	9.0(7)	0.3(6)	0.5(5)	-0.2(6)
C58	11.6(7)	11.3(8)	14.0(8)	-0.4(7)	1.5(6)	1.6(6)
C59	15.7(8)	12.9(8)	15.9(8)	-4.2(7)	1.5(6)	2.1(7)
C60	15.9(8)	16.8(9)	10.8(8)	-3.8(7)	2.3(6)	2.4(7)
C61	12.2(7)	14.8(8)	9.6(7)	-1.4(7)	0.0(6)	0.8(7)
C62	10.3(7)	8.9(7)	9.0(7)	-0.5(6)	1.3(6)	-0.2(6)
C63	9.2(7)	11.4(8)	9.8(7)	-1.5(6)	0.0(6)	-0.2(6)
C64	11.9(7)	10.2(8)	10.1(7)	0.1(6)	-0.4(6)	-0.8(6)
C65	9.7(7)	10.9(8)	14.0(8)	-1.7(6)	-0.9(6)	1.7(6)
C66	9.8(7)	14.7(8)	12.4(8)	-3.6(7)	1.5(6)	-0.1(7)
C67	11.8(7)	14.1(9)	10.9(8)	-0.8(6)	2.9(6)	-0.8(6)
C68	9.3(7)	11.0(8)	10.1(7)	-1.1(6)	0.1(6)	0.0(6)
C69	18.4(9)	15.4(9)	18.2(9)	3.6(7)	-1.2(7)	-7.2(7)
C70	18.3(9)	18.4(10)	18.0(9)	8.8(8)	-4.1(7)	-2.9(8)
C71	21.3(9)	13.4(8)	19.5(9)	-4.0(8)	-0.8(7)	3.3(8)
C72	18.8(9)	31.0(12)	18.0(9)	4.3(9)	8.2(7)	4.1(9)

Table 11: Bond Lengths in Å for **NM24014**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C3	1.371(2)	O4	C16	1.364(2)
O1	C19	1.425(2)	O4	C22	1.428(2)
O2	C4	1.378(2)	N1	C1	1.404(2)
O2	C20	1.424(2)	N1	C12	1.476(2)
O3	C15	1.377(2)	N2	C7	1.489(2)
O3	C21	1.427(2)	N2	C18	1.410(2)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.397(2)	O54	C66	1.372(2)
C1	C6	1.387(2)	O54	C72	1.430(3)
C2	C3	1.392(3)	N51	C51	1.423(2)
C3	C4	1.411(3)	N51	C62	1.487(2)
C4	C5	1.396(2)	N52	C57	1.474(2)
C5	C6	1.398(2)	N52	C68	1.398(2)
C6	C7	1.524(2)	C51	C52	1.398(2)
C7	C8	1.535(2)	C51	C56	1.381(3)
C7	C12	1.578(2)	C52	C53	1.396(2)
C8	C9	1.529(3)	C53	C54	1.412(3)
C9	C10	1.532(3)	C54	C55	1.391(2)
C10	C11	1.528(3)	C55	C56	1.397(2)
C11	C12	1.540(2)	C56	C57	1.523(2)
C12	C13	1.518(2)	C57	C58	1.532(3)
C13	C14	1.392(2)	C57	C62	1.579(2)
C13	C18	1.387(2)	C58	C59	1.531(3)
C14	C15	1.391(2)	C59	C60	1.532(3)
C15	C16	1.410(2)	C60	C61	1.526(3)
C16	C17	1.399(2)	C61	C62	1.539(2)
C17	C18	1.396(2)	C62	C63	1.520(2)
O51	C53	1.370(2)	C63	C64	1.388(2)
O51	C69	1.428(2)	C63	C68	1.389(2)
O52	C54	1.377(2)	C64	C65	1.390(2)
O52	C70	1.427(2)	C65	C66	1.407(3)
O53	C65	1.386(2)	C66	C67	1.400(3)
O53	C71	1.424(2)	C67	C68	1.396(2)

Table 12: Bond Angles in ° for **NM24014**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	O1	C19	116.51(15)	C6	C7	C8	110.26(14)
C4	O2	C20	115.95(14)	C6	C7	C12	100.21(13)
C15	O3	C21	115.96(15)	C8	C7	C12	116.26(15)
C16	O4	C22	116.75(14)	C9	C8	C7	112.29(14)
C1	N1	C12	106.75(14)	C8	C9	C10	109.83(15)
C18	N2	C7	106.99(14)	C11	C10	C9	110.04(16)
C2	C1	N1	126.81(16)	C10	C11	C12	113.98(15)
C6	C1	N1	111.64(15)	N1	C12	C7	104.23(13)
C6	C1	C2	121.34(17)	N1	C12	C11	110.89(15)
C3	C2	C1	118.20(17)	N1	C12	C13	114.84(14)
O1	C3	C2	124.15(17)	C11	C12	C7	115.57(14)
O1	C3	C4	114.87(16)	C13	C12	C7	100.54(14)
C2	C3	C4	120.98(16)	C13	C12	C11	110.42(14)
O2	C4	C3	115.97(15)	C14	C13	C12	129.77(16)
O2	C4	C5	124.04(16)	C18	C13	C12	109.68(15)
C5	C4	C3	119.97(16)	C18	C13	C14	120.51(16)
C4	C5	C6	118.88(16)	C15	C14	C13	118.95(16)
C1	C6	C5	120.60(16)	O3	C15	C14	124.20(16)
C1	C6	C7	109.23(15)	O3	C15	C16	115.52(15)
C5	C6	C7	129.79(16)	C14	C15	C16	120.25(15)
N2	C7	C6	116.25(15)	O4	C16	C15	114.60(15)
N2	C7	C8	110.33(14)	O4	C16	C17	124.48(16)
N2	C7	C12	103.29(13)	C17	C16	C15	120.87(16)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C18	C17	C16	117.58(16)	C56	C57	C58	110.96(14)
C13	C18	N2	110.93(15)	C56	C57	C62	99.58(14)
C13	C18	C17	121.78(16)	C58	C57	C62	115.49(14)
C17	C18	N2	127.24(16)	C59	C58	C57	113.29(15)
C53	O51	C69	116.77(14)	C58	C59	C60	110.60(16)
C54	O52	C70	116.40(15)	C61	C60	C59	110.09(15)
C65	O53	C71	112.81(14)	C60	C61	C62	113.39(15)
C66	O54	C72	116.40(16)	N51	C62	C57	106.22(13)
C51	N51	C62	105.59(14)	N51	C62	C61	111.74(14)
C68	N52	C57	107.24(14)	N51	C62	C63	112.83(15)
C52	C51	N51	125.83(16)	C61	C62	C57	116.10(15)
C56	C51	N51	112.61(16)	C63	C62	C57	100.29(13)
C56	C51	C52	121.46(16)	C63	C62	C61	109.23(14)
C53	C52	C51	117.93(17)	C64	C63	C62	129.82(16)
O51	C53	C52	124.50(16)	C64	C63	C68	120.14(16)
O51	C53	C54	114.74(15)	C68	C63	C62	109.43(15)
C52	C53	C54	120.71(16)	C63	C64	C65	119.38(17)
O52	C54	C53	114.76(15)	O53	C65	C64	120.64(17)
O52	C54	C55	124.90(16)	O53	C65	C66	119.11(16)
C55	C54	C53	120.32(16)	C64	C65	C66	120.23(16)
C54	C55	C56	118.67(16)	O54	C66	C65	115.84(16)
C51	C56	C55	120.89(16)	O54	C66	C67	123.50(17)
C51	C56	C57	109.83(15)	C67	C66	C65	120.65(16)
C55	C56	C57	129.23(16)	C68	C67	C66	117.80(17)
N52	C57	C56	114.56(14)	C63	C68	N52	111.47(15)
N52	C57	C58	111.52(15)	C63	C68	C67	121.72(16)
N52	C57	C62	104.17(13)	C67	C68	N52	126.66(17)

Table 13: Torsion Angles in ° for **NM24014**.

Atom	Atom	Atom	Atom	Angle/°
O1	C3	C4	O2	-0.4(2)
O1	C3	C4	C5	178.65(16)
O2	C4	C5	C6	-179.14(16)
O3	C15	C16	O4	-1.4(2)
O3	C15	C16	C17	176.36(16)
O4	C16	C17	C18	176.74(16)
N1	C1	C2	C3	174.15(16)
N1	C1	C6	C5	-174.26(15)
N1	C1	C6	C7	-0.7(2)
N1	C12	C13	C14	-53.0(2)
N1	C12	C13	C18	129.39(16)
N2	C7	C8	C9	-76.92(19)
N2	C7	C12	N1	-146.47(14)
N2	C7	C12	C11	91.57(16)
N2	C7	C12	C13	-27.27(16)
C1	N1	C12	C7	27.37(17)
C1	N1	C12	C11	152.36(14)
C1	N1	C12	C13	-81.62(18)
C1	C2	C3	O1	-179.51(16)
C1	C2	C3	C4	0.4(3)
C1	C6	C7	N2	127.28(16)
C1	C6	C7	C8	-106.23(17)

Atom	Atom	Atom	Atom	Angle/°
C1	C6	C7	C12	16.84(17)
C2	C1	C6	C5	0.9(3)
C2	C1	C6	C7	174.48(16)
C2	C3	C4	O2	179.69(16)
C2	C3	C4	C5	-1.3(3)
C3	C4	C5	C6	1.9(3)
C4	C5	C6	C1	-1.7(3)
C4	C5	C6	C7	-173.84(17)
C5	C6	C7	N2	-59.9(2)
C5	C6	C7	C8	66.6(2)
C5	C6	C7	C12	-170.32(17)
C6	C1	C2	C3	-0.2(3)
C6	C7	C8	C9	153.34(15)
C6	C7	C12	N1	-26.20(16)
C6	C7	C12	C11	-148.15(14)
C6	C7	C12	C13	93.01(14)
C7	N2	C18	C13	-17.61(19)
C7	N2	C18	C17	164.87(17)
C7	C8	C9	C10	-58.0(2)
C7	C12	C13	C14	-164.21(18)
C7	C12	C13	C18	18.18(17)
C8	C7	C12	N1	92.56(17)
C8	C7	C12	C11	-29.4(2)
C8	C7	C12	C13	-148.23(14)
C8	C9	C10	C11	65.22(19)
C9	C10	C11	C12	-54.1(2)
C10	C11	C12	N1	-82.13(18)
C10	C11	C12	C7	36.2(2)
C10	C11	C12	C13	149.42(15)
C11	C12	C13	C14	73.3(2)
C11	C12	C13	C18	-104.35(17)
C12	N1	C1	C2	167.69(17)
C12	N1	C1	C6	-17.49(19)
C12	C7	C8	C9	40.2(2)
C12	C13	C14	C15	-178.29(17)
C12	C13	C18	N2	-1.4(2)
C12	C13	C18	C17	176.29(16)
C13	C14	C15	O3	-175.37(16)
C13	C14	C15	C16	2.5(3)
C14	C13	C18	N2	-179.25(16)
C14	C13	C18	C17	-1.6(3)
C14	C15	C16	O4	-179.39(16)
C14	C15	C16	C17	-1.7(3)
C15	C16	C17	C18	-0.7(3)
C16	C17	C18	N2	179.64(16)
C16	C17	C18	C13	2.4(3)
C18	N2	C7	C6	-80.50(18)
C18	N2	C7	C8	153.04(15)
C18	N2	C7	C12	28.13(17)
C18	C13	C14	C15	-0.9(3)
C19	O1	C3	C2	5.4(3)
C19	O1	C3	C4	-174.53(17)
C20	O2	C4	C3	-153.78(16)
C20	O2	C4	C5	27.2(3)
C21	O3	C15	C14	-31.2(2)

Atom	Atom	Atom	Atom	Angle/°
C21	O3	C15	C16	150.87(16)
C22	O4	C16	C15	-172.73(16)
C22	O4	C16	C17	9.6(3)
O51	C53	C54	O52	0.8(2)
O51	C53	C54	C55	-177.52(16)
O52	C54	C55	C56	-177.82(16)
O53	C65	C66	O54	2.5(3)
O53	C65	C66	C67	-176.50(16)
O54	C66	C67	C68	-179.73(17)
N51	C51	C52	C53	-174.47(16)
N51	C51	C56	C55	175.40(16)
N51	C51	C56	C57	-6.9(2)
N51	C62	C63	C64	-60.2(2)
N51	C62	C63	C68	128.91(16)
N52	C57	C58	C59	-79.81(19)
N52	C57	C62	N51	-142.88(14)
N52	C57	C62	C61	92.23(17)
N52	C57	C62	C63	-25.27(16)
C51	N51	C62	C57	21.74(18)
C51	N51	C62	C61	149.28(15)
C51	N51	C62	C63	-87.18(17)
C51	C52	C53	O51	176.32(16)
C51	C52	C53	C54	-1.1(3)
C51	C56	C57	N52	129.57(16)
C51	C56	C57	C58	-103.05(17)
C51	C56	C57	C62	19.09(18)
C52	C51	C56	C55	-1.2(3)
C52	C51	C56	C57	176.56(16)
C52	C53	C54	O52	178.49(16)
C52	C53	C54	C55	0.1(3)
C53	C54	C55	C56	0.3(3)
C54	C55	C56	C51	0.1(3)
C54	C55	C56	C57	-177.08(17)
C55	C56	C57	N52	-53.0(2)
C55	C56	C57	C58	74.4(2)
C55	C56	C57	C62	-163.44(18)
C56	C51	C52	C53	1.6(3)
C56	C57	C58	C59	151.18(16)
C56	C57	C62	N51	-24.37(16)
C56	C57	C62	C61	-149.26(14)
C56	C57	C62	C63	93.24(14)
C57	N52	C68	C63	-16.96(19)
C57	N52	C68	C67	167.37(17)
C57	C58	C59	C60	-55.8(2)
C57	C62	C63	C64	-172.84(18)
C57	C62	C63	C68	16.30(18)
C58	C57	C62	N51	94.47(17)
C58	C57	C62	C61	-30.4(2)
C58	C57	C62	C63	-147.92(15)
C58	C59	C60	C61	63.9(2)
C59	C60	C61	C62	-54.9(2)
C60	C61	C62	N51	-83.52(19)
C60	C61	C62	C57	38.5(2)
C60	C61	C62	C63	150.93(16)
C61	C62	C63	C64	64.7(2)

Atom	Atom	Atom	Atom	Angle/°
C61	C62	C63	C68	-106.17(17)
C62	N51	C51	C52	166.55(17)
C62	N51	C51	C56	-9.8(2)
C62	C57	C58	C59	38.8(2)
C62	C63	C64	C65	-172.71(17)
C62	C63	C68	N52	-0.7(2)
C62	C63	C68	C67	175.25(16)
C63	C64	C65	O53	178.25(16)
C63	C64	C65	C66	0.3(3)
C64	C63	C68	N52	-172.55(16)
C64	C63	C68	C67	3.4(3)
C64	C65	C66	O54	-179.57(16)
C64	C65	C66	C67	1.5(3)
C65	C66	C67	C68	-0.8(3)
C66	C67	C68	N52	173.70(17)
C66	C67	C68	C63	-1.6(3)
C68	N52	C57	C56	-81.20(18)
C68	N52	C57	C58	151.71(15)
C68	N52	C57	C62	26.50(17)
C68	C63	C64	C65	-2.7(3)
C69	O51	C53	C52	7.7(3)
C69	O51	C53	C54	-174.76(16)
C70	O52	C54	C53	166.66(16)
C70	O52	C54	C55	-15.1(3)
C71	O53	C65	C64	81.9(2)
C71	O53	C65	C66	-100.2(2)
C72	O54	C66	C65	-169.03(17)
C72	O54	C66	C67	9.9(3)

Table 14: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **NM24014**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H2	7710(20)	8500(40)	9158(13)	22(7)
H1	8350(20)	3600(40)	7773(12)	16(6)
H2A	5829.22	7181.46	9474.03	14
H5	6138.58	2901.13	7884.84	11
H8A	6912.46	5505.9	6977.41	14
H8B	6289.34	7055.67	7295.62	14
H9A	7283.29	8377.16	6569.14	17
H9B	8446.94	7474.34	6937.35	17
H10A	8300.54	10589.88	7242.82	17
H10B	7205.74	10075.54	7522.31	17
H11A	8788.71	10107.69	8371.54	15
H11B	9468.24	8776.91	7998.51	15
H14	9882.32	7869.7	9580.14	12
H17	10419.6	2572.26	8450.33	13
H19A	3985.31	6950.81	9605.07	29
H19B	4852.61	5959.22	10168.44	29
H19C	3532.69	5446.91	10026.55	29
H20A	4860.82	559.34	7833.6	24
H20B	4451.62	-562.18	8382.98	24
H20C	5717.51	218.22	8502.03	24

Atom	x	y	z	U_{eq}
H21A	12059.4	8304.43	10068.18	26
H21B	12418.6	7616.82	10790.5	26
H21C	11128.14	8163.29	10500.85	26
H22A	12405.82	1922.48	8820.95	25
H22B	11538.49	664.46	9094.89	25
H22C	12832.08	820.87	9469.23	25
H4	860(20)	4610(40)	7498(13)	23(7)
H3	2140(20)	8400(40)	5937(12)	14(6)
H52A	-678.72	2487.78	6572.05	13
H55	-9.95	7673.74	5420.59	13
H58A	930.96	10004.23	6639.13	15
H58B	253.17	8688.97	7019.22	15
H59A	1405.03	10598.67	7757.77	18
H59B	2509.76	10020.13	7498.94	18
H60A	2412.32	8455.39	8470.32	17
H60B	1237.13	7555.06	8118.38	17
H61A	2707.57	5485.8	8105.02	15
H61B	3401.91	6952.83	7794.48	15
H64	3611.97	2885.5	7267.79	13
H67	4032.48	7002.91	5651.99	15
H69A	-2942.4	562.06	5489.05	27
H69B	-2642.05	1710.56	6134.98	27
H69C	-1681.33	524.14	5915.25	27
H70A	-2281.39	7321.62	4093.28	29
H70B	-962.47	7563	4407.63	29
H70C	-1905.59	8261.75	4777.44	29
H71A	4678.41	494.77	5996.7	28
H71B	4170.14	63.25	6613.71	28
H71C	5426.5	-582.27	6584.58	28
H72A	5134.35	5885.34	5039.42	33
H72B	6441.78	5299.15	5212.11	33
H72C	5977.89	6792.64	5632.92	33

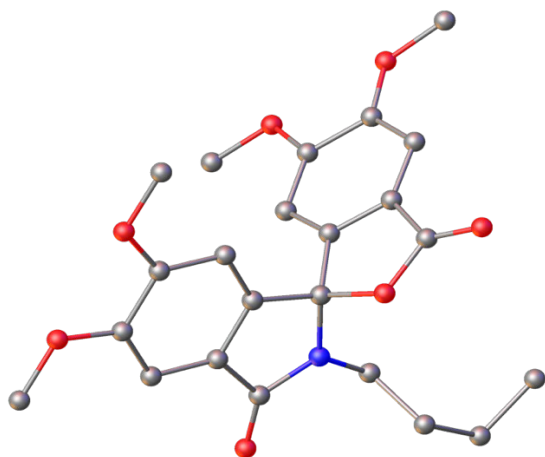
Table 15: Hydrogen Bond information for **NM24014**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N1	H2	O3 ¹	0.93(3)	2.25(3)	3.106(2)	153(2)
N52	H3	O52 ²	0.88(3)	2.26(3)	3.095(2)	159(2)

¹2-x,1/2+y,2-z; ²-x,1/2+y,1-z

$$R_1=6.53\%$$

Crystal Data and Experimental



Experimental. Single colourless needle crystals of **NM20021** recrystallised from a mixture of methanol and chloroform by solvent layering. A suitable crystal with dimensions $0.07 \times 0.03 \times 0.02 \text{ mm}^3$ was selected and mounted on a MITIGEN holder in Paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at a steady $T = 120.00(10) \text{ K}$ during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{23}\text{H}_{25}\text{NO}_7$, $M_r = 427.44$, triclinic, $P-1$ (No. 2), $a = 8.7717(9) \text{ \AA}$, $b = 11.0529(12) \text{ \AA}$, $c = 12.0254(14) \text{ \AA}$, $\alpha = 64.180(11)^\circ$, $\beta = 86.636(9)^\circ$, $\gamma = 84.205(9)^\circ$, $V = 1044.0(2) \text{ \AA}^3$, $T = 120.00(10) \text{ K}$, $Z = 2$, $Z' = 1$, $d(\text{Cu K}\alpha) = 0.840$, 11290 reflections measured, 2553 unique ($R_{\text{int}} = 0.1293$) which were used in all calculations. The final wR_2 was 0.1845 (all data) and R_1 was 0.0653 ($I \geq 2\sigma(I)$).

Compound	NM20021
Formula	$\text{C}_{23}\text{H}_{25}\text{NO}_7$
$D_{\text{calc.}} / \text{g cm}^{-3}$	1.360
μ / mm^{-1}	0.840
Formula Weight	427.44
Colour	colourless
Shape	needle
Size/ mm^3	$0.07 \times 0.03 \times 0.02$
T/K	120.00(10)
Crystal System	triclinic
Space Group	$P-1$
$a/\text{\AA}$	8.7717(9)
$b/\text{\AA}$	11.0529(12)
$c/\text{\AA}$	12.0254(14)
$\alpha/^\circ$	64.180(11)
$\beta/^\circ$	86.636(9)
$\gamma/^\circ$	84.205(9)
$V/\text{\AA}^3$	1044.0(2)
Z	2
Z'	1
Wavelength/ $\text{\AA}$	1.54184
Radiation type	Cu K α
$2\theta_{\text{min}}/^\circ$	4.084
$2\theta_{\text{max}}/^\circ$	54.228
Measured Refl's.	11290
Indep't Refl's	2553
Refl's $I \geq 2\sigma(I)$	1795
R_{int}	0.1293
Parameters	286
Restraints	0
Largest Peak	0.342
Deepest Hole	-0.317
GooF	0.984
wR_2 (all data)	0.1845
wR_2	0.1633
R_1 (all data)	0.0926
R_1	0.0653

Structure Quality Indicators

Reflections:	d min (Cu) 0.95	I/ σ (I) 9.8	Rint 12.93%	complete 100% (IUCr) 100%
Refinement:	Shift 0.000	Max Peak 0.3	Min Peak -0.3	Goof 0.984

A colourless needle-shaped crystal with dimensions $0.07 \times 0.03 \times 0.02 \text{ mm}^3$ was mounted on a MITIGEN holder in Paratone oil. Data were collected using a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature device operating at $T = 120.00(10) \text{ K}$.

Data were measured using φ scans using Cu K α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.84a, 2020). The maximum resolution that was achieved was $\vartheta = 54.228^\circ$ (0.95 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.84a, 2020). The unit cell was refined using CrysAlisPro (Rigaku, V1.171.40.84a, 2020) on 2060 reflections, 18% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.40.84a, 2020). The final completeness is 100.00 % out to 54.228° in ϑ . A multi-scan absorption correction was performed using CrysAlisPro 1.171.40.84a (Rigaku Oxford Diffraction, 2020) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.. The absorption coefficient μ of this material is 0.840 mm^{-1} at this wavelength ($\lambda = 1.54184 \text{ Å}$) and the minimum and maximum transmissions are 0.833 and 1.000.

The structure was solved and the space group $P-1$ (# 2) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: This weak data set was trimmed to 0.95 Å resolution during refinement.

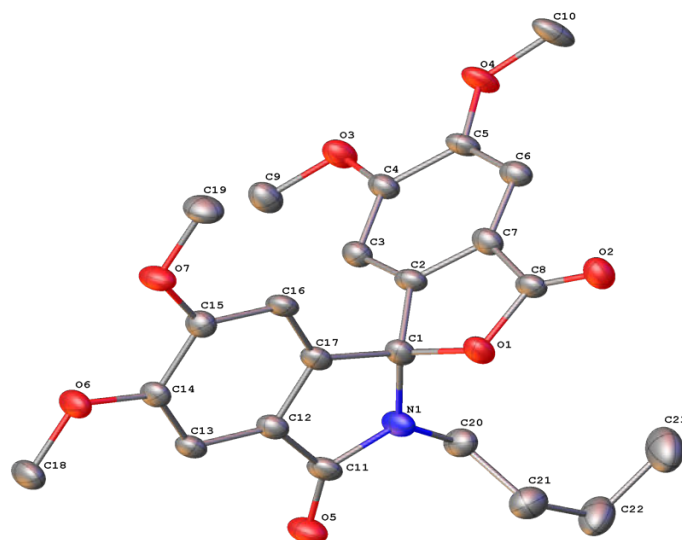
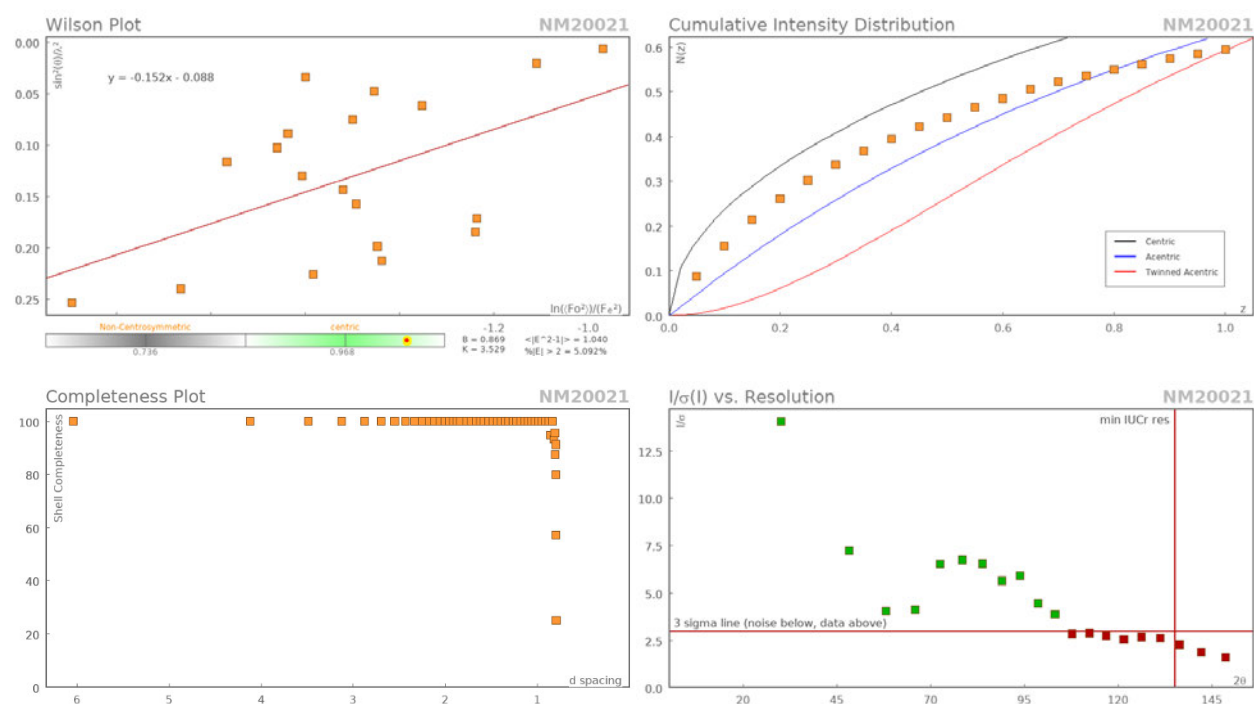


Figure 11: The molecular structure of NM20021. Displacement ellipsoids are at the 50% probability level. H atoms are not shown.

Data Plots: Diffraction Data



Data Plots: Refinement and Data

Failed to make fobs_fcalc plot

```
Python argument types in
double __imul__(double, NoneType)
did not match C++ signature:
__imul__(class scitbx::af::versa<double, class scitbx::af::flex_grid<class scitbx::af::small<long, 10> > > {Ivalue}
__imul__(class scitbx::af::versa<double, class scitbx::af::flex_grid<class scitbx::af::small<long, 10> > > {Ivalue}
```

Failed to make normal_probability plot

```
Python argument types in
double __imul__(double, NoneType)
did not match C++ signature:
__imul__(class scitbx::af::versa<double, class scitbx::af::flex_grid<class scitbx::af::small<long, 10> > > {Ivalue}
__imul__(class scitbx::af::versa<double, class scitbx::af::flex_grid<class scitbx::af::small<long, 10> > > {Ivalue}
```

Reflection Statistics

Total reflections (after filtering)	11290	Unique reflections	2553
Completeness	1.0	Mean I/ σ	6.09
hkl _{max} collected	(10, 13, 14)	hkl _{min} collected	(-8, -13, -15)
hkl _{max} used	(9, 11, 12)	hkl _{min} used	(-9, -10, 0)
Lim d _{max} collected	999.0	Lim d _{min} collected	0.95
d _{max} used	10.82	d _{min} used	0.95
Friedel pairs	1945	Friedel pairs merged	1
Inconsistent equivalents	0	R _{int}	0.1293
R _{sigma}	0.1025	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(2112, 1613, 970, 581, 382, 236, 129, 72, 45, 32, 23, 22, 15, 11, 5, 1)	Maximum multiplicity	18
Removed systematic absences	0	Filtered off (Shel/OMIT)	5769

Table 16: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **NM20021**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
O1	951(3)	3736(3)	3433(3)	24.3(7)
O2	116(3)	2850(3)	2238(3)	28.9(8)
O3	7138(3)	779(3)	3974(3)	25.7(8)
O4	5746(3)	-60(3)	2662(3)	27.3(8)
O5	3461(3)	6424(3)	4432(3)	31.9(8)
O6	1416(3)	2828(3)	9020(3)	29.8(8)
O7	685(3)	949(3)	8514(3)	28.5(8)
N1	2921(4)	4946(4)	3665(3)	24.5(9)
C1	2350(4)	3631(4)	4097(4)	22.0(10)
C2	3404(4)	2636(4)	3809(4)	20.5(10)
C3	4928(4)	2197(4)	4148(4)	20.7(10)
C4	5663(4)	1289(4)	3738(4)	21.0(10)
C5	4885(4)	827(4)	2995(4)	22.0(10)
C6	3385(4)	1310(4)	2653(4)	20.8(10)
C7	2676(4)	2214(5)	3082(4)	22.4(10)
C8	1129(5)	2914(4)	2833(4)	22.2(10)
C9	8002(5)	1318(5)	4607(4)	28.3(11)
C10	4972(5)	-649(5)	2030(5)	33.0(12)
C11	2965(5)	5373(5)	4574(4)	24.9(10)
C12	2351(4)	4305(4)	5703(4)	20.1(10)
C13	2179(4)	4233(4)	6892(4)	21.5(10)
C14	1618(4)	3077(5)	7803(4)	21.9(10)

Atom	x	y	z	U_{eq}
C15	1203(4)	2024(5)	7523(4)	23.1(10)
C16	1403(4)	2127(4)	6333(4)	23.0(10)
C17	1981(4)	3281(4)	5435(4)	21.1(10)
C18	1778(6)	3875(5)	9328(4)	33.2(11)
C19	155(5)	-99(5)	8266(4)	32.5(11)
C20	3591(5)	5680(5)	2432(4)	28.7(11)
C21	2546(5)	6837(5)	1610(5)	36.4(12)
C22	3259(6)	7515(6)	296(5)	46.2(14)
C23	3149(7)	6675(6)	-421(5)	54.2(16)

Table 17: Anisotropic Displacement Parameters ($\times 10^4$) for **NM20021**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	31.2(15)	23.2(19)	22.6(16)	-14.8(15)	-2.0(12)	3.3(12)
O2	36.6(16)	32(2)	24.3(17)	-18.2(16)	-0.5(14)	-1.2(13)
O3	28.7(15)	29(2)	27.5(17)	-20.7(16)	-0.2(12)	1.2(13)
O4	33.8(15)	25.7(19)	34.4(18)	-25.0(16)	1.4(13)	1.1(13)
O5	49.7(18)	23(2)	29.6(18)	-17.5(16)	6.8(14)	-10.0(15)
O6	48.5(17)	27(2)	20.1(17)	-15.8(15)	3.9(13)	-5.2(14)
O7	44.1(16)	22.2(19)	24.1(17)	-14.7(16)	8.5(13)	-7.5(13)
N1	40(2)	20(2)	14.3(19)	-9.0(18)	8.1(15)	-3.0(16)
C1	26(2)	20(3)	22(2)	-12(2)	1.1(17)	3.4(18)
C2	31(2)	14(2)	19(2)	-11(2)	6.2(17)	-3.7(18)
C3	30(2)	18(3)	17(2)	-10(2)	2.0(16)	-3.7(17)
C4	30(2)	17(3)	18(2)	-10(2)	2.2(17)	-1.4(18)
C5	30(2)	18(3)	21(2)	-12(2)	6.8(17)	-0.2(18)
C6	31(2)	18(3)	17(2)	-11(2)	4.1(17)	-4.1(18)
C7	31(2)	24(3)	18(2)	-14(2)	7.3(17)	-6.3(18)
C8	35(2)	19(3)	19(2)	-13(2)	5.5(19)	-4.6(18)
C9	30(2)	29(3)	33(3)	-20(2)	1.6(19)	-1.2(18)
C10	38(2)	34(3)	43(3)	-33(3)	1(2)	-1(2)
C11	35(2)	19(3)	28(3)	-18(2)	1.6(18)	3(2)
C12	25.1(19)	17(3)	21(2)	-11(2)	3.6(17)	-1.6(17)
C13	32(2)	18(3)	22(2)	-16(2)	-1.0(17)	1.0(18)
C14	31(2)	21(3)	14(2)	-10(2)	3.0(17)	3.3(18)
C15	33(2)	17(3)	19(2)	-8(2)	3.1(17)	-0.2(18)
C16	32(2)	20(3)	25(2)	-17(2)	0.4(18)	0.2(18)
C17	25(2)	21(3)	22(2)	-15(2)	0.1(17)	5.4(18)
C18	56(3)	27(3)	22(3)	-15(2)	4(2)	-5(2)
C19	50(3)	20(3)	27(3)	-9(2)	3(2)	-10(2)
C20	43(2)	22(3)	23(2)	-12(2)	4.6(19)	-2(2)
C21	42(3)	34(3)	34(3)	-15(3)	-3(2)	-1(2)
C22	63(3)	37(4)	32(3)	-5(3)	-9(2)	-15(3)
C23	80(4)	54(4)	26(3)	-11(3)	2(3)	-24(3)

Table 18: Bond Lengths in Å for **NM20021**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.470(5)	O1	C8	1.378(5)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C8	1.199(5)	C2	C7	1.368(6)
O3	C4	1.352(5)	C3	C4	1.388(6)
O3	C9	1.436(5)	C4	C5	1.437(6)
O4	C5	1.359(5)	C5	C6	1.385(6)
O4	C10	1.430(5)	C6	C7	1.392(6)
O5	C11	1.220(6)	C7	C8	1.471(6)
O6	C14	1.370(5)	C11	C12	1.474(6)
O6	C18	1.428(6)	C12	C13	1.397(6)
O7	C15	1.360(6)	C12	C17	1.376(6)
O7	C19	1.440(6)	C13	C14	1.386(6)
N1	C1	1.446(6)	C14	C15	1.429(6)
N1	C11	1.371(6)	C15	C16	1.388(6)
N1	C20	1.466(6)	C16	C17	1.384(7)
C1	C2	1.507(6)	C20	C21	1.490(7)
C1	C17	1.506(6)	C21	C22	1.548(7)
C2	C3	1.396(6)	C22	C23	1.530(8)

Table 19: Bond Angles in ° for **NM20021**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	O1	C1	110.7(3)	C2	C7	C8	108.2(4)
C4	O3	C9	116.1(3)	C6	C7	C8	129.1(4)
C5	O4	C10	116.5(3)	O1	C8	C7	108.1(3)
C14	O6	C18	115.9(4)	O2	C8	O1	121.4(4)
C15	O7	C19	116.4(3)	O2	C8	C7	130.5(4)
C1	N1	C20	124.1(3)	O5	C11	N1	124.6(4)
C11	N1	C1	113.3(4)	O5	C11	C12	129.3(4)
C11	N1	C20	122.1(4)	N1	C11	C12	106.1(4)
O1	C1	C2	102.9(3)	C13	C12	C11	129.1(4)
O1	C1	C17	110.4(3)	C17	C12	C11	108.8(4)
N1	C1	O1	109.9(3)	C17	C12	C13	122.0(4)
N1	C1	C2	113.9(3)	C14	C13	C12	117.1(4)
N1	C1	C17	102.3(3)	O6	C14	C13	124.7(4)
C17	C1	C2	117.6(4)	O6	C14	C15	114.3(4)
C3	C2	C1	128.4(4)	C13	C14	C15	121.0(4)
C7	C2	C1	110.0(4)	O7	C15	C14	114.2(4)
C7	C2	C3	121.5(4)	O7	C15	C16	125.5(4)
C4	C3	C2	117.1(4)	C16	C15	C14	120.2(4)
O3	C4	C3	124.4(4)	C17	C16	C15	118.1(4)
O3	C4	C5	114.3(3)	C12	C17	C1	109.5(4)
C3	C4	C5	121.3(4)	C12	C17	C16	121.6(4)
O4	C5	C4	114.8(3)	C16	C17	C1	129.0(4)
O4	C5	C6	125.3(4)	N1	C20	C21	112.5(4)
C6	C5	C4	119.9(4)	C20	C21	C22	110.4(4)
C5	C6	C7	117.5(4)	C23	C22	C21	111.7(5)
C2	C7	C6	122.7(4)				

Table 20: Torsion Angles in ° for **NM20021**.

Atom	Atom	Atom	Atom	Angle/°
O1	C1	C2	C3	176.7(4)

Atom	Atom	Atom	Atom	Angle/°
O1	C1	C2	C7	-0.8(4)
O1	C1	C17	C12	-118.0(4)
O1	C1	C17	C16	63.8(5)
O3	C4	C5	O4	0.8(5)
O3	C4	C5	C6	-177.8(4)
O4	C5	C6	C7	179.8(4)
O5	C11	C12	C13	0.3(7)
O5	C11	C12	C17	-177.7(4)
O6	C14	C15	O7	-0.4(5)
O6	C14	C15	C16	-177.7(3)
O7	C15	C16	C17	-178.3(4)
N1	C1	C2	C3	57.8(6)
N1	C1	C2	C7	-119.7(4)
N1	C1	C17	C12	-1.1(4)
N1	C1	C17	C16	-179.3(4)
N1	C11	C12	C13	178.6(4)
N1	C11	C12	C17	0.6(5)
N1	C20	C21	C22	-176.1(4)
C1	O1	C8	O2	179.8(4)
C1	O1	C8	C7	0.3(4)
C1	N1	C11	O5	177.0(4)
C1	N1	C11	C12	-1.4(5)
C1	N1	C20	C21	106.4(5)
C1	C2	C3	C4	-178.6(4)
C1	C2	C7	C6	178.8(4)
C1	C2	C7	C8	1.0(5)
C2	C1	C17	C12	124.4(4)
C2	C1	C17	C16	-53.8(6)
C2	C3	C4	O3	179.2(4)
C2	C3	C4	C5	0.1(6)
C2	C7	C8	O1	-0.8(5)
C2	C7	C8	O2	179.7(5)
C3	C2	C7	C6	1.1(7)
C3	C2	C7	C8	-176.7(4)
C3	C4	C5	O4	-180.0(4)
C3	C4	C5	C6	1.4(6)
C4	C5	C6	C7	-1.6(6)
C5	C6	C7	C2	0.5(6)
C5	C6	C7	C8	177.7(4)
C6	C7	C8	O1	-178.4(4)
C6	C7	C8	O2	2.1(8)
C7	C2	C3	C4	-1.3(6)
C8	O1	C1	N1	122.0(3)
C8	O1	C1	C2	0.3(4)
C8	O1	C1	C17	-126.0(4)
C9	O3	C4	C3	-5.3(6)
C9	O3	C4	C5	173.9(4)
C10	O4	C5	C4	173.8(4)
C10	O4	C5	C6	-7.6(6)
C11	N1	C1	O1	118.9(4)
C11	N1	C1	C2	-126.4(4)
C11	N1	C1	C17	1.6(4)
C11	N1	C20	C21	-82.4(5)
C11	C12	C13	C14	-177.6(4)
C11	C12	C17	C1	0.4(5)

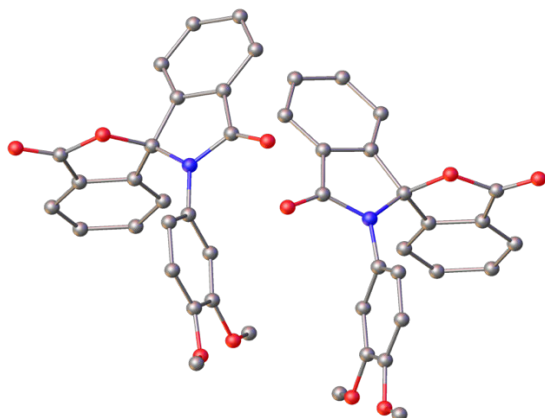
Atom	Atom	Atom	Atom	Angle/°
C11	C12	C17	C16	178.7(4)
C12	C13	C14	O6	178.3(3)
C12	C13	C14	C15	-1.5(6)
C13	C12	C17	C1	-177.8(4)
C13	C12	C17	C16	0.6(6)
C13	C14	C15	O7	179.4(3)
C13	C14	C15	C16	2.1(6)
C14	C15	C16	C17	-1.4(6)
C15	C16	C17	C1	178.0(4)
C15	C16	C17	C12	0.0(6)
C17	C1	C2	C3	-61.8(6)
C17	C1	C2	C7	120.7(4)
C17	C12	C13	C14	0.2(6)
C18	O6	C14	C13	1.9(6)
C18	O6	C14	C15	-178.3(4)
C19	O7	C15	C14	176.0(4)
C19	O7	C15	C16	-6.9(6)
C20	N1	C1	O1	-69.2(4)
C20	N1	C1	C2	45.6(5)
C20	N1	C1	C17	173.5(4)
C20	N1	C11	O5	4.9(7)
C20	N1	C11	C12	-173.5(4)
C20	C21	C22	C23	75.5(6)

Table 21: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **NM20021**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H3	5440.29	2505.21	4638.1	25
H6	2859.04	1035.2	2143.96	25
H9A	7990.74	2298.51	4130.23	43
H9B	9062.4	915.85	4694.5	43
H9C	7544.2	1107.55	5426.46	43
H10A	4559.88	62.56	1255.88	50
H10B	4130.35	-1135.82	2552.79	50
H10C	5694.67	-1278.54	1848.63	50
H13	2435.09	4945.64	7068.39	26
H16	1151.67	1424.87	6139.15	28
H18A	1185.44	4718.15	8811.43	50
H18B	2875.4	3997.39	9183.29	50
H18C	1523.47	3628.84	10200.19	50
H19A	-675.81	281.84	7668.82	49
H19B	-223.57	-803.65	9035.65	49
H19C	1002.6	-490.09	7926.17	49
H20A	3835.38	5051.43	2047.42	34
H20B	4561.08	6019.28	2511.65	34
H21A	2360.4	7505.01	1955.91	44
H21B	1548.86	6513.51	1566.94	44
H22A	2721.53	8418.88	-160.48	55
H22B	4349.1	7633.88	359.5	55
H23A	3598.59	7138.51	-1249.83	81
H23B	2070.63	6559.55	-489.86	81
H23C	3707.47	5788.65	15.46	81

$$R_1 = 9.62\%$$

Crystal Data and Experimental



Experimental. Single colourless needle crystals of **NM20011** recrystallised from methanol by slow evaporation. A suitable crystal with dimensions $0.58 \times 0.09 \times 0.04 \text{ mm}^3$ was selected and mounted on a MITIGEN holder in Paratone oil. on a Bruker D8 VENTURE diffractometer. The crystal was kept at a steady $T = 100.0 \text{ K}$ during data collection. The structure was solved with the ShelXT (Sheldrick, 2015) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{23}\text{H}_{17}\text{NO}_5$, $M_r = 387.38$, monoclinic, $P2_1/c$ (No. 14), $a = 22.885(2) \text{ \AA}$, $b = 7.7704(7) \text{ \AA}$, $c = 23.886(2) \text{ \AA}$, $\beta = 117.016(3)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 3784.2(6) \text{ \AA}^3$, $T = 100.0 \text{ K}$, $Z = 8$, $Z' = 2$, $d(\text{MoK}\alpha) = 0.097$, 189566 reflections measured, 8701 unique ($R_{\text{int}} = 0.1535$) which were used in all calculations. The final wR_2 was 0.2521 (all data) and R_1 was 0.0962 ($I \geq 2 \sigma(I)$).

Compound	NM20011
Formula	$\text{C}_{23}\text{H}_{17}\text{NO}_5$
$D_{\text{calc.}} / \text{g cm}^{-3}$	1.360
μ / mm^{-1}	0.097
Formula Weight	387.38
Colour	colourless
Shape	needle
Size/ mm^3	$0.58 \times 0.09 \times 0.04$
T / K	100.0
Crystal System	monoclinic
Space Group	$P2_1/c$
$a / \text{\AA}$	22.885(2)
$b / \text{\AA}$	7.7704(7)
$c / \text{\AA}$	23.886(2)
$\beta / ^\circ$	90
$\alpha / ^\circ$	117.016(3)
$\gamma / ^\circ$	90
$V / \text{\AA}^3$	3784.2(6)
Z	8
Z'	2
Wavelength/ $\text{\AA}$	0.71073
Radiation type	MoK α
$2\theta_{\text{min}} / ^\circ$	2.530
$2\theta_{\text{max}} / ^\circ$	25.505
Measured Refl's.	189566
Indep't Refl's	8701
Refl's $I \geq 2 \sigma(I)$	5872
R_{int}	0.1535
Parameters	529
Restraints	0
Largest Peak	0.535
Deepest Hole	-0.362
GooF	1.064
wR_2 (all data)	0.2521
wR_2	0.2200
R_1 (all data)	0.1487
R_1	0.0962

Structure Quality Indicators

Reflections:	d min (Mo)	0.83	I/ σ (I)	16.7	R _{int}	15.35%	complete	100%
Refinement:	Shift	0.000	Max Peak	0.5	Min Peak	-0.4	Goof	1.064

A colourless needle-shaped crystal with dimensions $0.58 \times 0.09 \times 0.04 \text{ mm}^3$ was mounted on a MITIGEN holder in Paratone oil.. Data were collected using a Bruker D8 VENTURE diffractometer equipped with an Oxford Cryosystems Cryostream 800 low-temperature device operating at $T = 100.0 \text{ K}$.

Data were measured using ω and φ scans using MoK α radiation. . The maximum resolution that was achieved was $\theta = 25.505^\circ$ ($0.83 \text{ \AA}$).

. The unit cell was refined using SAINT (Bruker, V8.40A, after 2013) on 4108 reflections, 2% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.40A, after 2013). The final completeness is 99.50 % out to 25.505° in θ . A multi-scan absorption correction was performed using TWINABS-2012/1 (Bruker, 2012) was used for absorption correction. Final HKLF 4 output contains 189566 reflections, $R_{int} = 0.1535$ (26694 with $I > 3\sigma(I)$, $R_{int} = 0.0759$). The absorption coefficient μ of this material is 0.097 mm^{-1} at this wavelength ($\lambda = 0.71073 \text{ \AA}$) and the minimum and maximum transmissions are 0.504 and 0.745.

The structure was solved and the space group $P2_1/c$ (# 14) determined by the ShelXT (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: The crystal used was a non-merohedral twin. Twinning was deconvoluted with CELL_NOW and SAINT. Twin law $[-1 \ 0 \ 0 / 0 \ -1 \ 0 / -0.949 \ 0 \ -1]$ and twin scale factor 0.353(2).

The value of Z' is 2. This means that there are two independent molecules in the asymmetric unit.

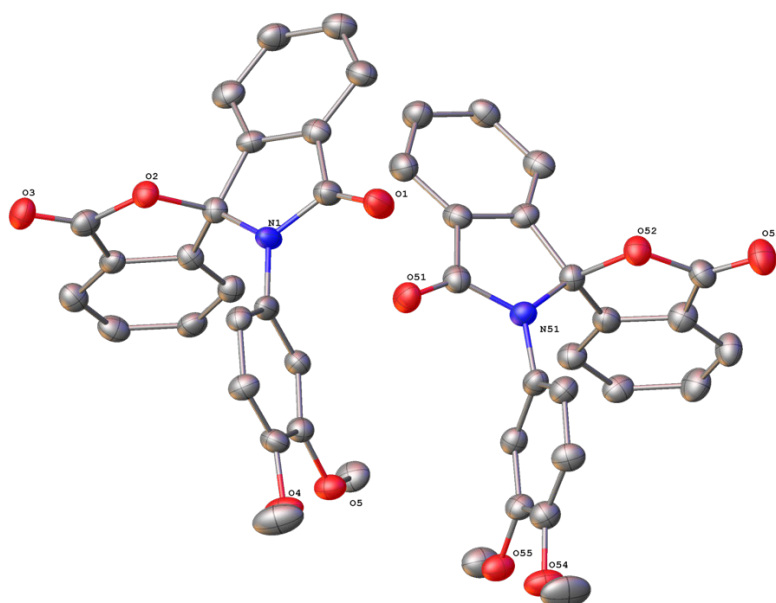
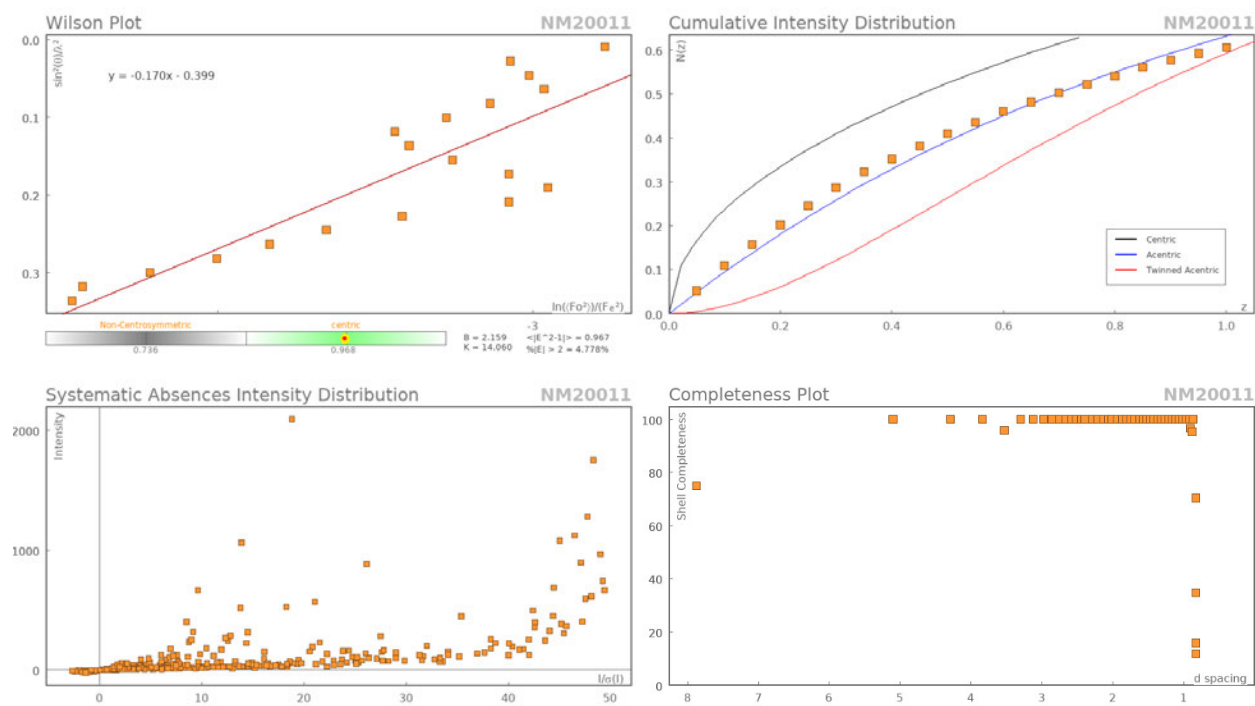
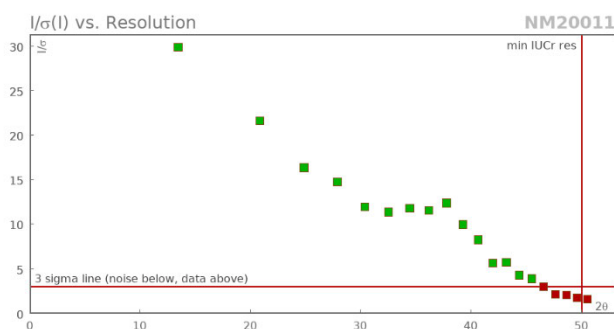


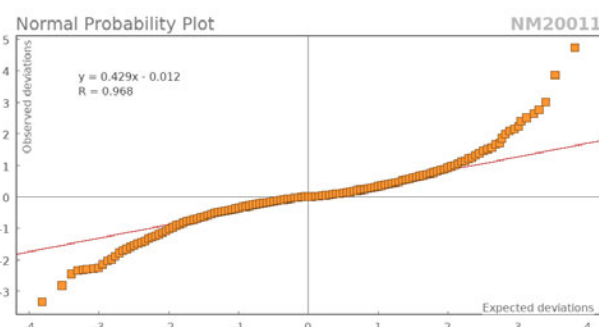
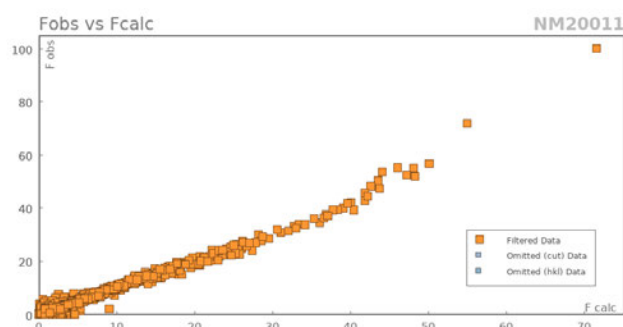
Figure 12: The asymmetric unit of NM20011. Displacement ellipsoids are at the 50% probability level and H atoms are not shown.

Data Plots: Diffraction Data





Data Plots: Refinement and Data



Reflection Statistics

Total reflections (after filtering)	18182	Unique reflections	6970
Completeness	0.987	Mean I/σ	6.43
$hkl_{\max}$ collected	(24, 9, 28)	$hkl_{\min}$ collected	(-27, 0, 0)
$hkl_{\max}$ used	(24, 9, 28)	$hkl_{\min}$ used	(-27, 0, 0)
Lim $d_{\max}$ collected	100.0	Lim $d_{\min}$ collected	0.36
$d_{\max}$ used	8.05	$d_{\min}$ used	0.83
Friedel pairs	0	Friedel pairs merged	1
Inconsistent equivalents	0	R_{int}	0.0
R_{sigma}	0.0599	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(97, 5231, 1413, 711, 85, 18, 1)	Maximum multiplicity	0
Removed systematic absences	1236	Filtered off (Shel/OMIT)	0

Table 22: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **NM20011**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
O1	2822(2)	9161(6)	5490(2)	38.6(11)
O2	4857.5(19)	8098(5)	5921.1(19)	28.7(9)
O3	5811(2)	7715(6)	5872(2)	34.7(11)
O4	2467(2)	7090(6)	2870.2(19)	38.4(11)
O5	2433(2)	4549(5)	3546.2(19)	33.0(10)
N1	3704(2)	7740(7)	5479(2)	26.9(11)
C1	4329(3)	7030(8)	5926(3)	25.7(13)
C2	4308(3)	7274(8)	6546(3)	27.2(13)
C3	4751(3)	6713(9)	7143(3)	35.8(15)
C4	4597(3)	7065(9)	7626(3)	36.8(15)
C5	4027(3)	7932(9)	7530(3)	36.2(15)

Atom	x	y	z	U_{eq}
C6	3591(3)	8476(9)	6939(3)	35.1(14)
C7	3741(3)	8120(8)	6450(3)	28.8(13)
C8	3354(3)	8428(9)	5767(3)	30.7(14)
C9	5320(3)	7081(9)	5862(3)	30.0(14)
C10	5107(3)	5284(8)	5798(3)	27.6(14)
C11	5410(3)	3811(8)	5743(3)	32.1(14)
C12	5099(3)	2267(9)	5702(3)	32.9(15)
C13	4486(3)	2204(9)	5707(3)	31.4(14)
C14	4180(3)	3712(8)	5759(3)	28.7(13)
C15	4498(3)	5243(8)	5809(3)	25.6(13)
C16	3431(3)	7591(8)	4805(3)	26.8(12)
C17	3087(3)	6093(8)	4522(3)	27.9(13)
C18	2787(3)	5946(8)	3874(3)	27.7(13)
C19	2811(3)	7336(8)	3511(3)	30.4(13)
C20	3155(3)	8795(8)	3792(3)	29.4(13)
C21	3477(3)	8927(8)	4457(3)	25.5(12)
C22	2326(4)	8580(10)	2483(3)	56(2)
C23	2441(3)	3086(8)	3919(3)	37.4(15)
O51	2671(2)	4135(6)	5488(2)	35.5(10)
O52	1099(2)	3144(6)	6014(2)	32.6(10)
O53	93(2)	2806(6)	5943(2)	41.1(12)
O54	513(2)	2143(6)	2918.2(19)	41.8(11)
O55	1199(2)	-395(5)	3583.7(19)	34.0(10)
N51	1791(2)	2746(7)	5522(2)	26.5(11)
C51	1617(3)	2057(8)	5987(3)	27.3(13)
C52	2250(3)	2286(8)	6595(3)	27.8(13)
C53	2407(3)	1769(8)	7202(3)	34.5(14)
C54	3035(3)	2125(9)	7677(3)	33.0(14)
C55	3489(3)	2992(9)	7536(3)	34.5(14)
C56	3326(3)	3500(9)	6923(3)	34.3(14)
C57	2711(3)	3129(8)	6468(3)	30.0(14)
C58	2414(3)	3444(8)	5776(3)	30.6(14)
C59	569(3)	2146(8)	5935(3)	29.9(14)
C60	714(3)	353(8)	5853(3)	32.9(15)
C61	345(3)	-1130(8)	5785(3)	35.3(15)
C62	607(3)	-2649(9)	5738(3)	39.6(17)
C63	1227(3)	-2738(8)	5761(3)	32.2(14)
C64	1598(3)	-1259(8)	5831(3)	30.7(13)
C65	1326(3)	292(9)	5881(3)	31.1(14)
C66	1408(3)	2598(8)	4853(3)	27.6(13)
C67	1018(3)	3937(8)	4504(3)	31.3(14)
C68	699(3)	3815(8)	3848(3)	32.9(14)
C69	778(3)	2372(8)	3555(3)	33.2(14)
C70	1155(3)	989(8)	3918(3)	28.4(13)
C71	1474(3)	1110(8)	4561(3)	27.6(13)
C72	161(4)	3569(11)	2542(3)	57(2)
C73	1509(3)	-1915(9)	3935(3)	42.6(16)

Table 23: Anisotropic Displacement Parameters ($\times 10^4$) for **NM20011**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	34(2)	48(3)	32(2)	3(2)	14(2)	10(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	28(2)	26(2)	32(2)	-0.7(18)	13.7(18)	-2.3(18)
O3	26(2)	40(3)	37(2)	5(2)	13.2(19)	-4(2)
O4	50(3)	36(3)	24(2)	-2.8(18)	12(2)	-9(2)
O5	37(2)	31(2)	30(2)	-3.4(18)	13.7(19)	-4(2)
N1	25(2)	33(3)	21(2)	-2(2)	9(2)	5(2)
C1	26(3)	24(3)	28(3)	2(2)	13(2)	0(3)
C2	29(3)	25(3)	23(3)	-2(2)	8(2)	-1(3)
C3	38(3)	32(4)	34(3)	-2(3)	14(3)	-7(3)
C4	35(3)	40(4)	27(3)	1(3)	8(3)	3(3)
C5	44(4)	35(4)	28(3)	-1(3)	15(3)	1(3)
C6	39(3)	36(4)	33(3)	-5(3)	19(3)	-3(3)
C7	34(3)	24(3)	30(3)	-1(3)	15(3)	-3(3)
C8	30(3)	35(4)	27(3)	-1(3)	12(3)	1(3)
C9	27(3)	31(3)	27(3)	2(3)	7(2)	3(3)
C10	27(3)	34(4)	21(3)	-1(2)	11(2)	-6(3)
C11	32(3)	34(4)	30(3)	4(3)	15(3)	6(3)
C12	40(4)	29(4)	31(3)	0(3)	18(3)	7(3)
C13	29(3)	36(4)	23(3)	-1(3)	7(3)	-3(3)
C14	26(3)	32(3)	26(3)	4(3)	10(2)	1(3)
C15	28(3)	24(3)	24(3)	5(2)	12(2)	4(3)
C16	21(3)	33(3)	24(3)	0(3)	8(2)	5(3)
C17	28(3)	32(3)	27(3)	-1(3)	15(2)	0(3)
C18	28(3)	27(3)	29(3)	-2(2)	13(2)	-1(3)
C19	35(3)	32(3)	28(3)	-3(3)	17(3)	0(3)
C20	33(3)	25(3)	27(3)	3(2)	11(3)	-2(3)
C21	26(3)	21(3)	30(3)	-2(2)	13(2)	-2(2)
C22	78(6)	40(4)	32(4)	6(3)	10(4)	-11(4)
C23	44(4)	26(3)	41(4)	1(3)	19(3)	-8(3)
O51	32(2)	43(3)	33(2)	4(2)	15.9(19)	-6(2)
O52	31(2)	29(2)	40(2)	-0.7(19)	17.6(19)	0.9(19)
O53	38(3)	36(3)	57(3)	2(2)	28(2)	4(2)
O54	49(3)	37(3)	28(2)	-0.5(19)	7(2)	1(2)
O55	33(2)	31(2)	31(2)	-1.0(18)	7.7(19)	5(2)
N51	26(2)	28(3)	24(2)	1(2)	10(2)	-1(2)
C51	27(3)	28(3)	28(3)	2(3)	13(2)	1(3)
C52	30(3)	22(3)	29(3)	-1(2)	11(2)	-1(3)
C53	43(3)	29(3)	36(4)	-1(3)	21(3)	-2(3)
C54	40(3)	33(4)	29(3)	5(3)	18(3)	6(3)
C55	34(3)	39(4)	29(3)	1(3)	13(3)	-2(3)
C56	35(3)	37(4)	35(3)	-1(3)	19(3)	-4(3)
C57	36(3)	28(3)	29(3)	-2(3)	17(3)	-3(3)
C58	31(3)	27(3)	36(3)	-1(3)	17(3)	0(3)
C59	32(3)	28(3)	34(3)	1(3)	19(3)	3(3)
C60	33(3)	28(3)	36(3)	3(3)	14(3)	1(3)
C61	33(3)	29(4)	49(4)	2(3)	22(3)	-2(3)
C62	35(3)	34(4)	48(4)	1(3)	18(3)	-7(3)
C63	34(3)	25(3)	34(3)	0(3)	12(3)	1(3)
C64	33(3)	28(3)	32(3)	-1(3)	15(3)	-2(3)
C65	30(3)	37(4)	27(3)	1(3)	13(3)	1(3)
C66	24(3)	33(3)	25(3)	3(3)	10(2)	-1(3)
C67	29(3)	31(3)	32(3)	-1(3)	12(3)	-2(3)
C68	39(3)	28(3)	28(3)	6(3)	12(3)	1(3)
C69	33(3)	32(4)	32(3)	2(3)	13(3)	0(3)
C70	30(3)	23(3)	32(3)	-2(2)	13(3)	-2(3)
C71	26(3)	28(3)	26(3)	5(2)	10(2)	0(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C72	66(5)	48(5)	33(4)	8(3)	1(4)	15(4)
C73	46(4)	36(4)	39(4)	0(3)	13(3)	6(3)

Table 24: Bond Lengths in Å for **NM20011**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C8	1.231(7)	O51	C58	1.216(7)
O2	C1	1.471(7)	O52	C51	1.481(7)
O2	C9	1.380(8)	O52	C59	1.379(8)
O3	C9	1.217(8)	O53	C59	1.211(8)
O4	C19	1.380(7)	O54	C69	1.369(7)
O4	C22	1.425(8)	O54	C72	1.423(9)
O5	C18	1.369(7)	O55	C70	1.370(7)
O5	C23	1.439(7)	O55	C73	1.436(8)
N1	C1	1.451(7)	N51	C51	1.443(7)
N1	C8	1.378(8)	N51	C58	1.382(8)
N1	C16	1.442(7)	N51	C66	1.437(7)
C1	C2	1.516(8)	C51	C52	1.525(8)
C1	C15	1.501(8)	C51	C65	1.495(9)
C2	C3	1.391(9)	C52	C53	1.385(9)
C2	C7	1.379(8)	C52	C57	1.388(8)
C3	C4	1.378(9)	C53	C54	1.397(9)
C4	C5	1.393(9)	C54	C55	1.401(9)
C5	C6	1.373(9)	C55	C56	1.392(9)
C6	C7	1.385(9)	C56	C57	1.361(9)
C7	C8	1.480(8)	C57	C58	1.494(8)
C9	C10	1.464(9)	C59	C60	1.466(9)
C10	C11	1.375(9)	C60	C61	1.394(9)
C10	C15	1.406(8)	C60	C65	1.372(9)
C11	C12	1.376(9)	C61	C62	1.351(10)
C12	C13	1.408(9)	C62	C63	1.397(10)
C13	C14	1.399(9)	C63	C64	1.393(9)
C14	C15	1.372(9)	C64	C65	1.387(9)
C16	C17	1.395(8)	C66	C67	1.377(8)
C16	C21	1.364(8)	C66	C71	1.393(9)
C17	C18	1.384(8)	C67	C68	1.399(8)
C18	C19	1.400(9)	C68	C69	1.377(9)
C19	C20	1.369(9)	C69	C70	1.404(9)
C20	C21	1.419(8)	C70	C71	1.372(8)

Table 25: Bond Angles in ° for **NM20011**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O2	C1	110.4(4)	O2	C1	C15	103.8(4)
C19	O4	C22	117.1(5)	N1	C1	O2	108.6(5)
C18	O5	C23	115.8(4)	N1	C1	C2	102.3(4)
C8	N1	C1	112.5(5)	N1	C1	C15	117.8(5)
C8	N1	C16	122.1(5)	C15	C1	C2	115.0(5)
C16	N1	C1	125.0(4)	C3	C2	C1	129.1(6)
O2	C1	C2	109.1(5)	C7	C2	C1	110.0(5)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	C2	C3	120.8(6)	O52	C51	C65	103.1(4)
C4	C3	C2	116.9(6)	N51	C51	O52	109.1(5)
C3	C4	C5	122.3(6)	N51	C51	C52	102.4(5)
C6	C5	C4	120.4(6)	N51	C51	C65	117.8(5)
C5	C6	C7	117.6(6)	C65	C51	C52	115.2(5)
C2	C7	C6	122.0(6)	C53	C52	C51	130.2(6)
C2	C7	C8	107.9(5)	C53	C52	C57	120.2(5)
C6	C7	C8	130.1(6)	C57	C52	C51	109.6(5)
O1	C8	N1	124.6(5)	C52	C53	C54	118.4(6)
O1	C8	C7	128.2(6)	C53	C54	C55	120.1(6)
N1	C8	C7	107.2(5)	C56	C55	C54	121.0(6)
O2	C9	C10	108.8(5)	C57	C56	C55	117.8(6)
O3	C9	O2	120.7(6)	C52	C57	C58	108.0(5)
O3	C9	C10	130.5(6)	C56	C57	C52	122.5(6)
C11	C10	C9	130.1(5)	C56	C57	C58	129.4(6)
C11	C10	C15	122.0(6)	O51	C58	N51	126.4(6)
C15	C10	C9	107.8(6)	O51	C58	C57	127.2(6)
C10	C11	C12	117.7(5)	N51	C58	C57	106.4(5)
C11	C12	C13	121.0(6)	O52	C59	C60	108.3(5)
C14	C13	C12	120.8(7)	O53	C59	O52	120.0(6)
C15	C14	C13	117.8(5)	O53	C59	C60	131.7(6)
C10	C15	C1	108.9(5)	C61	C60	C59	129.7(6)
C14	C15	C1	130.3(5)	C65	C60	C59	108.4(6)
C14	C15	C10	120.7(6)	C65	C60	C61	121.8(6)
C17	C16	N1	118.1(5)	C62	C61	C60	117.6(6)
C21	C16	N1	120.3(5)	C61	C62	C63	121.4(6)
C21	C16	C17	121.5(5)	C64	C63	C62	121.1(6)
C18	C17	C16	119.7(6)	C65	C64	C63	117.0(5)
O5	C18	C17	124.7(5)	C60	C65	C51	110.0(6)
O5	C18	C19	116.0(5)	C60	C65	C64	121.0(6)
C17	C18	C19	119.3(6)	C64	C65	C51	129.0(5)
O4	C19	C18	114.6(5)	C67	C66	N51	120.8(6)
C20	C19	O4	124.7(6)	C67	C66	C71	120.8(5)
C20	C19	C18	120.7(5)	C71	C66	N51	118.3(5)
C19	C20	C21	120.0(5)	C66	C67	C68	119.4(6)
C16	C21	C20	118.8(5)	C69	C68	C67	120.2(6)
C59	O52	C51	110.2(4)	O54	C69	C68	125.3(6)
C69	O54	C72	116.0(5)	O54	C69	C70	115.1(5)
C70	O55	C73	117.0(5)	C68	C69	C70	119.7(5)
C58	N51	C51	113.4(5)	O55	C70	C69	115.4(5)
C58	N51	C66	120.5(5)	O55	C70	C71	124.3(5)
C66	N51	C51	125.8(5)	C71	C70	C69	120.3(5)
O52	C51	C52	109.0(5)	C70	C71	C66	119.6(5)

Table 26: Torsion Angles in ° for **NM20011**.

Atom	Atom	Atom	Atom	Angle/°
O2	C1	C2	C3	-70.9(8)
O2	C1	C2	C7	112.0(5)
O2	C1	C15	C10	5.0(6)
O2	C1	C15	C14	-179.5(6)
O2	C9	C10	C11	-178.2(6)
O2	C9	C10	C15	1.0(7)

Atom	Atom	Atom	Atom	Angle/°
O3	C9	C10	C11	1.4(11)
O3	C9	C10	C15	-179.4(6)
O4	C19	C20	C21	178.4(5)
O5	C18	C19	O4	0.2(8)
O5	C18	C19	C20	-179.7(5)
N1	C1	C2	C3	174.2(6)
N1	C1	C2	C7	-2.9(6)
N1	C1	C15	C10	125.1(5)
N1	C1	C15	C14	-59.4(8)
N1	C16	C17	C18	176.5(5)
N1	C16	C21	C20	-174.7(5)
C1	O2	C9	O3	-177.3(5)
C1	O2	C9	C10	2.3(6)
C1	N1	C8	O1	177.2(6)
C1	N1	C8	C7	-2.5(7)
C1	N1	C16	C17	83.6(7)
C1	N1	C16	C21	-100.1(7)
C1	C2	C3	C4	-177.7(6)
C1	C2	C7	C6	178.6(6)
C1	C2	C7	C8	1.6(7)
C2	C1	C15	C10	-114.1(6)
C2	C1	C15	C14	61.4(8)
C2	C3	C4	C5	0.4(10)
C2	C7	C8	O1	-179.2(7)
C2	C7	C8	N1	0.5(7)
C3	C2	C7	C6	1.2(9)
C3	C2	C7	C8	-175.8(6)
C3	C4	C5	C6	-0.1(10)
C4	C5	C6	C7	0.3(10)
C5	C6	C7	C2	-0.9(9)
C5	C6	C7	C8	175.4(6)
C6	C7	C8	O1	4.2(12)
C6	C7	C8	N1	-176.2(6)
C7	C2	C3	C4	-0.9(9)
C8	N1	C1	O2	-112.0(5)
C8	N1	C1	C2	3.2(7)
C8	N1	C1	C15	130.4(6)
C8	N1	C16	C17	-89.0(7)
C8	N1	C16	C21	87.2(7)
C9	O2	C1	N1	-130.6(5)
C9	O2	C1	C2	118.6(5)
C9	O2	C1	C15	-4.5(6)
C9	C10	C11	C12	178.6(6)
C9	C10	C15	C1	-3.8(7)
C9	C10	C15	C14	-179.8(5)
C10	C11	C12	C13	1.0(9)
C11	C10	C15	C1	175.4(5)
C11	C10	C15	C14	-0.6(9)
C11	C12	C13	C14	-0.5(10)
C12	C13	C14	C15	-0.5(9)
C13	C14	C15	C1	-174.0(6)
C13	C14	C15	C10	1.0(9)
C15	C1	C2	C3	45.3(9)
C15	C1	C2	C7	-131.8(5)
C15	C10	C11	C12	-0.4(9)

Atom	Atom	Atom	Atom	Angle/°
C16	N1	C1	O2	74.7(7)
C16	N1	C1	C2	-170.0(5)
C16	N1	C1	C15	-42.8(8)
C16	N1	C8	O1	-9.3(10)
C16	N1	C8	C7	171.0(5)
C16	C17	C18	O5	-179.3(5)
C16	C17	C18	C19	-2.7(8)
C17	C16	C21	C20	1.5(8)
C17	C18	C19	O4	-176.7(5)
C17	C18	C19	C20	3.4(9)
C18	C19	C20	C21	-1.7(9)
C19	C20	C21	C16	-0.7(8)
C21	C16	C17	C18	0.2(8)
C22	O4	C19	C18	163.9(6)
C22	O4	C19	C20	-16.2(9)
C23	O5	C18	C17	-6.7(8)
C23	O5	C18	C19	176.6(5)
O52	C51	C52	C53	69.2(8)
O52	C51	C52	C57	-112.0(5)
O52	C51	C65	C60	-0.4(7)
O52	C51	C65	C64	-178.5(6)
O52	C59	C60	C61	177.0(6)
O52	C59	C60	C65	-0.2(7)
O53	C59	C60	C61	-2.9(12)
O53	C59	C60	C65	179.8(7)
O54	C69	C70	O55	-0.5(8)
O54	C69	C70	C71	176.5(5)
O55	C70	C71	C66	178.3(5)
N51	C51	C52	C53	-175.3(6)
N51	C51	C52	C57	3.4(6)
N51	C51	C65	C60	-120.6(6)
N51	C51	C65	C64	61.4(8)
N51	C66	C67	C68	174.0(5)
N51	C66	C71	C70	-174.8(5)
C51	O52	C59	O53	179.9(6)
C51	O52	C59	C60	0.0(7)
C51	N51	C58	O51	-178.4(6)
C51	N51	C58	C57	3.4(7)
C51	N51	C66	C67	99.6(7)
C51	N51	C66	C71	-84.4(7)
C51	C52	C53	C54	179.0(6)
C51	C52	C57	C56	-179.6(6)
C51	C52	C57	C58	-1.6(7)
C52	C51	C65	C60	118.3(6)
C52	C51	C65	C64	-59.8(8)
C52	C53	C54	C55	0.3(9)
C52	C57	C58	O51	-179.2(6)
C52	C57	C58	N51	-0.9(7)
C53	C52	C57	C56	-0.7(10)
C53	C52	C57	C58	177.2(6)
C53	C54	C55	C56	-0.5(10)
C54	C55	C56	C57	0.2(10)
C55	C56	C57	C52	0.4(10)
C55	C56	C57	C58	-177.0(6)
C56	C57	C58	O51	-1.4(11)

Atom	Atom	Atom	Atom	Angle/°
C56	C57	C58	N51	176.8(7)
C57	C52	C53	C54	0.3(9)
C58	N51	C51	O52	111.2(5)
C58	N51	C51	C52	-4.2(6)
C58	N51	C51	C65	-131.7(5)
C58	N51	C66	C67	-87.4(7)
C58	N51	C66	C71	88.6(7)
C59	O52	C51	N51	126.2(5)
C59	O52	C51	C52	-122.7(5)
C59	O52	C51	C65	0.2(6)
C59	C60	C61	C62	-177.7(7)
C59	C60	C65	C51	0.4(7)
C59	C60	C65	C64	178.6(5)
C60	C61	C62	C63	0.3(11)
C61	C60	C65	C51	-177.1(6)
C61	C60	C65	C64	1.1(10)
C61	C62	C63	C64	-0.2(11)
C62	C63	C64	C65	0.5(9)
C63	C64	C65	C51	176.9(6)
C63	C64	C65	C60	-1.0(9)
C65	C51	C52	C53	-46.1(9)
C65	C51	C52	C57	132.6(5)
C65	C60	C61	C62	-0.8(10)
C66	N51	C51	O52	-75.3(7)
C66	N51	C51	C52	169.3(5)
C66	N51	C51	C65	41.7(8)
C66	N51	C58	O51	7.8(10)
C66	N51	C58	C57	-170.5(5)
C66	C67	C68	C69	-0.2(9)
C67	C66	C71	C70	1.1(9)
C67	C68	C69	O54	-177.2(6)
C67	C68	C69	C70	2.9(9)
C68	C69	C70	O55	179.4(5)
C68	C69	C70	C71	-3.6(9)
C69	C70	C71	C66	1.6(9)
C71	C66	C67	C68	-1.8(9)
C72	O54	C69	C68	3.7(9)
C72	O54	C69	C70	-176.4(6)
C73	O55	C70	C69	-172.3(5)
C73	O55	C70	C71	10.9(8)

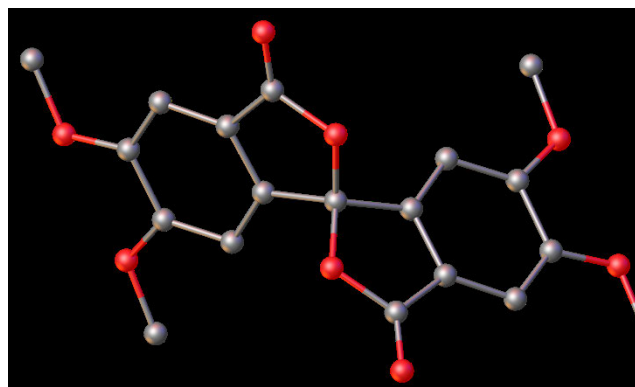
Table 27: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **NM20011**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H3	5140.34	6114.13	7213.57	43
H4	4891.3	6704.35	8039.12	44
H5	3937.96	8149.63	7874.98	43
H6	3201.24	9073.34	6867.39	42
H11	5820.24	3857.49	5733.38	39
H12	5300.05	1227.38	5670.72	39
H13	4278.41	1124.2	5675.43	38
H14	3764.71	3676.03	5758.92	34

Atom	x	y	z	U_{eq}
H17	3059.1	5179.26	4772.7	33
H20	3177.52	9717.83	3541.81	35
H21	3721.28	9928.73	4656.38	31
H22A	1993.66	8296.97	2056.14	83
H22B	2726.67	8973.01	2470.35	83
H22C	2159.73	9494.05	2654.85	83
H23A	2173.62	2161	3642.29	56
H23B	2260.91	3418.5	4205.62	56
H23C	2892.78	2683.2	4163.17	56
H53	2094.95	1185.63	7292.46	41
H54	3155.77	1778.45	8096.77	40
H55	3913.72	3238.13	7862.62	41
H56	3632.64	4085.53	6826.36	41
H61	-75.8	-1075.23	5771.11	42
H62	364.59	-3678.16	5688.92	47
H63	1399.28	-3825.54	5728.86	39
H64	2018.71	-1310.74	5842.79	37
H67	965.34	4933.35	4707.57	38
H68	427.86	4731.04	3604.85	39
H71	1737.53	184.51	4805.38	33
H72A	25.36	3309.52	2098.37	86
H72B	444.03	4589.14	2665.14	86
H72C	-227.37	3790.51	2603.08	86
H73A	1477.19	-2842.5	3644.14	64
H73B	1289.59	-2268.24	4185.67	64
H73C	1971.86	-1672.36	4213.97	64

$R_1=5.64\%$

Crystal Data and Experimental



Experimental. Single colourless needle crystals of **nm20011b** recrystallised from methanol by slow evaporation. A suitable crystal with dimensions $0.28 \times 0.05 \times 0.03 \text{ mm}^3$ was selected and mounted on a MITIGEN holder in Paratone oil. on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at a steady $T = 120.00(10) \text{ K}$ during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{19}\text{H}_{16}\text{O}_8$, $M_r = 372.32$, orthorhombic, $Fdd2$ (No. 43), $a = 15.962(2) \text{ \AA}$, $b = 43.558(7) \text{ \AA}$, $c = 4.7954(5) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 3334.2(8) \text{ \AA}^3$, $T = 120.00(10) \text{ K}$, $Z = 8$, $Z' = 0.5$, $\mu(\text{Cu K}\alpha) = 0.996$, 13162 reflections measured, 1467 unique ($R_{\text{int}} = 0.0947$) which were used in all calculations. The final wR_2 was 0.1447 (all data) and R_1 was 0.0564 ($I \geq 2 \sigma(I)$).

Compound	nm20011b
Formula	$\text{C}_{19}\text{H}_{16}\text{O}_8$
$D_{\text{calc.}} / \text{g cm}^{-3}$	1.483
ρ / mm^{-1}	0.996
Formula Weight	372.32
Colour	colourless
Shape	needle
Size/ mm^3	$0.28 \times 0.05 \times 0.03$
T/K	120.00(10)
Crystal System	orthorhombic
Flack Parameter	-0.4(4)
Hooft Parameter	-0.6(3)
Space Group	$Fdd2$
$a/\text{\AA}$	15.962(2)
$b/\text{\AA}$	43.558(7)
$c/\text{\AA}$	4.7954(5)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$V/\text{\AA}^3$	3334.2(8)
Z	8
Z'	0.5
Wavelength/ $\text{\AA}$	1.54178
Radiation type	Cu $\text{K}\alpha$
$\rho_{\text{min}}/^\circ$	4.060
$\rho_{\text{max}}/^\circ$	76.261
Measured Refl's.	13162
Indep't Refl's	1467
Refl's $I \geq 2 \sigma(I)$	1298
R_{int}	0.0947
Parameters	125
Restraints	1
Largest Peak	0.214
Deepest Hole	-0.304
GooF	1.064
wR_2 (all data)	0.1447
wR_2	0.1387
R_1 (all data)	0.0657
R_1	0.0564

Structure Quality Indicators

Reflections:	d min (Cu)	0.79	I/ σ (I)	13.9	R _{int}	9.47%	complete	86%		
Refinement:	Shift	0.000	Max Peak	0.2	Min Peak	-0.3	Goof	1.064	Flack	-0.4(4)

A colourless needle-shaped crystal with dimensions $0.28 \times 0.05 \times 0.03 \text{ mm}^3$ was mounted on a MITIGEN holder in Paratone oil.. Data were collected using a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature device operating at $T = 120.00(10) \text{ K}$.

Data were measured using θ scans using Cu K α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.61a, 2019). The maximum resolution that was achieved was $\theta = 76.261^\circ$ ($0.79 \text{ \AA}$).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.61a, 2019). The unit cell was refined using CrysAlisPro (Rigaku, V1.171.40.61a, 2019) on 1962 reflections, 15% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.40.61a, 2019). The final completeness is 100.00 % out to 76.261° in θ . A multi-scan absorption correction was performed using SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. $wR_2(\text{int})$ was 0.1171 before and 0.0837 after correction. The Ratio of minimum to maximum transmission is 0.6572. The $\theta/2$ correction factor is Not present. . The absorption coefficient μ of this material is 0.996 mm^{-1} at this wavelength ($\lambda = 1.54178 \text{ \AA}$) and the minimum and maximum transmissions are 0.310 and 0.472.

The structure was solved and the space group $Fdd2$ (# 43) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: The identity of O4 was established by refinement of the occupancy and analysis of Fourier maps for H atoms.

The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

The Flack parameter was refined to -0.4(4). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in -0.6(3). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

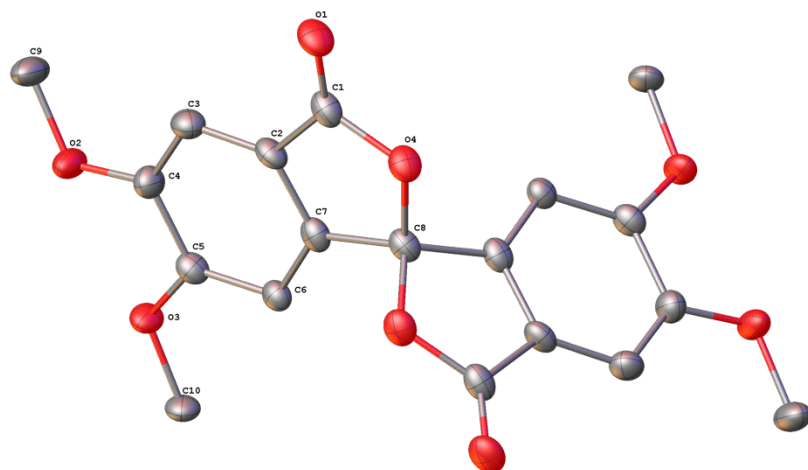
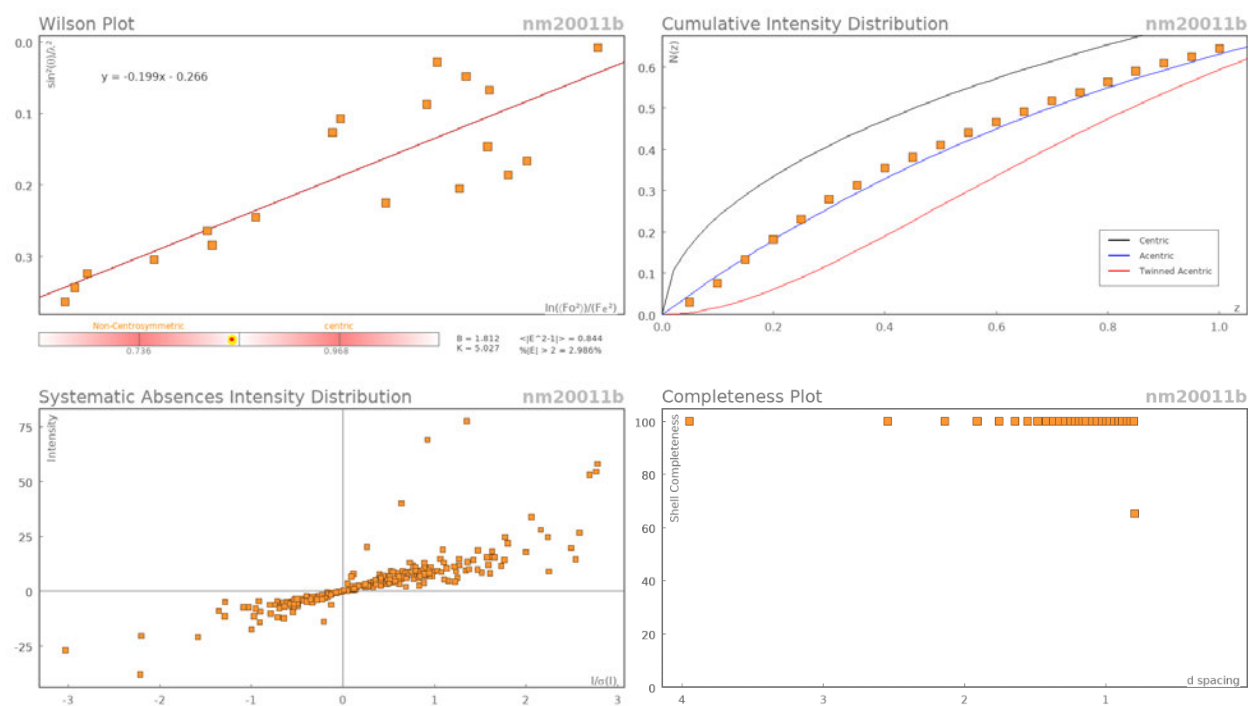
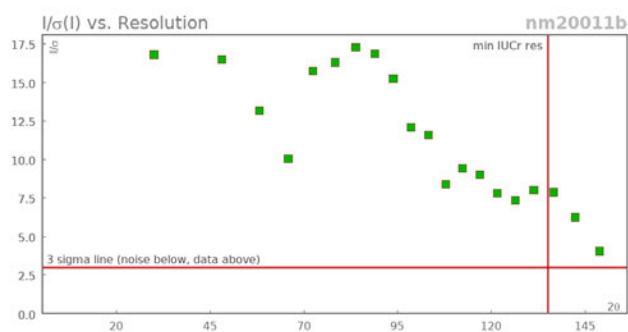


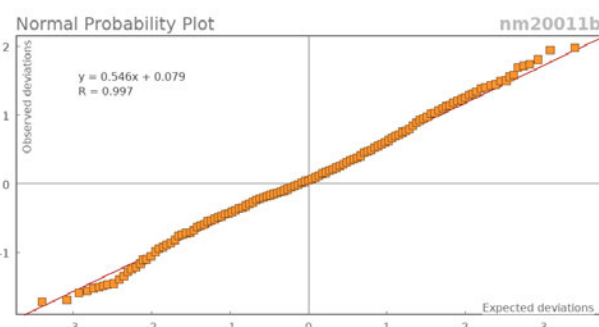
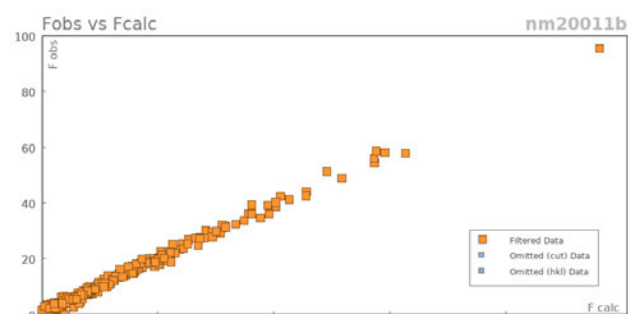
Figure 13: Twice the asymmetric unit (labelled) of NM20011b. Displacement ellipsoids are at the 50% probability level and H atoms are not shown.

Data Plots: Diffraction Data





Data Plots: Refinement and Data



Reflection Statistics

Total reflections (after filtering)	13598	Unique reflections	1467
Completeness	0.84	Mean I/σ	11.79
$hkl_{\max}$ collected	(20, 53, 4)	$hkl_{\min}$ collected	(-19, -54, -5)
$hkl_{\max}$ used	(20, 54, 4)	$hkl_{\min}$ used	(0, 0, -5)
Lim $d_{\max}$ collected	100.0	Lim $d_{\min}$ collected	0.77
$d_{\max}$ used	10.89	$d_{\min}$ used	0.79
Friedel pairs	1478	Friedel pairs merged	0
Inconsistent equivalents	0	R_{int}	0.0947
R_{sigma}	0.072	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(1730, 986, 887, 562, 283, 147, 108, 49, 47, 25, 25, 15, 15, 10, 2, 2, 1)	Maximum multiplicity	57
Removed systematic absences	436	Filtered off (Shel/OMIT)	0

Table 28: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **nm20011b**. U_{eq} is defined as $1/3$ of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
O3	3168.0(17)	5610.2(6)	780(6)	24.7(7)
O4	5633.0(17)	5136.0(7)	9032(6)	23.7(7)
O2	3987.1(18)	6089.2(6)	2059(7)	29.1(7)
O1	6172.0(18)	5600.5(7)	9924(6)	29.0(7)
C6	3982(2)	5278.3(9)	3826(8)	19.6(8)
C4	4234(2)	5831.8(9)	3415(9)	23.7(9)
C7	4644(2)	5270.6(9)	5726(9)	20.9(8)
C1	5672(2)	5450.2(10)	8624(9)	23.1(9)
C5	3782(2)	5563.5(9)	2695(8)	21.4(8)

Atom	x	y	z	U_{eq}
C2	5056(2)	5533.1(9)	6503(9)	21.3(8)
C3	4875(2)	5818.6(9)	5379(10)	24.5(9)
C10	2651(2)	5355.4(9)	58(10)	24.9(9)
C8	5000	5000	7276(12)	20.7(11)
C9	4500(3)	6358.3(9)	2414(12)	34.3(11)

Table 29: Anisotropic Displacement Parameters ($\times 10^4$) for **nm20011b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O3	21.2(14)	24.2(13)	28.5(16)	1.1(12)	-11.2(13)	-1.9(11)
O4	24.8(13)	28.7(14)	17.6(15)	-1.6(11)	-5.2(12)	4.4(11)
O2	24.9(13)	20.8(13)	41.6(19)	6.3(13)	-11.9(14)	-3.8(11)
O1	24.2(14)	36.4(15)	26.3(18)	-4.8(14)	-8.9(13)	3.4(12)
C6	17.9(17)	22.7(18)	18.1(19)	-2.1(14)	0.8(16)	2.2(14)
C4	23.6(18)	21.6(18)	26(2)	2.7(16)	-3.2(18)	1.2(14)
C7	20.5(17)	26.1(19)	16(2)	-0.5(15)	1.9(15)	5.2(14)
C1	21.4(18)	30.6(19)	17(2)	-2.6(16)	-0.6(16)	6.9(16)
C5	19.5(17)	28.0(19)	17(2)	-0.3(16)	-3.5(17)	1.5(15)
C2	15.9(16)	30.0(19)	18(2)	-2.9(16)	-2.9(16)	2.3(14)
C3	21.0(18)	25.2(19)	27(2)	-2.6(17)	-3.1(18)	-2.5(14)
C10	19.4(18)	24.8(18)	31(2)	-3.7(17)	-6.3(18)	-5.4(15)
C8	19(2)	28(3)	15(3)	0	0	3(2)
C9	27(2)	25(2)	51(3)	7(2)	-10(2)	-7.7(17)

Table 30: Bond Lengths in Å for **nm20011b**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	C5	1.358(5)	C6	C5	1.393(5)
O3	C10	1.426(4)	C4	C5	1.416(5)
O4	C1	1.384(5)	C4	C3	1.391(6)
O4	C8	1.443(5)	C7	C2	1.370(5)
O2	C4	1.355(5)	C7	C8	1.505(5)
O2	C9	1.440(5)	C1	C2	1.461(6)
O1	C1	1.205(5)	C2	C3	1.386(6)
C6	C7	1.396(6)			

Table 31: Bond Angles in ° for **nm20011b**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	O3	C10	117.7(3)	C2	C7	C8	109.8(3)
C1	O4	C8	110.8(3)	O4	C1	C2	108.2(3)
C4	O2	C9	116.8(3)	O1	C1	O4	119.6(4)
C5	C6	C7	116.7(4)	O1	C1	C2	132.2(4)
O2	C4	C5	114.7(4)	O3	C5	C6	124.2(3)
O2	C4	C3	125.0(4)	O3	C5	C4	114.1(3)
C3	C4	C5	120.4(3)	C6	C5	C4	121.6(3)
C6	C7	C8	128.8(3)	C7	C2	C1	107.8(4)
C2	C7	C6	121.4(4)	C7	C2	C3	122.9(4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	C2	C1	129.3(4)	O4	C8	C7 ¹	110.21(19)
C2	C3	C4	117.0(4)	O4	C8	C7	103.4(2)
O4	C8	O4 ¹	108.6(5)	C7	C8	C7 ¹	120.8(5)
O4 ¹	C8	C7	110.22(19)				
O4 ¹	C8	C7 ¹	103.4(2)	¹ 1-x,1-y,+z			

Table 32: Torsion Angles in ° for nm20011b.

Atom	Atom	Atom	Atom	Angle/°
O4	C1	C2	C7	1.5(5)
O4	C1	C2	C3	-179.0(4)
O2	C4	C5	O3	-0.7(5)
O2	C4	C5	C6	177.4(4)
O2	C4	C3	C2	-178.4(4)
O1	C1	C2	C7	-179.6(4)
O1	C1	C2	C3	0.0(8)
C6	C7	C2	C1	176.5(4)
C6	C7	C2	C3	-3.1(7)
C6	C7	C8	O4 ¹	-60.9(6)
C6	C7	C8	O4	-176.7(4)
C6	C7	C8	C7 ¹	59.6(4)
C7	C6	C5	O3	178.6(4)
C7	C6	C5	C4	0.7(6)
C7	C2	C3	C4	1.1(7)
C1	O4	C8	O4 ¹	-117.4(3)
C1	O4	C8	C7 ¹	130.1(3)
C1	O4	C8	C7	-0.3(4)
C1	C2	C3	C4	-178.4(4)
C5	C6	C7	C2	2.1(6)
C5	C6	C7	C8	179.9(4)
C5	C4	C3	C2	1.7(6)
C2	C7	C8	O4 ¹	117.2(4)
C2	C7	C8	O4	1.3(4)
C2	C7	C8	C7 ¹	-122.4(3)
C3	C4	C5	O3	179.2(4)
C3	C4	C5	C6	-2.6(6)
C10	O3	C5	C6	5.5(6)
C10	O3	C5	C4	-176.5(4)
C8	O4	C1	O1	-179.8(4)
C8	O4	C1	C2	-0.7(4)
C8	C7	C2	C1	-1.7(5)
C8	C7	C2	C3	178.7(4)
C9	O2	C4	C5	-171.5(4)
C9	O2	C4	C3	8.6(6)

¹1-x,1-y,+z

Table 33: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **nm20011b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H6	3682.92	5097.85	3328.17	23
H3	5174.71	5997.14	5923.97	29
H10A	2235.4	5419.88	-1328.77	37
H10B	2362.89	5280.07	1728.07	37
H10C	2998.43	5191.07	-723.12	37
H9A	4298.67	6521.77	1180.63	51
H9B	5082.41	6308.78	1947.58	51
H9C	4468.53	6427.41	4355.97	51