PhD PROJECT PROPOSAL

PhD PROJECT TITLE
Topological molecules for semiconducting materials.

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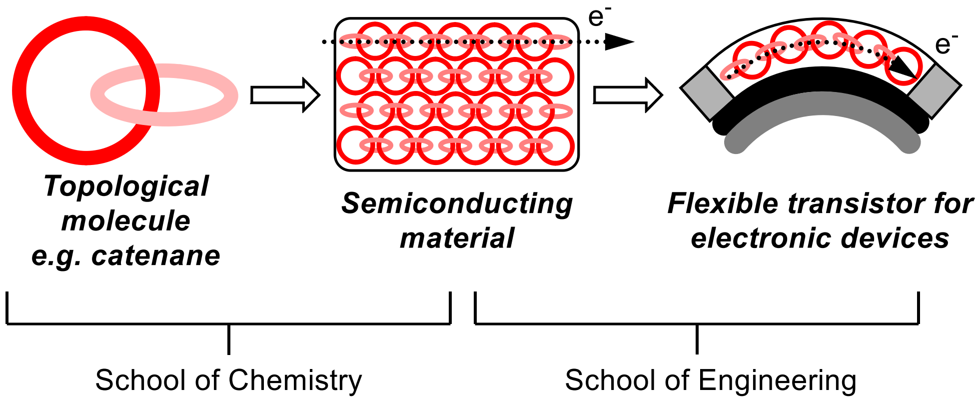
PROJECT ABSTRACT
The aim of this project is to use **molecular topology** to improve the **electrical properties** of materials (Fig.).

Molecules with **complex topologies** are fascinating because they contain the **newest bond** in chemistry**,** a molecular link! A good example is a **catenane** (Figure). You may have seen catenanes before because their development at Birmingham led to the 2016 **Nobel Prize in Chemistry**.

However, the topology of these molecules has never been used to control semiconductivity in materials. These electronic materials are critical for futuristic devices such as **foldable display screens**.

In this project we will make new catenane materials in the School of **Chemistry**. Then we will use their topology to optimise transistors in the School of **Engineering**.



APPLICATION OF TOPOLOGY

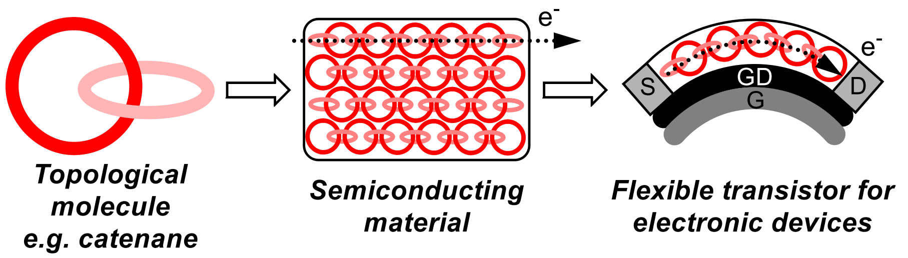
Topological design is central to this project. Initially, it uses molecules that have non-trivial topologies to strengthen intermolecular interactions. Secondly, molecular topology is used to increase the ordering of molecules in a material. For the first time, this work will enable us to understand how molecular topology is connected to the semiconductivity of an organic material.

This interdisciplinary project feeds into multiple themes of the CDT; i) Chemistry, ii) Mathematical, Computational and Data Sciences, iii) Manufacturing, Fabrication and 3D Printing and iv) Health and Life Sciences.

DETAILED PROJECT DESCRIPTION

Topological molecules for semiconducting materials.

In this project, the candidate will design and construct molecules with non-trivial topologies and use them to fabricate high-performance organic semiconducting materials and transistor devices.



Main location	Chemistry	Chemistry/Engineering	Engineering
Core Training	Molecular synthesis	Microfabrication	Electronic measurement

Fig. 1: Project outline. (e^- = electron, S = source, D = drain, G = gate, GD = gate dielectric)

Background: This project will address the limitations of organic semiconducting materials through **precise engineering of molecular topology** (Fig. 1). Lightweight and flexible, organic semiconducting (OSC) materials are integral to delivering next-generation electronic devices, such as point-of-care diagnostics, wearable sensors, and foldable displays.[1] Further benefits of OSCs include molecular-scale engineering and sustainable manufacturing. Therefore, OSCs represent ideal materials for constructing organic field-effect transistors (OFETs), essential components in the above devices.[2] However, OFET performance is currently restricted by charge mobility (i.e. conductivity), long-term stability and processability of OSCs.

Project outline: The properties of OSCs are intrinsically connected to the **topology of their constituent molecules**. For example, requirements for high charge mobility and stability have led to the use of spherical-shaped carbon nanomaterials (fullerenes) that increase intermolecular contacts (Fig. 2a).[3] This enhances hole-electron hopping and prevents ingress of unwanted degradants (O_2/H_2O). The **chiral topology** of molecules provides a further handle to optimise charge transport[4] and yet has barely been exploited for OSCs because almost all molecular building-blocks are achiral. This includes **1.1** (Fig. 2b), the parent molecule of a class of organic compounds known as perylene diimides (PDIs), ideally suited for plastic electronics on account of good conductivity, stability and availability.[5]
This project will synthesise a series of **PDI molecules with non-trivial topologies** (Fig. 2b), including chiral derivatives (**1.2**) and molecular links, also known as catenanes (**1.3**).[6] Molecular links are chemistry's newest type of bond yet are unexplored for OSCs. Molecular topology will maximise intermolecular contacts to enhance charge mobility and stability. Therefore, this project will map out the **topology-properties relationship** of OSCs, providing a blueprint for the development of future materials from the **bottom-up** by rational design.

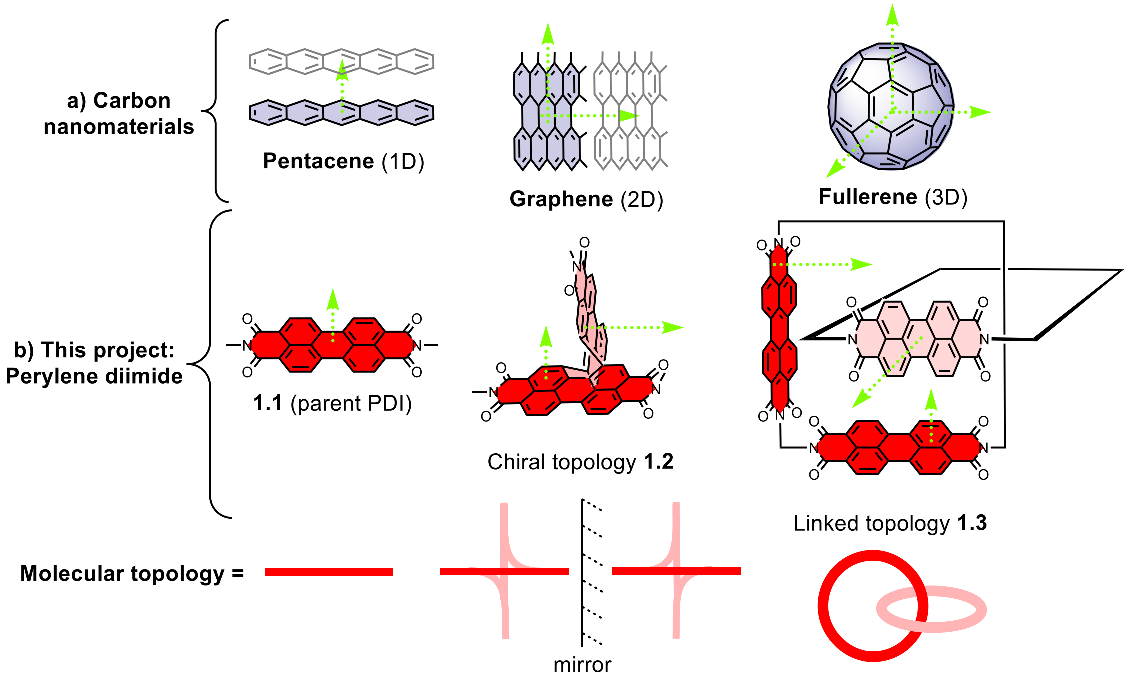


Fig. 2. Increasing intermolecular contacts by exploiting molecular topology.

Controlling the arrangement of molecules in OSCs is challenging, yet ordered structures are of central importance to device performance. Our recent work has shown that **molecular self-assembly** is a powerful tool for enhancing charge mobility, stability and processability.[7] Crucially, self-assembly relies on the **complementary topology** of molecules to direct their close association (Fig. 3a). Therefore, this project will also use molecular topology (e.g. **2.1**) to form **ordered polymer stacks** (**2.2**) and **polymers of molecular links** (**2.3**) of PDI, providing channels to facilitate charge transport. This is analogous to conduction down complementary strands of DNA (Fig. 3b).[8] Topology-directed self-assembly will form robust arrays of tightly-interacting molecules, delivering high-performance OSCs for flexible OFET devices.

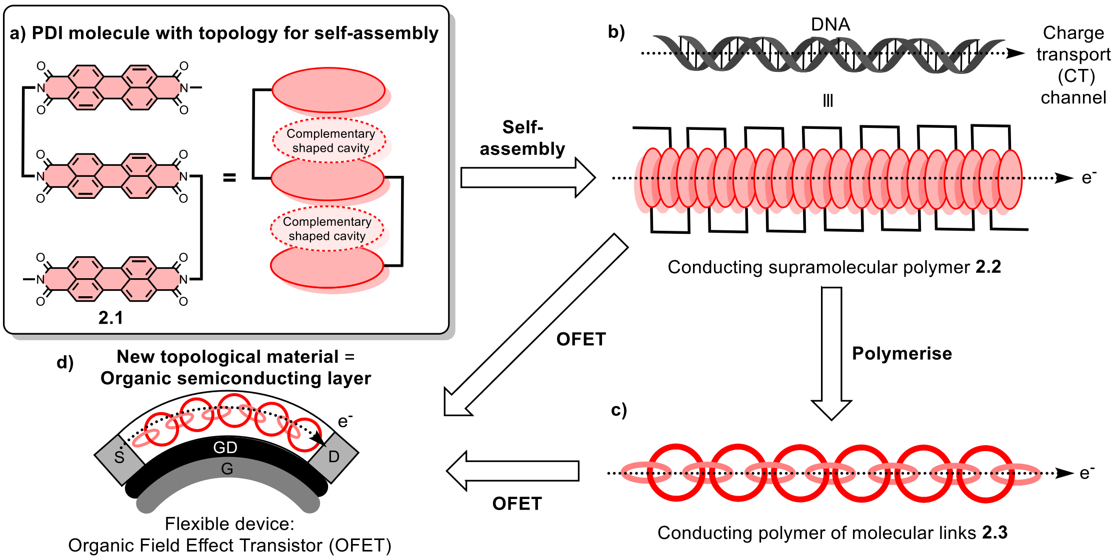


Fig. 3. a) Molecular topology enables: b) self-assembly into a supramolecular polymer and c) a polymer of molecular links, both semiconducting materials for d) flexible OFETs.

Aims:

1. **To fabricate high-performance OSC materials by exploiting molecular topology to enhance intermolecular contacts (WP1)**

2. **To use topology to direct molecular self-assembly and improve OSC crystallinity and performance in OFETs (WP2)**

Methodology: An integrated approach is required for each aim; hence the candidate will work in Chemistry and Engineering throughout the project, supervised by TB and GC respectively. In each work package (WP), topological molecular design is used to control material morphology and optimise OFET performance. The independence of these WPs reduces risk.

WP1: Topological PDI molecules are designed (Fig. 2b) and prepared in high analytical purity using straightforward syntheses in Chemistry (TB). From these, semiconducting materials are fabricated by spin-coating in Engineering (microfabrication cleanroom, GC) and characterised using in-house techniques across Schools (see skills). In collaboration with MJ, this will include mechanical properties (e.g. flexibility). Materials will then be integrated into OFETs (GC, Fig. 3d) to measure mobility and stability and map-out topology-function relationship (**Aim 1 – Yr. 2-3**).

WP2: PDIs designed with complementary topologies for molecular self-assembly will be prepared via well-established synthetic methods and subjected to rigorous purification and characterisation (TB. Fig. 3a). Self-assembly (Fig. 3b,c) will be quantified using in-house techniques in solution and solid-state (TB, see skills). OFETs will be fabricated from these OSCs (GC, Fig. 3d) and their performance correlated with degree of self-assembly (**Aim 2 – Yr. 3-4**).

Training and Skills: The candidate will be an integral member of TB (Chemistry) and GC (Engineering) research teams and be involved with associated supervision activities from both (e.g. group-meetings, seminars, problem-classes, literature presentations). The candidate will receive **extensive training** in modern synthetic chemistry, including cutting-edge purification (e.g. high-performance-liquid-chromatography, TB). Training will be on a range of analytical instruments for solution and solid-state characterisation (e.g. NMR, absorption/emission spectroscopies, mass-spectrometry, cyclic-voltammetry, X-ray diffraction, microscopy). Unique to this project, the candidate will learn to **quantify molecular interactions** using state-of-the-art instrumentation and **computational modelling**. The candidate will diversify skillsets by working across length scales; receiving training in microfabrication (spin-coating, sputtering and photolithography) of organic materials and devices as well as electronic measurement and parameter extraction (GC).

From molecule to material to device design, this project equips the candidate with a **multi-disciplinary skillset** that will be integral to working in plastic electronic manufacturing. This will be complemented by **interdisciplinary knowledge** and skills in **scientific communication**, making the candidate ideally qualified for employment in chemistry or engineering, fields where the UK is a world-leader. This includes both industry and academia. This project will develop advanced **critical thinking** and **problem-solving**, essential skills that translate outside of research and development.

Topological design: Topological design of molecules is at the core of this project; for example, molecular links are proposed because their unique topology will enhance charge carrier mobility in OSCs and OFETs. Molecular topology will also be vital to enabling material fabrication via molecular self-assembly. This links to several themes of the CDT (see above).

Research links: TB has extensive experience in chemical synthesis, molecular self-assembly and organic electronic materials (connecting to current OLED research). GC has an extensive background in microfabrication, printed, and flexible electronics and has measured and modelled the electrical behaviour of OSC devices.

Research strategies: Integral to this project, molecular self-assembly directly addresses the **EPSRC Phys. Sci. grand challenge** 'directed assembly of extended structures'. This project delivers materials for prototype OFET biosensors, devices with outstanding societal importance that fit the priority area of **'21st century products'** under the 'Manufacturing the future' theme. In line with **UoB's strategic research plans**, this project is challenege-led research that underpins innovative and collaborative materials development across three EPS Schools (Chemistry, Engineering, Met&Mat).

Candidate background and interests: This project would be suitable for any physical scientist or engineer with an interest in chemistry, materials or electronic engineering. The substantial training aspect means that previous experience in molecular synthesis or material/device fabrication is not required.

Refs: 1. *Royal Society of Chemistry*, **2012**. https://tinyurl.com/y4r6dtzf 2. *Chem. Rev*. **2019**, 119, 3. 3. *J. Mater. Chem. C.* **2018**, 6, 3514. 4. *ChemRxiv. Preprint*. **2020**, DOI: 10.26434/chemrxiv.12496040.v1. 5. *Acc. Chem. Res*. **2015**, 48, 2, 267. 6. *Angew. Chem. Int. Ed.* **2015**, 54, 6110. 7. *Chem. Eur. J.* **2020**, 26, 3744. 8. *Chem. Rev*. **2010**, 110, 3, 1642.