

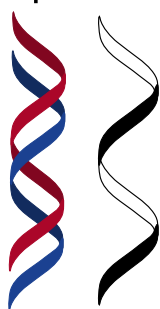
Helicene Radicals as Chiral Conductive Materials (HR-CCM)

The spin-selective transport of electrons through chiral materials (chiral induced spin selectivity, CISS) could revolutionise areas such as disruptive quantum technologies or spintronics computing, or more efficient hydrogen generation for carbon-neutral fuels. However, the study and real-world exploitation of the CISS effect is limited by the low conductivity and processability of the most commonly used materials, DNA and oligopeptides. Here, I propose open shell Helicene Radicals as Chiral Conductive Materials (HR-CCM) with improved device compatibility by combining good conductivities and chiral spin selectivity with solution or vacuum processing.

Vision

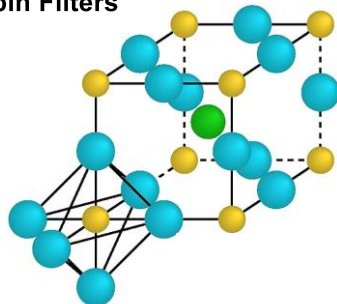
V1 Background and Challenges Spin-selective electron transport at room temperature could revolutionise computing through spintronics or quantum technologies, lead to more efficient hydrogen generation from water electrolysis, or even improve our understanding of electron transport in enzymes.^{1–3} In 2011, Naaman and co-workers demonstrated that such spin-filtering could be achieved using DNA due to the Chiral Induced Spin Selectivity (CISS) effect.⁴ Despite more than a decade of research interest, **a lack of suitable materials limits the exploitation of CISS at a device scale,⁵ or in other real-world applications.** The most commonly studied materials, self-assembled monolayers (SAM) of DNA or α -helix polyaniline (AHPA), are limited by low conductivities and not compatible with conventional device fabrication or operation conditions. Chiral perovskites are a rare example of more conductive CISS materials, but their use in spintronics applications is limited by low spin coherence times⁵ due to the presence of many heavy atoms.

Examples of Chiral Spin Filters



DNA & Oligopeptides

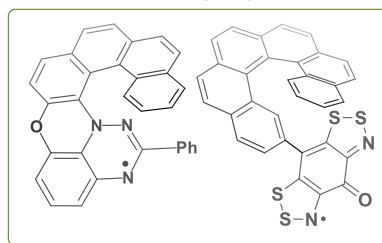
- ✓ Well-studied
- ✓ $\approx 60\%$ spin polarization
- ✗ low conductivity
- ✗ low processability



Chiral Perovskites

- ✗ low spin coherence
- ✓ high conductivity
- ✓ solution processing
- ✓/✗ limited vacuum processing

This proposal



Radical Helicenes

- ✓ high spin coherence
- ✓ high conductivity
- ✓ solution processing
- ✓ vacuum processing

More processable materials are needed to maintain spin filtering in bulk measurements.

Impressive spin filtering $>80\%$ has been measured using magnetic conductive atomic force microscopy (mC-AFM) at the nanoscale.⁶

However, the

spin filtering is not maintained in bulk measurements such as magnetoresistance (MR), where MR values between 0.01% and $<5\%$ have been reported.^{6,7} This discrepancy is due to the limited coverage observed with the SAM or fibres typically used for these experiments, which cannot form perfect layers on the μm length scale of devices.⁸ Through these imperfections (pinholes), the bulk of the current is transported with little or no spin control.⁷ To overcome these limitations, the materials proposed here avoid the use of SAM and are designed to form thin films through solution- or vacuum-processing (cf. WP2 and C2.2).

Highly conductive chiral materials could enable CISS in real-world applications. In traditional spintronics, organic materials possess long spin lifetimes but short spin-diffusion lengths due to the reduced mobilities compared to inorganic materials.⁹ While the impact of mobility on spin-filtering in CISS is not yet known, high charge mobilities would let spin-polarised electrons travel further over the same spin-diffusion time and thus help preserve spin coherence over device dimensions,¹⁰ particularly if CISS originates in the spinterface between the metal and the chiral material.¹¹ Additionally, high conductivities are a necessary (though not sufficient) requirement for the current densities in real-world applications such as circularly polarised (CP) light emitting spin-LEDs⁵ or the CISS-driven low-overpotential oxygen evolution reaction in water splitting.^{12,13}

V2 Research Aim: design and synthesise radical helicenes that combine technologically relevant processability and conductivities with chiral spin filtering. It should be stressed that it is not the goal to rival neither the best existing non-chiral single-component radical conductors (SCRC), nor the highest levels of spin filtering reported. Instead, the aim is to identify architectures and compound classes that can combine room temperature spin filtering *and* high conductivities in

solution- or vacuum-processable molecules, eventually leading to applications such as water splitting, single-layer spin valves for spintronics, or charge transport materials for CP spin-OLEDs.

Objective 1 Design and synthesise helicene radicals based on known SCRCs. Neutral helicene monoradicals are rare and have not been assessed for their charge transport abilities.¹⁴ To reduce risk, the helicenes proposed here will be based on three different families of persistent radicals for which high conductivities ($\sigma > 10^{-2}$ S/cm) have been reported.^{15,16} A high-throughput computational modelling of radical helicenes will be developed in parallel and select the most promising second-generation candidates for synthesis.

Objective 2 Determine electronic properties and structure. The electronic (optical, spin) and structural (X-ray diffraction, advanced microscopies) properties of the compounds from WP1 will be measured in solution, thin films and single crystals. The results will be used to validate the computational modelling from WP1.

Objective 3 Identify materials that combine spin filtering and high conductivities. Both spin filtering and conductivities will be measured for the most promising candidates identified through the work on Objectives 1&2. The results will again be used to validate the computational modelling and, subsequently, predict high-performing second-generation materials.

V3 Project Design The proposed combination of synthesis, (modelling-guided) design, and characterization (cf. Fig. 1) is unique and only possible because of my ability to drive high-impact collaborations based on innovative synthetic chemistry. *I am targeting helicenes because they are perfect chiral conducting materials that enable both room temperature spin filtering and device fabrication.* Strong spin filtering values of 45–85 % have been reported for oriented helicene systems;^{17,18} similar orientational control could be achieved in thin films of more device-relevant helicenes through blade coating or vacuum processing.¹⁹ Moreover, helicenes are compatible with device fabrication and operation, as demonstrated by their use in solution-processed organic field effect transistors (OFETs)²⁰ or CP-light emitters,²¹ and -detectors.²² The origin for both spin filtering and device performance could lie in the helically twisted extended π -system. The twisted aromatic system results in strong chiroptical properties,²³ which in turn has been linked to CISS spin filtering.²⁴ Additionally, the twisted aromatic system could explain helicenes' improved processability (helicenes are more soluble than their planar analogues²⁵) and improved charge mobilities through the reduction of sp^3 -hybridised carbon atoms (no requirement for chiral induction from sp^3 -hybridised asymmetric carbon centres and reduced need for solubilising alkyl chains).

The use of open shell helicenes as chiral SCRCs (cSCRCs) will improve spin filtering,²⁶ as well as the predictability and processability compared to conventional chiral conductors. SCRCs do not require doping to improve conductivity and therefore avoid issues due to the disruption of the (chiral) bulk structure.¹⁵ The proposed molecules have a net-neutral charge and should be suitable for solution- and vacuum-processing, thus avoiding the electrocrystallization conditions often necessary for the popular chiral conductors based on TTF²⁷ or metal-dithiolene complexes.²⁸ Finally, left- and right-handed helicenes are both readily accessible, in contrast to chiral inorganic systems, where chirality can be difficult to control.

Beneficiaries: Academic *HR-CCM will open new directions of research for CISS and its real-world applications.* The development of CISS-active materials suitable for device fabrication and operation will lead to a paradigm change in the field and allow researchers to move away from proof-of-concept materials to real-world applications. HR-CCM will contribute to a better understanding of CISS and the development of applications not achievable with low conductivity materials.

Beneficiaries: National Importance *CISS materials such as HR-CCM will allow the control of electron and photon spin and thus enable disruptive quantum and spintronics technologies.* Quantum computing and sensing have been predicted to be worth \$10-15bn by 2030, rising to \$450-850bn in the next 15–30 years. The UK National Quantum Strategy aims to secure the UK's position as a leading quantum-enabled economy, and involves £2.5bn of public and £1bn of private investment by 2034.²⁹ *HR-CCM can contribute to quantum technologies by creating a new generation of CISS-enabled materials that manipulate and read out spin states at room temperature.^{2,3}* Additionally, the development of high conductivity CISS materials will enable low-overpotential water splitting^{12,13} at industrially relevant current densities, helping to deliver the 7–20 GW of hydrogen production capacity need projected for the UK in 2035 as part of the road to net zero.³⁰ Finally, the development of a reliable computational design pipeline and the synthetic optimisation for *HR-CCM* will contribute to the UK chemical industry, which had a revenue of over £70bn in 2020. The research of *HR-CCM* is also closely aligned with many of the strategic themes and priorities of the EPSRC. The synthetic

work and the overarching vision align with the *science & simulation and design* components of the *Manufacturing the future* theme and its *sustainability and function* priority; the *Physical Sciences* theme with the Chemistry grand challenges *dial-a-molecule – 100% efficient synthesis* and *directed assembly of extended structures with targeted properties*; as well as the *Spintronics*, and *Synthetic organic chemistry* research areas. The room-temperature quantum applications of CISS fit the *Quantum technologies* theme, the Physics Grand Challenges *Quantum physics for new quantum technologies* and *Nanoscale design of functional materials*, as well as the *Quantum devices, components and systems* research area. The potential development of low-overpotential water splitting fits the *Energy and decarbonisation* theme with the *hydrogen and alternative energy vectors* research area.

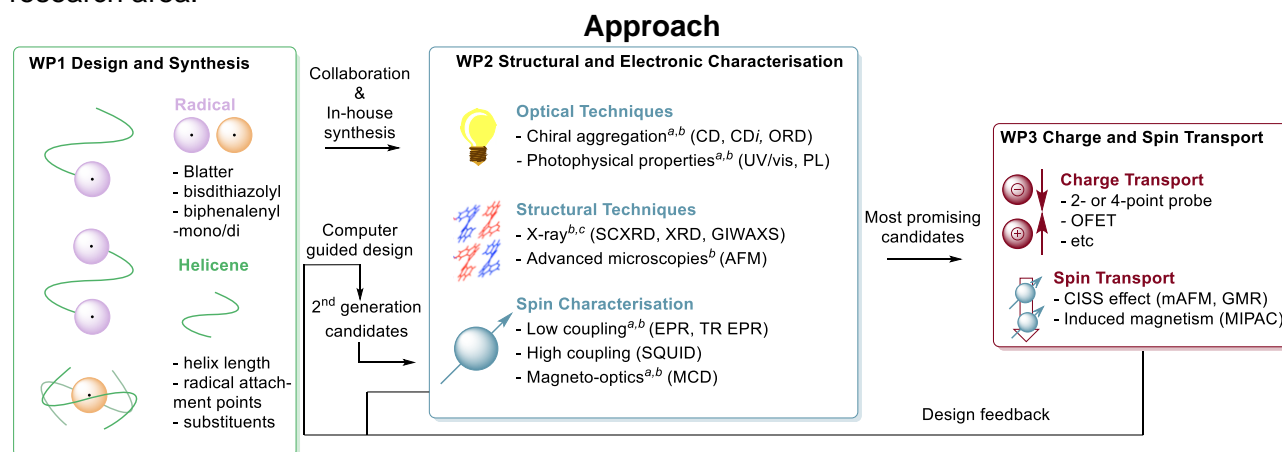


Figure 1 Diagram of the proposed approach. ^aSolution; ^bThin Film (Templated & Untemplated); ^cSingle Crystal.

This project is divided into three work packages (WPs) that cover the *Design and Synthesis* (Figure 2 & 3, WP1), *Structural and Electronic Characterisation* (WP2), and *Charge and Spin Transport* (WP3). Each WP includes milestones (M), deliverables, (D), risks (R), and contingency plans (C) and are described in the following:

WP1 Design and Synthesis of Conductive Open-Shell Helicenes

Time Frame: months 0–27	Team: PDRA & PhD
Objective 1: Design and synthesise helicene radicals based on known SCRCs	
Deliverables and Milestones: D1.1 Synthesis of open shell helicenes. D1.2 Identification of priority candidates in each radical class through modelling. D1.3 Draft publications and report on the modelling and synthesis at international conferences. M1.1 Synthesis of initial cSCRC candidates for characterisation and model validation. M1.2 Development and validation of modelling suite for high-throughput computational prediction of charge transport for cSCRCs. M1.3 Synthesis of highly ranked 2 nd generation cSCRC candidates.	
Risks and Contingencies: R1.1 Candidate radicals are not stable. R1.2 Challenging synthesis of open shell helicenes. R1.3 Difficulties in modelling charge transport behaviour. C1.1 If some radicals show poor stability (R1.1), we will focus on other radical classes, for example, air-stable Blatter radicals. C1.2 The synthetic risk (R1.2) will be mitigated through a mixture of collaborations (Blatter), elaboration of known helicenes (phenalenyl), and the cross-coupling of easily accessible helicene precursors (bisdithiazolyl). C1.3 In case of unreliable modelling (R1.3), the 2 nd generation cSCRCs can be designed based solely on the 1 st generation's performance.	

WP1.1 Design of SCRCs based on known radical conductors. Although the presence of radicals may help in the development of conductive chiral materials, there is a risk that magnetically ordered (Mott) insulators could be formed (cf. R3.1 and C3.1 in WP3). To reduce this risk, we are basing their design on known conductors ($\sigma > 10^{-2}$ S/cm),^{15,16} which should (at minimum) provide an “inter-regnum” state between Mott insulating and metallic, as found for other SCRC.³¹ Figure 2 illustrates how the bisdithiazolyl and Blatter-type^{16,32} cSCRC¹⁵ candidates (2a) will be assembled. The radical groups will be placed as mono- or diradicals (2b) at the terminal rings of different carbo- and heterohelicenes. Variation of both the attachment position (2c) and the helix length (2d) provides a unique opportunity to tune the conductivity *via* the: 1) bulk packing; 2) the intra- and intermolecular distance and angle of the radical groups; 3) the exchange interaction between the two radical groups; and 4) the presence or absence of quantum interference.^{33–35}

To mitigate project risk, a third type of cSCRC structures based on boron spiro-biphenalenyl structures will be investigated (Fig. 3a). These molecules are based on the non-chiral mixed-

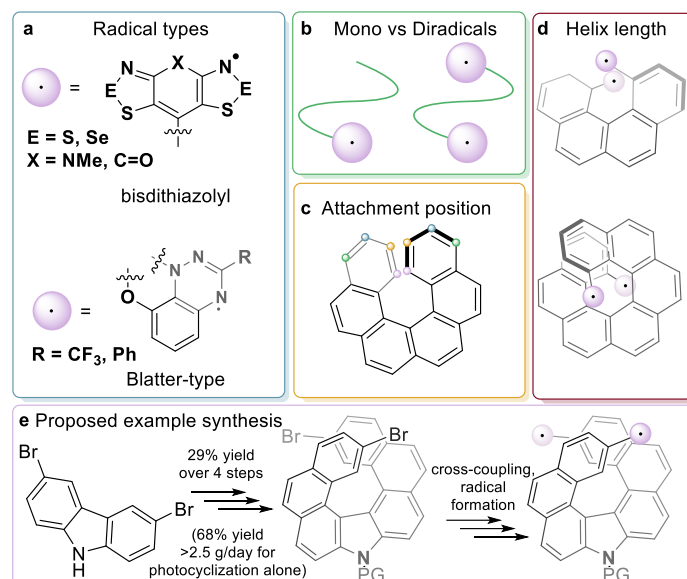


Figure 2 Approach for the design & synthesis of chiral bisdithiazolyl and Blatter-type radicals.

into the interaction of spin and chirality. For the bisdithiazolyl radicals, the delocalisation into the helicene backbone will be low, which will likely limit the chiroptical properties in solution. In the solid state, however, a helical spin arrangement could be achieved through the controlled columnar stacking using thin film templating (cf. WP2).¹⁹ In contrast, the influence of delocalisation across the helical backbone can be explored with both Blatter⁴¹ and *i*DMQA-based spiro-biphenalenyl radicals,³⁸ which will likely display spin density in the terminal or central parts of the helicenes, respectively. Finally, a highly localised radical within the central parts of the helicene can be explored with *a*DMQA-based spiro-biphenalenyl radicals.³⁹

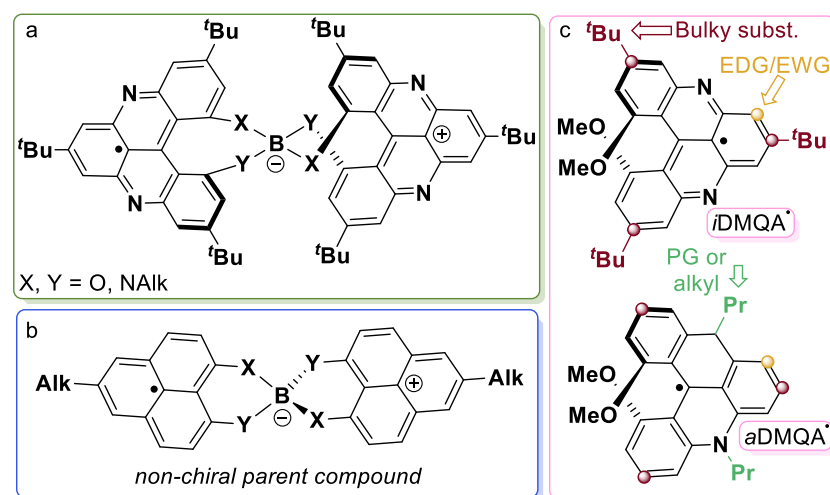


Figure 3 Approach for the design & synthesis of chiral biphenalenyl-type radicals.

to develop a suite of computational approaches that will calculate conductivities based on the chemical structure of potential cSCRCs, allowing us to focus our synthetic efforts on the most promising materials. While this work is ambitious, it will be based on the combination of previous simulations of radicals⁴² and the high-throughput prediction of charge transport for functionalised closed shell helicenes.⁴³

WP1.2 Synthesis of cSCRCs To reduce the risk associated with the synthesis of the proposed cSCRCs, different synthetic strategies will be pursued for each radical class. First, we will leverage our in-house expertise on helicene synthesis with our group's scalable (>2.5 g/day) method for continuous flow photocyclization (Fig. 2e, unpublished results, 68% yield for the photocyclization) to synthesise helicenes containing aryl halides. From these common intermediates, a subsequent C-C

valence³⁶ spiro-biphenalenyl SCRCs (3b), for which conductivities of up to 0.3 S/cm have been reported.³⁷ As the extension of π -conjugation has been predicted to lead to increased conductivity,¹⁵ the known conformationally stable chiral DMQA[•] (DiMethoxyQuinAcridinyl) [4]helicenes will be used as phenalenyl surrogates. The impact of high³⁸ (imino DMQA[•], *i*DMQA[•], 3c top) or low radical delocalisation (amino DMQA[•], *a*DMQA[•], 3c bottom),³⁹ bulky and/or solubilising substituents (red arrows, 3c), the introduction of electron donating or withdrawing substituents⁴⁰ (yellow arrows) or the use of coordinating or solubilising side-chains (green arrows) on the conductivity can be probed.

In the proposed structures, the different positions of spin density and the degree of delocalisation will provide exciting insight

While some general design rules for SCRCs exist (e.g. increasing aromaticity can improve conductivity), these rules are insufficient to predict, for example, the 10⁵-fold reduction observed when going from a butyl- or hexyl-chain on a spiro-biphenalenyl boron radical (Figure 3b) to the intermediate length pentyl chain.¹⁵ To avoid such pitfalls in the design of cSCRCs and increase robustness, I will collaborate with Dr Jarvist Frost Moore (an expert in the modelling of electronic states, Imperial College London)

cross-coupling, followed by cyclisation, anion metathesis and oxidation will afford the desired bisdithiazolyl structures.⁴⁴ The Blatter-type radicals⁴⁵ will be synthesised from the same aryl bromide helicenes through a method currently being developed in an unpublished collaboration with Prof Piotr Kaszyński (an expert in the synthesis and characterization of Blatter-type radicals, Polish Academy of Sciences).

The synthesis of the proposed spiro-biphenalenyl radicals (e.g. Fig 3a) will be based on cationic aDMQA⁺ (cf. 3c bottom) compounds. These compounds are 1) conformationally and chemically stable, 2) can be obtained in two steps from commercially available materials, 3) can be transformed to /DMQA structures,³⁸ 4) are compatible with late-stage functionalisations⁴⁰ and 5) can be readily resolved into the enantiomers on scale by using a chiral auxiliary.⁴⁶ Treating these DMQA⁺ structures with boron halides should cleave the methyl ethers to afford dicationic spiro-biphenalenyls, which could be reduced to the desired mixed valence with a mild reductant.⁴⁷ Alternatively, a two-step deprotection/boronate formation strategy could be employed using acid, fluoride, or oxidant-labile protecting groups for the phenol groups.

The proposed helicenes will be synthesised as racemic mixtures and then resolved using either a chiral auxiliary⁴⁶ or a semi-preparative recycling HPLC with chiral stationary phase that is already present in the department. For the most promising candidates, funds have been requested to allow the outsourced chiral resolution on multi-gram scale. A chiral resolution approach is the best choice for this project; firstly, access to both enantiomers is required for device studies. Secondly, there is currently no general asymmetric synthesis of helicenes despite significant research interest.

WP2 Structural and Electronic Characterisation

Time Frame: months 6–30	Team: PDRA & PhD
Objective 2: Determine electronic properties and structure	
Deliverables and Milestones: D2.1 Elucidate electronic properties through (magneto-)optical, electronic and spin measurements in solution and solid state. D2.2 Elucidate (chiral) solid-state structure through optical and structural characterisation. D2.3 Report the synthesis and characterisation of open shell helicenes as publications and at conferences. M2.1 Generate single crystals and uniform thin films. M2.2 Control orientation of helicenes in ordered thin films. M2.3 Confirm predicted molecular and bulk properties of modelled open shell helicenes.	
Risks and Contingencies: R2.1 Modelling does not accurately predict electronic properties or solid-state structure. R2.2 Materials do not form uniform thin films. C2.1 Experimental data will be fed back into the modelling approach to improve computational results (R2.1). C2.2 Better films (R2.2) could be obtained through vacuum deposition (e.g. organic molecular beam deposition, OMBD), or chemical modifications to improve solubility for solution processing. Additionally, the cSCRCs could be characterised as additives in polymer hosts or as single crystals.	

The structural identity and purity of all synthesised materials will be confirmed through standard in-house analytical techniques such as HPLC, high resolution mass spectrometry, and vibrational spectroscopy; closed-shell systems will additionally be characterised through 1D- (¹H, ¹³C) and 2D-NMR (COSY, HMBC, HMQC) techniques. Further characterisation for the synthesised cSCRC candidates will be obtained in solution and the solid state (thin films & single crystals). Through my collaboration with Dr Jessica Wade (an expert in the fabrication and chiral characterisation of organic materials, Imperial College London), I will be able to generate highly ordered thin films of the cSCRCs with controlled orientation relative to the substrates.¹⁹

Information on the electronic structure of the materials will be gathered through electrochemistry (cyclic voltammetry) and optical techniques (UV/vis, photoluminescence). In-house chiroptical (circular dichroism (CD), optical rotatory dispersion (ORD)) and magneto-optical techniques (magnetic circular dichroism (MCD), Faraday rotation) both in the solution and solid state will provide information on the dissymmetry of the electronic transitions and will be compared to the percentage of spin-filtration in WP3.²⁴ As in my previous work, I will use these techniques to obtain information on chiral aggregation and phase changes in the solid state.⁴⁸ The use of structural techniques based on X-ray measurements (SCXRD, XRD, GIWAXS) or scanning probe microscopies (e.g. AFM) will provide further understanding of the thin film and crystal structures of the materials. The experimental results will be compared to the structural and molecular properties obtained through the modelling performed in WP1.1 to validate and improve the computational approach.

The characterisation of the unpaired spin in cSCRC materials will be performed in the low coupling (electron paramagnetic resonance (EPR)) and strong coupling (Superconducting Quantum Interference Device (SQUID)) regimes in collaboration with Dr Wade at SPIN-Lab. We will explore

(circularly polarised) light-dependent spin properties in EPR and SQUID, which will improve our understanding of the electronic structure and any potential influence of CISS on spin dynamics.⁴⁹ Theoretical modelling will be employed to calculate spin density, electronic structure, and magnetic coupling. These predicted values will be compared to the experimental results obtained via EPR, and magnetic susceptibility. These results will also show the degree of spin delocalisation over the helically chiral aromatic system, illustrating the different chiral environments provided by the proposed cSCRC materials (cf. WP1.1).

WP3 Charge and Spin Transport

Time Frame: months 18–36	Team: PDRA & PhD
Objective 3: Identify materials that combine spin filtering and high conductivities	
Deliverables and Milestones: D3.1 Measure conductivity and charge mobilities. D3.2 Measure percentage of chiral spin filtering dependent on helicene orientation. D3.3 Report the conductivities and spin filtering of cSCRCs as well as their computational modelling (WP1.1) as publications and at conferences. M3.1 Develop high conductivity cSCRCs. M3.2 Obtain materials with high conductivity and percentage spin filtering.	
Risks and Contingencies: R3.1 Mott insulating behaviour prevents efficient charge transport. R3.2 Rapid spin-relaxation prevents chiral spin filtering. C3.1 The risk of dominating insulating behaviour is minimised through the computational modelling and the use of known SCRC motives (WP1). However, if any magnetically ordered (Mott) insulators were obtained, these would be very interesting for measurements of spin transport through magnons. ⁵⁰ C3.2 Longer spin lifetimes and larger magnetoresistance ⁵¹ could be obtained with little synthetic effort through late-stage perdeuteration. ⁵²	

The conductivity and magnetoresistance of the cSCRC materials will be tested in collaboration with Prof Jan Mol and Dr James Thomas (experts in quantum technologies, QMUL). The conductive properties will be characterised for single crystals, thin films¹⁶ or cold-pressed pellets with a 2- or 4-point probe setup and through the fabrication of OFETs. The CISS effect will be assessed through three different approaches. Two complementary techniques will probe local effects, investigating spin-polarised currents (mCP-AFM with Dr Wade in SPIN-Lab) and magnetisation (Magnetism Induced by Proximity of Adsorbed Chiral molecules (MIPAC))^{53,54} with Dr Helena Knowles, an expert in quantum imaging at the nanometer scale, University of Cambridge). For spin filtering in bulk, magnetoresistance devices will be fabricated and characterised in-house. Where possible, different orientations of the helicene relative to the surface (cf. WP2) will be tested to identify the impact of molecular orientation on conductivity and spin filtering. As in WP2, results from this WP will feed back to the computational modelling (WP1.1) to improve the predictions for second generation materials.

Translation to Outcomes and Impacts through open data and materials. To ensure that the knowledge gained from this project will allow the research community to quickly adapt materials capable of real-world applications, we will make our data and materials freely available. Our data will be kept according to the FAIR (findable, accessible, interoperable, reusable) principles,⁵⁵ while our materials will be made available to other groups for collaborations and independent validation.

Outlook: Conductivity and spin-filtering optimised materials for CISS applications. Towards the end of this grant and beyond, the knowledge gained in HR-CCM for the design of chiral materials with high conductivity will be combined with my URF's complementary work on the mechanism of spin filtering to design and synthesise next-generation chiral materials that can combine excellent electronic properties and spin filtering, enabling the path to room-temperature organic spintronics and quantum technologies. To allow fast impact, we will initially target applications that would require little translational work, e.g. single-layer spin valves for spintronics, charge transport materials for CP spin-OLEDs or more efficient water splitting.

Research Environment: I am a Royal Society University Research Fellow and took up my proleptic appointment at the School of Physical and Chemical Sciences of QMUL in September 2022. QMUL is a member of the Russell group of UK universities and has world-class facilities that will enable my research. For the in-house fabrication and characterisation, I will have access to an X-ray diffraction facility (with single crystal, powder, and SAXS/WAXS/GiSAXS capabilities), NMR-spectroscopy (400 and 600 MHz), a CD instrument with ORD and MCD add-ons, LC/MS, recycling semi-preparative liquid chromatography, a clean room, optical and magneto-electrical characterisation facilities, organic deposition systems, photolithography, an evaporator, and a 7T cryomagnet suitable for measurements from 1.5-400 K.