Masters Thesis

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Abstract:

A high-throughput computational workflow utilising a Marcus theory derived approach is presented to comparatively estimate electron and hole charge hopping rate in radical and zwitterionic helicene derivatives in one dimension, screening all possible spin states. The Einstein-S diffusion equation is then utilised to calculate mobility from the calculated rates. Estimated transfer integrals are validated against state of the art density functional theory calculations, and all values against literature DFT reportingsfor similar helicenes. A database is constructed for the best performing molecules, containing electron and hole hopping rates at a wide variety of translations and rotations that mobility can be calculated from for a variety of common crystal packings observed for organic semiconductors. A 100 molecule box is constructed and optimised with periodic boundary conditions for both main classes of molecule investigated to further explore and predict packing motifs. Simulated annealing is undertook to investigate structural order changing with temperature. Results are analysed and explanations of trends attempted, such that the best candidates for synthesis and ideas for future synthetic design suggested.

Introduction

Organic semiconductors: why helicenes?

Organic semiconductors have garnered significant attention in recent years due to their potential for flexible, lightweight, and cost-effective electronic applications. Unlike traditional inorganic semiconductors such as silicon, organic semiconductors exhibit intrinsic advantages, including solution processability, mechanical flexibility, and tunable optoelectronic properties through chemical modifications (Brütting & Adachi, 2012). These properties have led to their integration into organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), and organic field-effect transistors (OFETs) (Facchetti, 2007). However, the challenge of optimizing charge transport in organic materials remains a central focus in the field, particularly for emerging materials such as helicenes.

Helicenes, a class of polycyclic aromatic hydrocarbons characterized by their helical π-conjugated structures, have recently attracted considerable interest due to their unique electronic and chiroptical properties (Rickhaus et al., 2020). Their inherently chiral nature allows for efficient spin filtering, a phenomenon associated with the chiral-induced spin selectivity (CISS) effect, which has been demonstrated to influence charge transport in molecular systems (Naaman & Waldeck, 2012). This effect suggests that helicenes, particularly radical and zwitterionic derivatives, could serve as promising candidates for spintronic applications, where spin-polarized charge carriers are exploited for device functionality (Mondal et al., 2021). Moreover, the extended π-conjugation in helicenes enables efficient charge delocalization, potentially improving charge carrier mobility—an essential parameter for high-performance organic semiconductors.

 Brütting, W., & Adachi, C. (Eds.). (2012). *Physics of Organic Semiconductors*. Wiley-VCH.

 Facchetti, A. (2007). π-Conjugated Polymers for Organic Electronics and Photovoltaic Cell Applications. *Chemistry of Materials*, *19*(18), 4381-4399.

 Mondal, P. C., Fontanesi, C., Waldeck, D. H., & Naaman, R. (2021). Spin-Dependent Transport and Electrochemical Reactions of Chiral Molecules. *Accounts of Chemical Research*, *54*(10), 1609-1620.

 Naaman, R., & Waldeck, D. H. (2012). Chiral-Induced Spin Selectivity Effect. *Journal of Physical Chemistry Letters*, *3*(16), 2178-2187.

 Rickhaus, M., Mayor, M., & Juríček, M. (2020). Strain-Induced Helicene Chirality: Synthesis and Properties. *Chemical Society Reviews*, *49*(9), 3504-3524.

 Shen, C., et al. (2021). High Mobility and High Stability of Helicene-Based Organic Semiconductors. *Advanced Materials*, *33*(5), 2006921.

Purpose of investigation:

The primary objective of this research is to systematically investigate the charge transport properties of radical and zwitterionic helicene derivatives through computational screening, with the ultimate goal of identifying key molecular candidates for experimental synthesis. This study is conducted in collaboration with Dr. Jochen Brandt at Queen Mary University of London, leveraging both theoretical and synthetic approaches to design high-performance organic semiconductors. By computationally evaluating a diverse library of helicene derivatives with varying functionalization patterns, we aim to determine structure–property relationships that govern charge carrier mobility, reorganization energy, and transfer integrals. These insights will guide the rational design of new helicene-based materials for next-generation organic electronic applications.

Outline of thesis:

Theory:

Methods:

All calculations were completed on an Apple iMac using xtb 6.7.1 unless otherwise stated.

Transfer integrals were calculated using the dimer projection method (DIPRO\_)([Andrienko2010](https://pubs.rsc.org/en/content/articlehtml/2010/cp/c002337j)) (J.Kohn, N.Gildemeister, D.Fazzi, S.Grimme, A.Hansen, Efficient Calculation of Electronic Coupling Integrals with the Dimer Projection Method via a Density Matrix Tight-Binding Potential, JCP **2023**, submitted). And the projective method REFERENCEusing Gaussian b3lyp calculations.

Reccomendations for future work:  
  
The avenues for future investigation in this field can be easily categorised into either further synthetic or computational study. On the synthetic front