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学位論文題目	Towards Benchmarking Chirality-Induced Spin Selectivity: The Case of Chiral Tetrapyrroles	
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Summary of Doctoral Thesis

Name in Full：Adrian Joe Urban

Title：Towards Benchmarking Chirality-Induced Spin Selectivity: The Case of Chiral Tetrapyrroles

Summary: Chiral molecules are able to preferably transmit electrons with either spin and down, in a phenomenon called “chirality-induced spin selectivity” or CISS in short. Despite being known for two decades and despite being observed in a variety of systems such as biomolecules, oligopeptides, supramolecular assemblies or inorganic structures, a concise theoretical explanation that can fully explain experimental observations is still missing. In order to aid in the development of such a theoretical framework, a method of benchmarking spin-selectivity with respect to several structural and electronic properties of a molecule is obviously of great interest. To this end, the author sought out to test helical tetrapyrroles for their suitability as benchmark platforms. After optimization of various synthetic protocols given in literature, the properties of complexes of 19-benzoyl-5,10,15-triphenyl-bilatrien-1-one (H_2TPBT) and 2,3,7,8,12,13,17,18-octaethylformylbiladiverdin (H_2OEFB) with nickel(II), as well as 5,10,15,20-tetraphenylbiliviolin (H_3TPBV) are explored using electronic circular dichroism (ECD) and magnetoconductive atomic force microscopy (mc-AFM), both having an established connection to the CISS effect. The results are compared with the expected CISS magnitudes of several prevailing theories, and augmented with predictions based on modern density functional theory (DFT) to investigate structural isomerism, frontier molecular orbitals, and surface adsorption behavior. In a collaborative effort, the molecules are investigated under ultrahigh vacuum (UHV) conditions with ultraviolet photoelectron spectroscopy (UPS) and Mott electron polarimetry, in order to make them accessible for future projects with more specialized experimental setups. In a future outlook, other prominent chiral tetrapyrroles are explored and evaluated as candidates for CISS-benchmark molecules, and the most promising routes for specifically tailored chiral tetrapyrroles are introduced based on literature review. The oxidative cleavage of tetraphenylporphyrinato iron(III) chloride Fe(TPP)Cl, according to literature, leads to the formation of both H_2TPBT and its product of addition of a water molecule (referred to as a “covalent hydrate” by the author). This hydrate – contrary to the water-free molecule – has an interrupted pi-conjugation pathway and its helicities are expected to quickly interconvert so that separation of both enantiomers becomes unfeasible for use in molecular electronics and investigation of the CISS effect.

Consequently, a sizeable amount of product would be lost in the form of the covalent hydrate. Moreover, the few literature pro tocols for dehydration have been found to actually be equilibrium reactions where water will attack the water-free H_2TPBT molecule again during workup. The author of this thesis shows that it is possible to eliminate the water molecule completely when boiling the crude of Fe(TPP)Cl cleavage with glacial acetic acid in the presence of a copper(II) or nickel(II) acetate, resulting in Cu(TPBT) or Ni(TPBT) which possess inherent helical chirality. The copper complex easily racemizes after enantioseparation with chiral high-performance liquid chromatography (HPLC), likely due to noninnocenct behavior observable in electron spin resonance spectroscopy (ESR) and cyclic voltammetry (CV). The nickel complex, on the other hand, can indeed be separated and its enantiomers are stable in solution over the course of at least four weeks. Its crystal structure, obtained via x-ray crystallography, shows that the TPBT molecule retains its helicity upon coordination with nickel, spanning one-and-a-quarter turns with a 5.7 Å radius and a 3.2 Å pitch, and all 26 participating atoms being sp^2-hybridized. Contrary to prior literature prediction, the terminal benzoyl group is pointing alongside the rest of the helix in a syn-periplanar configuration (*sp*, compared to anti-periplanar, or *ap*). Using DFT calculations with a large functional and basis set study, and the obtained crystal structure as a benchmark, it was found that the sp-isomer is energetically favored by 11.9 ± 6.3 kJ/mol, with an activation barrier (*sp* to *ap*) of 26.7 ± 7.7 kJ/mol. The frontier orbitals of the experimentally obtained Ni(TPBT) show well-defined helicity. Intramolecular overlap, which would close the helix into a circle, is strongly limited. The ECD-active HOMO-LUMO transition, located in the near infrared at 800 nm with a large absorption symmetry value of $g_{\mathrm{Abs}} = \Delta\varepsilon/\varepsilon = 3 \cdot 10^{-3}$, is tunable by varying the coordinated metal atom and involes ligand-centered molecular orbitals, indicating a strong susceptibility of the TPBT ligand towards external perturbations such as the *d* electrons of a coordinated metal. DFT-based predictions reveal that Ni(TPBT) predominantly adsorbs onto gold surfaces with via its lactam ring on one end of the TPBT helix, instead of the benzoyl ring. When using highly ordered pyrolytic graphene (HOPG), the behavior is opposite and the molecule binds to the surface via its benzoyl group. These findings are especially promising, as several theories ascribe a large role of surface dipole interactions to the CISS effect, both in magnitude and direction. The adsoroption geometries can also be expected to be clearly distinguishable, based on predicted scanning tunnel microscopy (STM) images. Collaborative UPS experiments with Cu(TPBT) under UHV conditions show that the molecule can easily be evaporated onto Cu(111) at temperatures around 200 °C. Subsequent thermodesorption reveals and additional surface state at $E_{\mathrm{kin}} = 6.5$ eV. This state is stable until a substrate temperature of 300 °C at which the states of native the bare Cu(111) are completely restored, indicating the formation and decomposition free desorption of a mono - or bilayer. Both in mc-AFM and Mott polarimetry, theoretical predictions for the magnitude of the CISS effect in these molecules (least 6-14 %) are exceeded by all investigated molecules with values ranging as high as 30 % (H_3TPBV) in mc-AFM and 35 % [Ni(TPBT)] in Mott polarimetry. The collaborative effort is currently ongoing and expected to yield even larger numbers for the spin polarization, as not all of the targeted molecules have been measured yet.

（別紙１ Separate Sheet 1）

Results of the doctoral thesis defense

博士論文審査結果

Name in Full
氏　　名　Adrian Joe Urban

Title
論文題目　Towards Benchmarking Chirality-Induced Spin Selectivity: The Case of Chiral Tetrapyrroles

テトラピロールはポルフィリンの代謝産物として広く天然に存在し、ビリルビンなど人体にも関わる分子群としても知られているが、その合成研究やキラリティに注目した物性計測については、未知の点が多い。本博士論文で出願者は、様々な中心金属や周辺置換基を有するキラルテトラピロールを用いることによって、キラルな有機分子に電流を通すとスピン偏極が生じる Chirality-Induced Spin Selectivity（CISS）効果のベンチマークテストを行うことが可能である、との仮説のもと、テトラピロール類の合成・計算・物性計測研究を進めた。

第一章では、CISS 効果について、これまで実験的に知られている事実とその解釈を述べた後、テトラピロールの化学について記述し、この両者を組み合わせることの意義について論じている。

第二章では、CISS 効果の理論紹介と、その周辺にある類似現象について記述し、理論の妥当性を検証するためにはキラル分子の構造や構成元素を系統的に変化させる必要があることを述べている。

第三章では、テトラピロールの合成や電子状態計算のほか、円偏光二色性測定・電気化学測定・X 線構造解析・スピン依存伝導性測定などの手法についてその詳細を記述している。

第四章では、実験結果と計算結果について記述しており、テトラピロール錯体の中心金属が銅の場合はリガンドがラジカル性を帯びることや、中心金属がニッケルの場合は錯体が安定で、キラル分割をした後も常温でラセミ化が起きないことが記されている。興味深い点として、円偏光二色性が比較的大きな異方性因子（ｇ値）を示し、特にこれが近赤外線領域で見られるという、他の分子であまり見られない特性を有していることを示した。また、真空中の分子だけでなく、表面に吸着した状態での分子の量子状態についても計算を行い、その結果を示している。

第五章では、プローブ顕微鏡を用いたスピン依存伝導性の測定結果と、光電子分光によるスピン選択性を示し、キラルなテトラピロールの CISS 効果を初めて観測したことが記されている。

第六章では、以上の結果をまとめて、これまでに分かったことと、将来調べるべき事柄について論じている。

本博士論文の上記の成果は、新たな光学活性分子の合成・分離・同定にとどまらず、キラル分子ならではの物性研究に発展する端緒となるものであり、学術的に価値ある成果であると判断された。また、本論文の内容は出願者を筆頭著者とする学術論文として査読付

き国際誌に掲載済みである。以上より、本博士論文は博士(理学)の学位授与に値すると審査委員全員一致で判断した。