氏　　名　Ruttapol MALATONG

学位(専攻分野)　博士(理学)

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学位授与の要件　物理科学研究科　構造分子科学専攻
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学 位 論 文 題 目　Development of Switchable Spin Selectivity Based on Controllable Organic Chirality

論 文 審 査 委 員　主　査　飯野 亮太
分子科学コース 教授
山本 浩史
分子科学コース 教授
横山 利彦
分子科学コース 教授
倉持 光
分子科学コース 准教授
井改 知幸
名古屋大学 大学院工学研究科 准教授

(Form 3)

Summary of Doctoral Thesis

Name in full: Ruttapol MALATONG

Title: Development of Switchable Spin Selectivity Based on Controllable Organic Chirality

A chiral symmetry, an ultimate form of broken symmetry lacking both inversion and mirror symmetries, has recently attracted growing interest due to its unique ability to compellingly tie the electron motion to its spin angular momentum. A recent striking example is a gigantic spin-polarized current that emerged in organic chiral molecules, which is often referred to as chiral-induced spin selectivity (CISS). The phenomenon is noticeable in that pure organic systems give a platform of the CISS with light elements where a spin-orbit interaction (SOI) is negligibly small. Conversely, a conventional charge-to-spin conversion such as the Edelstein effect is well associated with a large SOI in a heavy-element system [1,2]. Although the microscopic origin of the unexpectedly large spin polarization of CISS is still controversial, the CISS effect potentially paves the way to a novel method of embedding organic chiral materials into solid-state spintronic and optical devices.

Because most of the chiral materials used in the CISS experiment-based solid-state devices are static molecules, in which the handedness molecules are fixed by their chemical bonds which are unable to invert spin polarization (SP) direction, spin polarization (SP) direction manipulation by efficiently controlling the chiral handedness with external excitation in “single device’’ has yet to be intensively studied to date. In this thesis, developing switchable organic molecules with external controllability, capable of inversion of spin polarization, is highly desired to study challengingly. It is anticipated that this switchable organic molecule would allow for constructing the responsive spintronic devices as well as representing a huge step forward in the field of organic spintronic applications.

Therefore, considerable interest in CISS lies in switchable chiral molecules with external controllability as first presented in a chapter **"(i) Highly Durable Spin Filter Switching Based on Self-Assembled Chiral Molecular Motor"**. By studying molecular motors known as overcrowded alkenes (OCAs), their handedness are switched by light irradiation and heat treatments [3,4]. In a previous study, OCA-based devices that exhibit CISS remains far from completion in terms of practical use, and rather fundamental obstacles such as (i) external controllability of spin, (ii) function durability, and (iii) improvement of spin-polarization efficiency have yet to be surmounted. Therefore, I aim to prepare new molecular systems based on overcrowded alkene that can address the three obstacles mentioned above to develop the practical utilization of CISS effect. I developed a self-assembled monolayer (SAM) of overcrowded alkene (OCA)-based molecular motor. With this system, I successfully demonstrate that the direction of spin polarization can be externally and repeatedly manipulated in an extremely stable manner by switching the molecular chirality, which is achieved by a formation of the covalent bonds between the molecules and electrode (see in Fig. 1). In addition, by focusing on the stereo architecture of the SAM of the OCAs, I pursue a new route to enhance the spin polarization efficiency per a single OCA molecule. The present experimental investigations report the creditable feasibility study towards the versatile CISS-based spintronic molecular devices with controllability, durability, and high efficiency.

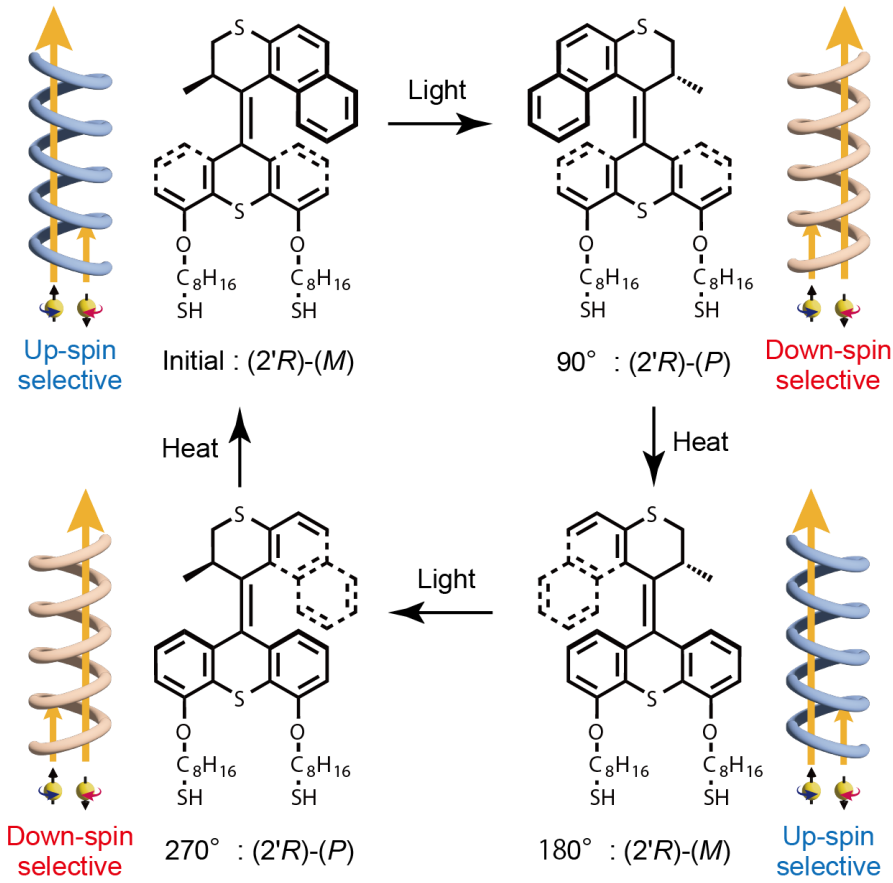

Fig. 1 Four-cycle 360° unidirectional rotations of the OCA molecule driven by light irradiation and heat application. (*2'R*)-(*M*)-OCA and (*2'R*)-(*P*)-OCA are characterized by the opposite handedness, and thus exhibit a spin selectivity with opposite directions.

Thus far, most CISS studies have intensively focused on chiral metals or insulating organic monomolecular layers to experimentally discuss spin-polarized current. Then a fundamental question arises on CISS effect in chiral ferroelectric materials because charge transport in macroscopic ferroelectric materials is only possible with displacement current. Therefore, an emergent spin-polarized current, if any, is likely due to the displacement current. In the second work, my significant research interest focuses on chiral dielectric materials as triglycine sulfate (TGS) **"(ii) Engineering Surface Spin Based on Chiral dielectric Materials"**.

Triglycine sulfate (TGS) crystals are composed of achiral molecules, and the handedness of the chiral room temperature phase is undefined, determined by random

crystal defects, and the crystal breaks up in domains of opposite handedness. A homogeneous handedness can be imposed throughout the entire crystal by cooling it (poling process) from the achiral high temperature phase in a strong electric field [5]. Thus, it is reasonable to hypothesize the CISS in TGS after poling, which can be measured as spin accumulation. Since TGS has demonstrated magnetochiral anisotropy (MChA) in a previous report, the interplay between chirality and magnetism also opens a whole new window on this material [6]. I studied alternating current (AC)-induced CISS effect in TGS under AC current excitation by detecting the spin accumulation with direct current (DC) voltage at the interface. The results demonstrate the antisymmetric signal profiles with temperature dependence close to transition temperature (321.7 K) as the function of the magnetic field (see in Fig. 2). Unfortunately, the TGS-based devices with different handedness, switched by an opposite poling process, exhibit similar behavior. This phenomenon is not likely due to CISS, in which spin accumulation could not be detected, even if the chirality is switched. In this thesis, the possible antisymmetric curves and why CISS undetected will be discussed in detail.

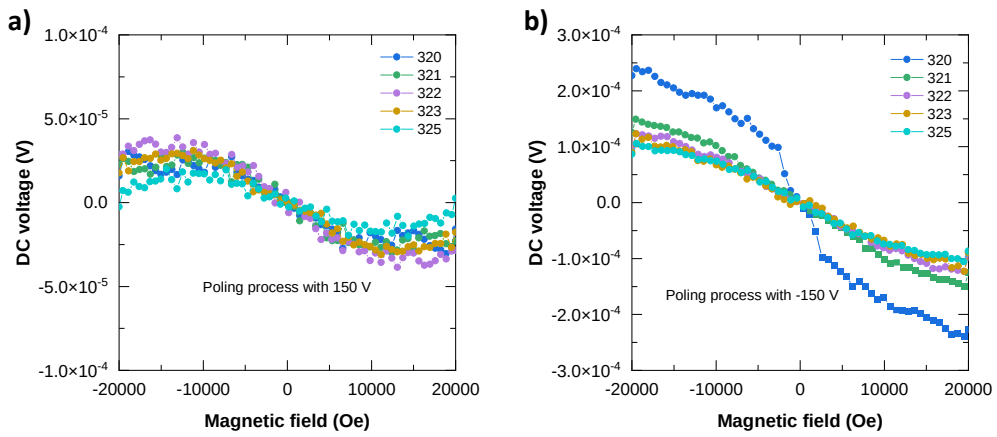

Fig. 2 a) Asymmetric curve, poling process @150V, b) Asymmetric curve, poling process @-150V at the function of magnetic field.

In summary, this thesis reports studies on **i) Highly Durable Spin Filter**

Switching Based on Self-Assembled Chiral Molecular Motor and **ii) Engineering Surface Spin Based on Chiral dielectric Materials**. In both topics, I have shown various organic materials-based devices, in which energetic stimuli externally control chirality, to experimentally study and to verify CISS effect. It is anticipated these works will be crucial in understanding and in utilizing CISS in further practical applications.

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（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　Ruttapol MALATONG

Title
論文題目　Development of Switchable Spin Selectivity Based on Controllable Organic Chirality

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）効果を利用した有機分子スピントロニクスの研究が近年盛んに行われている。本博士論文で出願者は、光と熱によってキラリティ反転可能な人工分子モーター overcrowded alkene（OCA）を基板上に並べることで、電子スピン選択的な伝導性制御の安定性と効率の改善に成功した。さらに、電場によってキラリティ反転可能な硫酸トリグリシン結晶を用いた電子スピン選択的な伝導性の制御を試みた。

第１章では、CISS 効果について、その発見から近年の理論研究および実験研究の成果が概説されている。

第２章では、本博士論文で利用している CISS を示す代表的な有機分子である OCA および硫酸トリグリシン結晶について、その構造や外場応答特性について概説されている。

第３章では、チオール基を末端に有するアルキル鎖で修飾された OCA を新規に合成して金基板上に自己集合化単分子膜として並べることに成功し、光と熱でそのキラリティを制御することで、電子スピン選択的な伝導性のスイッチング制御を達成している。さらに、アルカンチオールを添加することで基板上のアルキル鎖修飾 OCA の配向性を改善し、OCA 単分子当たりのスピン選択的伝導性制御の安定性と効率の改善に成功している。

第４章では、電場によってキラリティ反転可能な硫酸トリグリシン結晶を用い、電場による電子スピン選択的な伝導性の制御を試みている。現状では、伝導性の制御には至っていないが、電場によりキラリティが反転し、キラル結晶とアキラル結晶の転移温度 323K で焦電電流のピークが逆転することが確認されている。

本博士論文の上記の成果は、有機分子スピントロニクスの発展に大きく寄与すると判断された。また、第３章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。