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科学研究費助成事業　　研究成果報告書

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研究課題名（和文）Photoinduced macroscopic polarization change with long-lived metastable state

研究課題名（英文）Photoinduced macroscopic polarization change with long-lived metastable state

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研究成果の概要（和文）：励起状態から基底状態への緩和過程中に、電流出力とともに光誘起された巨視的な分極変化を実現するために。私たちは、極性Fe(II)スピンクロスオーバーコンプレックスを得ました。このコンプレックスはLIESST効果を示し、光励起後にFe(II)の28%が基底状態の低スピン状態から励起状態の高スピン状態に変化します。励起状態が基底状態に戻ると、電流が検出されます。その後、私たちは光照射に対応して、基底状態から励起状態への100%変換を持つ三核[Fe2Co]プルシャンブルー類似体を開発しました。このプロセス中に、出力電流が観測されました。

研究成果の学術的意義や社会的意義
This study combined the photo-responsive molecular magnetic materials and polar molecular crystals realizing the conversion of light energy to electrical energy. It paves the way to develop opto-electric multifunctional materials, next generation memories and energy saving and conversion materials.

研究成果の概要（英文）：To realize photo-induced macroscopic polarization change with current output during the relaxation process from excited state to the ground state. We focused on the spin crossover complexes with Light-Induced Excited Spin-State Trapping effect (LIESST) and Prussian blue analogues with photo-induced electron-transfer-coupled spin transition (ETCST) process. We have obtained a polar Fe(II) spin crossover complex exhibited LIESST effect, in which 28% of Fe(II) changes from the low spin state of the ground state to the high spin state of the excited state after photoexcitation. When the excited state returned to the ground state, the current was detected. Then, we developed a trinuclear [Fe2Co] Prussian blue analogue with 100% conversion from ground state to excited state in response to the light irradiation. During this process, the output current was observed. This study will benefit the development of multifunctional optoelectronic materials and energy conversion materials.

研究分野：coordination chemistry

キーワード：spin transition　electron transfer　magnetic change　polarization change　electric current　light

１．研究開始当初の背景

Polarization switching can be generated in response to an electric field, mechanical stress, and temperature, which is known as ferroelectricity, piezoelectricity, and pyroelectricity, respectively. Those materials are widely used in energy harvesting, data storage media, capacitors, and sensors. Light is also an effective way to induce polarization switching indirectly or directly. For example, light can indirectly induce the ferroelectric phase via the photoflexoelectric effect, and more commonly, polarization via the pyroelectric effect; however, both approaches make full use of the thermal effect of light to modulate the temperature of the lattice modes. Meanwhile, a photoinduced polarization change from the ground to the excited state by direct excitation with laser pulse was confirmed with the help of femtosecond technology in charge-transfer organic crystals and valence tautomeric cobalt complexes. Compared with the indirect way, directly photoinduced polarization switching is faster and more effective. Unfortunately, the short lifetime of the excited state hinders the analysis of its structure and physical properties, the realization of photoinduced polarization change in the macroscale with pyroelectric current output. In addition, it is not conducive to the application of photoinduced polarization change in data storage and energy storage and conversion.

２．研究の目的

The aim of the proposed research is to develop crystals of spin crossover complexes with LIESST effect that exhibit photoinduced polarization change from ground states to excited states with long-lived metastable states. Moreover, to elucidate the mechanism of this process, we expect to identify the differences in the chemical and electronic structures between ground states and excited states.

３．研究の方法

To realize the photoinduced macroscopic polarization change with long-lived excited states, in this project, we will focus on molecular crystals with LIESST, which offers a reversible way of photo-switching the electronic configuration of spin crossover (SCO) systems having long-lived excited states. The SCO phenomenon is a change of the electronic configuration of a metal ion in response to external stimuli such as temperature and light. This transition usually is associated with drastic modifications not only in the magnetic but also in the structural properties as a result of the change in the population of the antibonding eg orbitals. The abrupt shrinkage or expansion of the metal–ligand bonds can cause great changes in the crystal packing and symmetry of the corresponding crystal structure. In addition, [FeCo] Prussian blue compounds capable of electron transfer coupled spin transition (ETCST) are also ideal candidates. In the ETCST process, the electronic structure of the molecules involved change as the electrons are transferred between them, and this results in significant changes of the molecular dipole moment, thereby switching the polarization of the crystal.

４．研究成果

In this project, an Fe(II) spin crossover crystal (Figure 1A), $[Fe(L)_2(ClO_4)_2]$ (L=propyl-2,6-di(1Hpyrazol-1-yl)isonicotinate), that exhibits photoinduced macroscopic polarization change upon excitation by green light. When the excited crystal relaxes to the ground state, the corresponding pyroelectric current was directly detected (Figure 1B). An analysis of the structures, magnetic properties and the Mössbauer and infrared spectra of the complex, supported by calculations, revealed that the polarization change is dictated by the directional relative movement of ions during the spin transition process, which shows that the light-induced ion movement in a polar crystal is also realized.

This study indicates that the combination of the LIESST effect and macroscopic polarization is a feasible way to realize photoinduced persistent polarization change by harnessing the photoexcitation effect rather than the thermal effect of light. It demonstrates the enormous potential of polar spin crossover systems in the field of optoelectronic materials (Angew. Chem. Int. Ed. 2022, 61, e202208771).

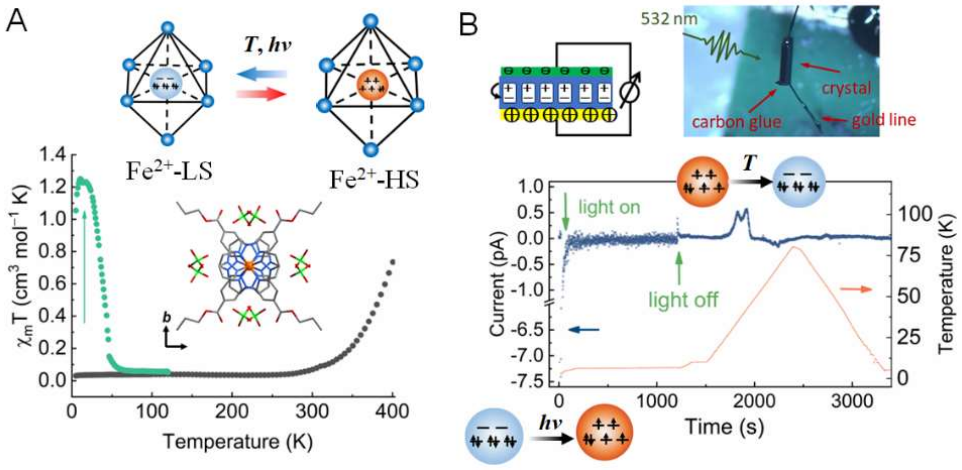

Fig. 1. Photoinduced spin transformation (A) accompanied by changes in macroscopic polarization (B, single crystal pyroelectric current).

In addition, a cyanidebridged compound [Fe(Tp)(CN)3]2(Co(dpa)2) ·2H2O ·IPA ([Fe2Co]) (Tp = trispyrazolylborate, dpa = 2,2′ -dipyridylamine, and IPA = isopropanol) exhibited light-induced polarization switching behavior was developed (Figure 2). A ferroelectric-type phase transition, was confirmed by single-crystal X-ray diffraction, characterized by a directional electron transfer and the reorientation of the solvent molecules. This process yielded a polar phase at low temperatures. Interestingly, the directional electron transfer process and polarization of the crystal can be controlled by irradiating the compound with 785 nm light without needing an electric field. The electric current signal, corresponding to the polarization switching from the excited state to ground state, can be detected clearly after irradiation using a conventional pyroelectric measurement system. This achievement realizes the direct electric detection of a light-controlled ferroelectric phase transition in the molecular Prussian blue analogues (J. Am. Chem. Soc. 2024, 146, 201-209).

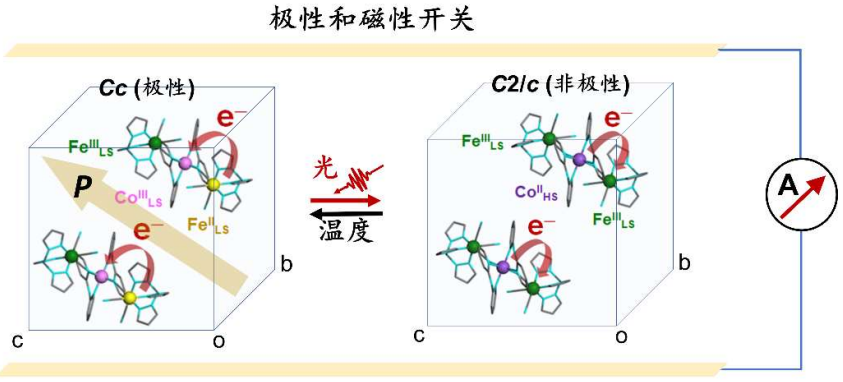

Fig. 2. Photoinduced charge transfer accompanied by changes in macroscopic polarization.

５．主な発表論文等

〔雑誌論文〕　計7件（うち査読付論文　7件／うち国際共著　7件／うちオープンアクセス　1件）

１．著者名 Sadhukhan Pritam、Wu Shu-Qi、Kanegawa Shinji、Su Sheng-Qun、Zhang Xiaopeng、Nakanishi Takumi、Long Jeremy Ian、Gao Kaige、Shimada Rintaro、Okajima Hajime、Sakamoto Akira、Chiappella Joy G.、Huzan Myron S.、Kroll Thomas、Sokaras Dimosthenis、Baker Michael L.、Sato Osamu	４．巻 14
２．論文標題 Energy conversion and storage via photoinduced polarization change in non-ferroelectric molecular [CoGa] crystals	５．発行年 2023年
３．雑誌名 Nature Communications	６．最初と最後の頁 3394
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１．著者名 Huang Yu-Bo、Li Jun-Qiu、Xu Wen-Huang、Zheng Wenwei、Zhang Xiaopeng、Gao Kai-Ge、Ji Tianchi、Ikeda Taisuke、Nakanishi Takumi、Kanegawa Shinji、Wu Shu-Qi、Su Sheng-Qun、Sato Osamu	４．巻 146
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３．雑誌名 Journal of the American Chemical Society	６．最初と最後の頁 201～209
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1．著者名 Xu Wen-Huang、Huang Yu-Bo、Zheng Wen-Wei、Su Sheng-Qun、Kanegawa Shinji、Wu Shu-Qi、Sato Osamu	4．巻 53
2．論文標題 Photo-induced valence tautomerism and polarization switching in mononuclear cobalt complexes with an enantiopure chiral ligand	5．発行年 2024年
3．雑誌名 Dalton Transactions	6．最初と最後の頁 2512～2516
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2．論文標題 Photoinduced Persistent Polarization Change in a Spin Transition Crystal	5．発行年 2022年
3．雑誌名 Angewandte Chemie International Edition	6．最初と最後の頁 e202208771
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/anie.202208771	査読の有無 有
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1．著者名 Cheng Feng、Wu Shuqi、Zheng Wenwei、Su Shengqun、Nakanishi Takumi、Xu Wenhuang、Sadhukhan Pritam、Sejima Hibiki、Ikenaga Shimon、Yamamoto Kaoru、Gao Kaige、Kanegawa Shinji、Sato Osamu	4．巻 28
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3．雑誌名 Chemistry ? A European Journal	6．最初と最後の頁 e2022021
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/chem.202202161	査読の有無 有
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2．発表標題 Photoinduced Persistent Polarization Change in a Spin Transition Crystal
3．学会等名 JSCC 72nd Annual Meeting
4．発表年 2022年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関