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研究課題名（和文）Magnetic Field-Induced Polarization Change in Molecular Crystals

研究課題名（英文）Magnetic Field-Induced Polarization Change in Molecular Crystals

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研究成果の概要（和文）：分極は物質の重要な性質の一つです。本研究では、長距離秩序を持たない0次元分子性物質の磁場誘起分極スイッチングに焦点を当てました。特に、磁場で分極が制御可能な反強磁性やスピンフラストレーションを持つ極性多核錯体を研究しました。この2年間で、最大の磁場誘起分極を示すスピンクロスオーバー錯体を得ることに成功し、相転移に伴う分極変化を示す反強磁性鉄三核錯体は97テスラの磁場でスピン状態を切り替えることが明らかになりました。また、非平行スピン構造の単分子磁石は磁場誘起分極電流を示し、非線形磁電効果を示すことも確認されました。

研究成果の学術的意義や社会的意義
This research contributes to material science by synthesizing new materials with optimized performance. Moreover, it enhances our understanding of magnetic molecules with entangled magnetization and polarization. Development of these materials may lead to next-generation magnetoelectric devices.

研究成果の概要（英文）：Polarization is one of the most important property of materials. In this work, we focused on the magnetic field-induced polarization switching in molecular materials lacking long-range ordering (OD systems). Particularly, we investigated the polar polynuclear complexes with magnetic structures that could be tuned by magnetic fields (e.g. antiferromagnetic or frustrated systems). In these two years, we have successfully obtained a spin-crossover complex exhibiting largest field-induced polarization up to date. Besides, we also screened out an antiferromagnetic trinuclear Fe complex exhibiting polarization change during phase transition. Pulsed magnetic fields measurements revealed that it possesses a spin ground state that could be switched by magnetic field of 97 T. Another single-molecule magnet with a non-collinear spin structure was also shown to exhibit magnetic field-induced polarization current, featuring a clear non-linear effect.

研究分野：Coordination Chemistry

キーワード：Magnetoelectric Coupling　Electric Polarization　Molecular Materials

１．研究開始当初の背景

Polarization is a fundamental property of materials. Various stimuli can switch the magnitude and orientation of polarization, forming the basis for many technologies. Recently, magnetic field switching in multiferroic materials has attracted attention in condensed matter physics. This phenomenon, known as magnetoelectric coupling, provides an additional way to control these systems. For example, in $TbMnO_3$, a large magnetoelectric effect occurs during a cycloidal spiral spin ordering, which induces ferroelectric order (***Nature***, 2003, *426*, 55). This discovery spurred further research into magnetoelectric effects in spiral magnets (***Rep. Prog. Phys.***, 2014, *77*, 076501).

With the miniaturization of electronic devices and advances in molecular spintronics, a key challenge arises: how to obtain molecular materials without long-range ordering exhibit similar effects? Recently, magnetic fields have been shown to affect electric polarization hysteresis in molecular ferroelectric crystals (***Science***, 2020, *367*, 671). Additionally, single-molecule magnets have demonstrated the magnetodielectric effect (***J. Am. Chem. Soc.***, 2018, *140*, 7795). Furthermore, electric current release upon applying a magnetic field has been observed in a piezoelectric Mn(III) complex with spin crossover behavior (***Nat. Commun.***, 2019, 10, 4043; ***AIP Adv.***, 2019, *9*, 085219; ***Inorg. Chem.***, 2021, *60*, 6167). However, these studies focus either on second-order effect (e.g. magnetostriction) or specific condensed phases like the Jahn-Teller liquid.

In this context, we propose to investigate the direct magnetic field-induced polarization switching in polar molecular crystals with specific spin structures responsive to magnetic fields, paying particular attention to frustrated systems and spin crossover molecules that exhibits potential field-dependent electric dipoles at a molecular level.

２．研究の目的

The proposed research aims to explore magnetic field-induced polarization changes in the polar crystals composed of molecules with field-responsive magnetic structures, representing a new direction in molecular magnetoelectrics. Specifically, we seek to investigate new mechanisms beyond spiral spin ordering that could be applied to molecular crystals or even isolated molecules.

Taking advantage of the designability and tailorability of molecular systems, we aim to achieve more versatile physical behaviors not possible in conventional inorganic systems. Fundamentally, the uniformity of molecular crystals will help clarify the mechanisms of magnetoelectric coupling at the molecular level.

３．研究の方法

The methodology for this research involves several key steps. Firstly, an extensive literature survey will be conducted to identify potential candidate materials crystallized in polar space groups. These candidates will be screened to select crystals with suitable sizes and good integrity. Magnetometry will be employed to gain accurate knowledge of their magnetic properties.

Next, the standard methodology for measuring the magnetic field-dependent pyroelectric effect using various standard samples will be established, and then we will then record and analyze the current release from single crystals upon changing the magnetic field to investigate polarization changes induced by both conventional and pulsed magnetic fields. Additionally, we will measure the pyroelectric current in various magnetic fields and integrate these measurements to obtain information on temperature-dependent polarization changes, derived from the thermally induced population changes in the magnetic field.

４．研究成果

The first system that we focused on in this project is an oxo-bridged mixed-valence complexes, $[Fe_3O(piv)_6(py)_3]$. We unambiguously confirmed the electron localization/delocalization phase transition occurring at two inequivalent metal sites via variable-temperature Mössbauer spectroscopy and single-crystal diffraction analyses. Notably, as the compound crystallizes in a polar space group,

changes in molecular dipole moments lead to a measurable sharp pyroelectric current during the transition process, indicative of polarization switching. As we are aware, this is the first experimental observation of polarization switching behavior induced by electron delocalization in absence of external electric fields.

Furthermore, our theoretical analyses via density functional theory and point-charge calculations further elucidate the intramolecular electron transfer mechanism, affirming its crucial role in polarization behavior. This aligns with our theoretical simulation of the potential magnetoelectric effect, positing the system as an ideal model for single-molecule magnetoelectrics due to its polar crystal structure, slight asymmetry at valence-active sites and the antiferromagnetic interactions between them. Magnetization and polarization measurements under pulsed magnetic fields further estimate the critical field of *ca*. 97 T to observe these effects.

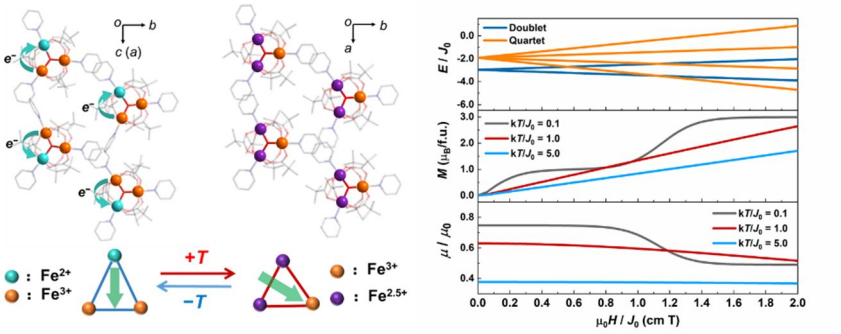

Fig.1 Thermally-induced polarization switching in a mixed valence Fe3 complex with non-collinear ground-state spin structure and the simulated magnetoelectric effect of it.

To summarize, we observe thermally induced polarization switching in a trinuclear mixed-valence Fe complex with non-collinear spin structures. Simulation suggests its potential as single-molecule magnetoelectrics with a mechanism similar to that for $LuFe_2O_4$, where spin-flop leads to change in the electronic charge on Fe ions at the domain boundary. Pulsed magnetic field measurements render the estimated critical fields for such effect (Fig. 1). This manuscript has been submitted and is now under review.

During the setup of our magnetoelectric measurement system with our MPMS system, we identified another complex, [(Fe(*SS*-cth))(Co(*RR*-cth))(*μ*-dhbq)]$(AsF_6)_3$, exhibits an abrupt SCO process at Fe site, which induces a redistribution of electron density owing to the change in the metal-ligand interaction. The resulting directional shift of electron density transfer, together with the directional alignment of molecules in lattice, lead to a large polarization change of 0.45 μC cm^{-2} observed during the SCO process. Interestingly, the same process can also be induced by pulsed magnetic field with the same polarization change, which sets a new record in the molecular crystals (ref. 0.12 μC cm^{-2} as the previous record). Even in various inorganic multiferroic crystals, the magnitude of polarization change of our crystal is competitive. This highlights the huge potential of our approach for realizing polarization change toward the threshold for practical applications (Fig. 2).

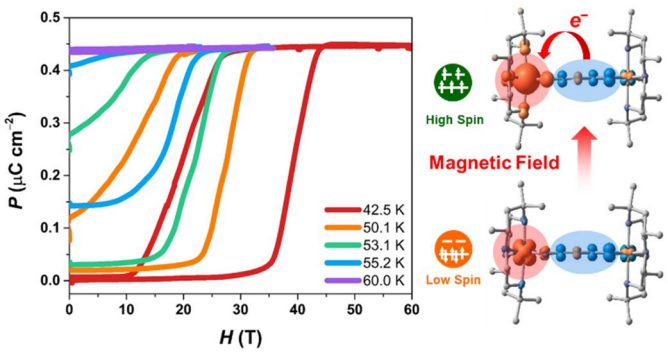

Fig. 2 Giant magnetic field-induced polarization in a [FeCo] crystal exhibiting SCO with strong metal-ligand covalency (***J. Am. Chem. Soc.*** 2023, *145*, 15647–15651, collaboration with M. Tokunaga at ISSP).

The strategy we proposed to achieve large polarization change, i.e. enhancing the change of metal-ligand covalency in the SCO process to induce a significant electron redistribution, is a significant step forward in the practical application of molecular materials with ME coupling. This strategy can be readily applied to molecular crystals with other electron dynamics, especially valence tautomeric materials that possess an even larger polarization change. This manuscript has been

published as ***J. Am. Chem. Soc.*** 2023, *145*, 29, 15647–15651.

Another system under intense investigation now is a transition metal-based chiral single-molecule magnet with frustrated spins in accord with our proposal. In measurements up to date, magnetic field-induced current release has been confirmed. However, more detailed characterizations to illustrate its origin is now in progress.

Besides these systems, during the preparation and characterization, many novel molecular crystals with polarization switching behavior induced by various stimuli have been found and characterized.

５．主な発表論文等

〔雑誌論文〕　計6件（うち査読付論文　6件／うち国際共著　6件／うちオープンアクセス　1件）

１．著者名 Zhang Xiaopeng、Xu Wen-Huang、Zheng Wenwei、Su Sheng-Qun、Huang Yu-Bo、Shui Qirui、Ji Tianchi、Uematsu Mikoto、Chen Qian、Tokunaga Masashi、Gao Kaige、Okazawa Atsushi、Kanegawa Shinji、Wu Shu-Qi、Sato Osamu	４．巻 145
２．論文標題 Magnetoelectricity Enhanced by Electron Redistribution in a Spin Crossover [FeCo] Complex	５．発行年 2023年
３．雑誌名 Journal of the American Chemical Society	６．最初と最後の頁 15647～15651
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/jacs.3c02977	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

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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オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

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
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D3DT03915C	査読の有無 有
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１．著者名 Kanegawa Shinji、Wu Shu-Qi、Zhou Ziqi、Shiota Yoshihito、Nakanishi Takumi、Yoshizawa Kazunari、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 -
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/jacs.4c02882	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
2．論文標題 Macroscopic Polarization Change of Mononuclear Valence Tautomeric Cobalt Complexes Through the Use of Enantiopure Ligand	5．発行年 2022年
3．雑誌名 Chemistry - A European Journal	6．最初と最後の頁 e202202161
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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1．著者名 Su Sheng‐Qun、Wu Shu‐Qi、Huang Yu‐Bo、Xu Wen‐Huang、Gao Kai‐Ge、Okazawa Atsushi、Okajima Hajime、Sakamoto Akira、Kanegawa Shinji、Sato Osamu	4．巻 61
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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〔学会発表〕　計2件（うち招待講演　0件／うち国際学会　2件）

1．発表者名 Shu-Qi Wu
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3．学会等名 The 18th International Conference on Molecule-Based Magnets（国際学会）
4．発表年 2023年

1．発表者名 Shu-Qi Wu, Pritam Sadhukhan, Shinji Kanegawa, Osamu Sato
2．発表標題 Electronic pyroelectricity in valence tautomeric complexes
3．学会等名 8th Asian Conference on Coordination Chemistry（国際学会）
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			
中国	Yangzhou University			