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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）Polar-axis-deformation induced molecular pyroelectrics for waste heat harvesting

研究課題名（英文）Polar-axis-deformation induced molecular pyroelectrics for waste heat harvesting

研究代表者
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交付決定額（研究期間全体）：（直接経費）　　3,600,000円

研究成果の概要（和文）：18-crown-6(18C6)とof3-R-adamantane-1-aminium 誘導体(HADA-R, R=H, F, Cl, Br, OH)を用いて、一連の結晶の合成に成功した。すべての(HADA-R)(18C6)ClO4結晶は類似した1次元超分子カラム構造を有していた。R=Hの場合、293 K付近HADA-Hと18C6で回転凍結転移を起こし、その結果、転移温度以上で大きな熱膨張が見られた。R=Fの場合、NH3とFが高温で無秩序化していた。従って、低温で結晶は強誘電相にあることが示唆された。R=Clの場合、結晶は18C6の回転-スイング-静止に伴い、負-ゼロ-正の熱膨張を示した。

研究成果の学術的意義や社会的意義
This research would a) enrich the design strategy of functional molecular materials, b) expand the area of high-performance pyroelectrics, and c) enlighten the application of molecular materials in energy problems.

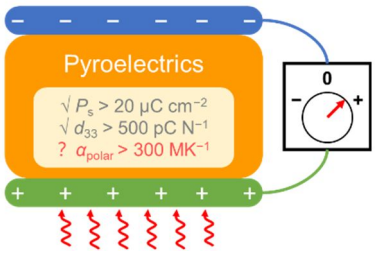
研究成果の概要（英文）：Using 18-crown-6 (18C6) and 3-R-adamantane-1-aminium (HADA-R, R = H, F, Cl, Br, OH), a series of crystals were successfully synthesized. All of the (HADA-R)(18C6)ClO4 crystals contain similar 1D supramolecular columns structure. For R = H, both HADA-H and 18C6 are rotating above room temperature, while undergo rotational-freezing transitions around 253-333 K, resulting in the significant thermal expansions along polar axis as designed. For R = F, the HADA-F exhibit flipping motion in the 1D column with disordered NH3 and F at above 373 K, indicating the crystal may be ferroelectric at lower temperature. For R = Cl, the one-dimensional columns in the crystal were reverse-arranged so the polarity is canceled, and so does for R = Br. The R = Cl crystal showed negative-zero-positive thermal expansion associated with the rotation-swing-stationary transition of 18C6, whereas this transition was not observed in the R = Br crystal, which has a larger atomic radius.

研究分野：機能物性化学関連

キーワード：Supramolecule　pyroelectricity　Structural flexibility　Thermal expansion

１．研究開始当初の背景

Low-grade waste heat (<150 °C) has been one of the major concerns in science and industry, because most of they are difficult to recycle. One of the most promising way to recycle low-grade waste heat is by pyroelectric materials (such as PVDF, TGS and ZnO), which can generate electric current during temperature fluctuation (T). The key parameter of pyroelectric materials is their pyroelectric coefficient (p), which can be describe as:



$$p = \partial P_s/\partial T + dc\alpha_{polar}. \quad (1)$$

In this formula, $\partial P_s/\partial T$ represents the change spontaneous polarization (P_s) over temperature (T). The product term $dc\alpha_{polar}$, is a multiplication of piezoelectric constant (d), elastic stiffness (c) and deformation coefficient (α_{polar}). For details, α_{polar}, the "polar axis deformation", is defined by the change of the length of polar axis over T. Massive progresses have been achieved by enlarging P_s (~20 μC cm^{-2}) and d (~500 pC N^{-1}). However, α_{polar} is usually small (~20 MK^{-1}) due to the rigid nature of inorganic materials.

Molecular materials are attracting extensive attention recently due to their diverse function by specific molecular groups. Some molecular materials can crystalize in polar state to exhibit distinguished piezoelectricity, pyroelectricity and ferroelectricity. On the other hand, molecular materials, especially MOFs and supramolecular crystals (*Chem. Commun.*, **2018**, 54, 5164) can exhibit extra-large structural flexibility with α > 300 MK^{-1}. However, it is rare to be structurally flexible and polar at the same time, because of the conflict nature that it usually requires strong dipole interactions to be polar while requires week intermolecular interactions to be structurally flexible.

We already synthesized [(HADA-OH)(18C6)]ClO_4 crystals with **a record-high thermal expansion in organic crystal (493 MK^{-1}) and large pyroelectric coefficient around room temperature (–540 μC m^{-2} K^{-1})**. These early results indicated a novel strategy for the design of high-performance pyroelectrics.

２．研究の目的

This research aims to obtain series of polar molecular materials whose polar axis undergoes large deformation, evaluate their pyroelectricity to build structure-performance relationship and explore their applications for waste heat harvesting.

３．研究の方法

The research methods include the following:

3.1 Design and Synthesis (Cation Modification)

3.2 Structure Analysis

3.3 Properties Analysis

3.4 Device Fabrication

4．研究成果

4.1 Design and Synthesis

We successfully synthesized the derivatives of 3-hydroxyl-adamantane-1-aminium (HADA-R, R = H, F, Cl, Br) by cation modification. By adopting 18-crown-6 (18C6) as the supramolecular assembly, we obtained a series of crystals, (HADA-R)(18C6)ClO_4.

4.2 Structure and Properties

All of the (HADA-R)(18C6)ClO_4 share similar 1D supramolecular columns formed by the packing of (HADA-R)(18C6) one to another, as shown in Fig 1. However, they exhibit significantly different properties.

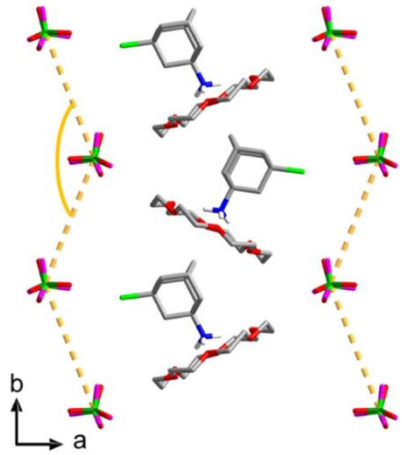


Fig 1. 1D supramolecular columns

1) The H-compound crystallizes in *CmC*2_1 at 353-433 K and *Pca*2_1 at 113-333 K. At 253-333 K, both HADA-H and 18C6 undergoes rotational-freezing transition, resulting in large thermal expansions. This compound exhibits large polar axis deformation as designed.

2) The F-compound crystallizes in *Cmcm* at 373 K, *Cmc*2_1 at 253 K, and *Pca*21 at 133 K. The disordered NH_3 and F in the higher-symmetry *Cmcm* phase indicate that HADA-F undergoes flipping motion in the 1D supramolecular column, and it is a potential 1D ferroelectric.

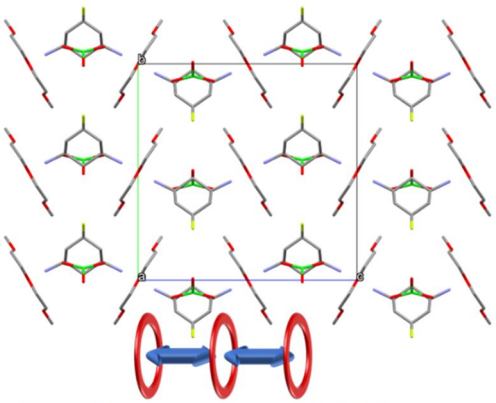


Fig 1. Flipping motion of HADA-F

3) The Cl-compound exhibits polymorphism. The majority polymorphism crystallizes in *Pbca* with reverse-arranged columns. We found that this nonpolar crystal exhibits a planar negative-zero-positive thermal expansion transition due to the rotation-swing-static transition of 18-crown-6. These results are enlightening in discovering novel kinds of zero thermal expansion, and the results are published in *Chemistry of Materials*. (10.1021/acs.chemmater.3c00358)

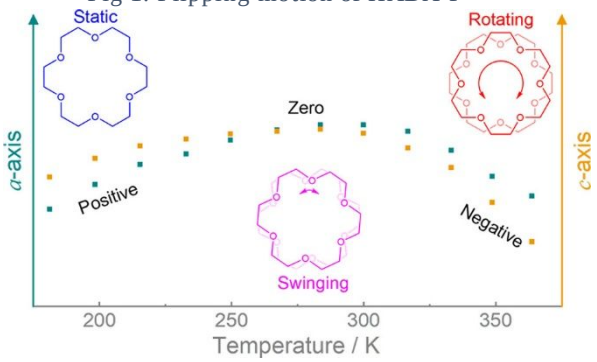


Fig 3. Thermal expansion of HADA-Cl

4) The Br-compound crystallizes in *Pmma* at 333-413 K and P212121 at 113-313 K. This compound did not show significant thermal expansion, which may be due to the large size Br atom that blocks the 18C6 from molecular motion.

5) For OH-compounds, we successfully establish a system that can measure the pyroelectric current corresponding to the change of temperature ranging from 77 K to 600 K, and suitable for powder, single-crystal and thin-film samples. We have explored the method of preparing OH-compound samples on thin films and trying to investigate the pyroelectric performance of the prepared thin films.

５．主な発表論文等

〔雑誌論文〕　計8件（うち査読付論文　8件／うち国際共著　3件／うちオープンアクセス　0件）

１．著者名 Kyoya Yuri、Takahashi Kiyonori、Kosaka Wataru、Huang Rui-Kang、Xue Chen、Wu Jia-bing、Miyasaka Hitoshi、Nakamura Takayoshi	４．巻 -
２．論文標題 Unlocking single molecule magnetism: a supramolecular strategy for isolating neutral MnIII salen-type dimer in crystalline environments	５．発行年 2024年
３．雑誌名 Dalton Transactions	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） 10.1039/d4dt00323c	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 －

１．著者名 Shao Bing、He Xing‐Lu、Huang Du、Xiang Yi‐Lei、Luo Yan、Wei Yan‐Mei、Jiang Linbin、Huang Rui‐Kang、Dong Min、Huang Jin	４．巻 -
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３．雑誌名 Advanced Functional Materials	６．最初と最後の頁 2315991
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/adfm.202315911	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

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２．論文標題 A Mixed Protonic?Electronic Conductor Base on the Host?Guest Architecture of 2D Metal?Organic Layers and Inorganic Layers	５．発行年 2023年
３．雑誌名 Advanced Science	６．最初と最後の頁 202205944
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2．論文標題 Multifunctional Triggering by Solid-Phase Molecular Motion: Relaxor Ferroelectricity, Modulation of Magnetic Exchange Interactions, and Enhancement of Negative Thermal Expansion	5．発行年 2023年
3．雑誌名 Chemistry of Materials	6．最初と最後の頁 2421～2428
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2．論文標題 A Proton Conductive Porous Framework of an 18-Crown-6-Ether Derivative Networked by Rigid Hydrogen Bonding Modules	5．発行年 2022年
3．雑誌名 Angewandte Chemie International Edition	6．最初と最後の頁 e202211686
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/anie.202211686	査読の有無 有
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2．論文標題 Fluoride-bridged dinuclear dysprosium complex showing single-molecule magnetic behavior: supramolecular approach to isolate magnetic molecules	5．発行年 2022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/D2DT01615J	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 －

〔学会発表〕　計3件（うち招待講演　0件／うち国際学会　2件）

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2．発表標題 Towards molecular multiferroics by supramolecular rotor and [MnCr(oxalate)3]− salts
3．学会等名 18th International Conference on Molecule-Based Magnets, ICMM2023（国際学会）
4．発表年 2023年

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4．発表年 2023年

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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