

ボウル状トリチアスマネン誘導体の強誘電性

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Ferroelectricity of bowl-shaped trithiasumanene derivatives

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【Abstract】 Organic ferroelectric materials have been widely used in the fields of sensors, nonvolatile memory storage, and intelligent information technology.^[1] In this work, a new concept for the organic ferroelectricity was pointed in a bowl-shaped non-planar π -functional molecule. Four kinds of alkoxy-substituted trithiasumanene derivatives (CnTSS) with $n = 6, 8, 10,$ and 16 were examined in terms of thermal stability, phase transition behavior, crystal structure, dielectric properties, and electric field–polarization curve. The ferroelectricity due to bowl-inversion was firstly observed in the solid state.

【Introduction】 Recent progress in organic synthesis expands a variation of new bowl-shaped π -molecular system such as sumanene and corannulene. However, physical functions of these π -curvature molecules have been insufficiently examined from the viewpoint of electrical conductivity, magnetism, optical, and ferroelectric properties, due to the limitation of synthetic difficulty. Herein, we focused on the bowl-shaped π -electronic system of trithiasumanene derivative to design ferroelectric response in the solid state. The ferroelectricity of trithiasumanene derivatives bearing six $-\text{OC}_n\text{H}_{2n+1}$ chains (**CnTSS**) was successfully observed, which became a candidate to form new class of organic ferroelectric nonvolatile and ultra-high density memory application.

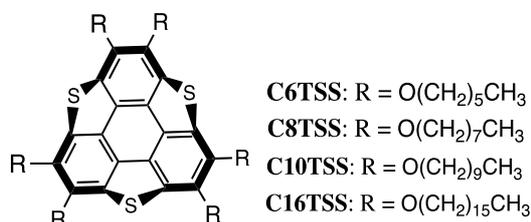


Fig. 1 TTS derivatives in this study.

【Experimental】 Four kinds of alkoxy-substituted TTS derivatives of C6TSS, C8TSS, C10TSS, and C16TSS were synthesized. Thermodynamic responses, dielectric properties, phase transition behaviors, and molecular assembly structures were evaluated by TG, DSC, and PXRD experiments, and the electric field – polarization (P - E) curves were examined in all CnTSS derivatives bearing different alkoxy chain length at $-\text{OC}_n\text{H}_{2n+1}$ with $n = 2, 6, 8, 10,$ and 16 (Fig. 1). Single crystals of short-chain derivative C2TSS were obtained to clarify the bowl-shaped molecular and packing structure.^[2]

【Results and Discussion】 Three derivatives of C6TSS, C8TSS, and C10TSS indicated one reversible solid-solid (S1-S2) phase transition at 400, 373, and 363 K, respectively, whereas the longest alkyl chain derivative of C16TSS showed the liquid crystalline M1 phase

before the melting. The PXRD pattern at M1 phase of **C16TSS** was consistent with the formation of discotic hexagonal columnar (Col_h) phase.

Single crystal X-ray structural analysis of **C2TSS** (Figs. 2b and 2c) indicated the formation of columnar π -stacking structure of each bowl-shaped molecule. The space group of acentric $P3c1$ generated a polar axis along the c axis, corresponding to the π -stacking direction. Each π -stack has a permanent dipole moment, and the number of polar π -stacks (A and B) was observed at 2:1 ration with a net dipole moment, which was consistent with the ferroelectric ground state. Temperature-dependent PXRD patterns of **C10TSS** indicated the melting state of $-\text{OC}_{10}\text{H}_{21}$ chains and same packing structure of all **CnTSS** derivatives to that of **C2TSS** (Fig. 2a).

The frequency (f) and temperature (T) dependent dielectric constants showed the anomalies around the S1-S2 and S2-M2 phase transitions. Both ϵ_1 and ϵ_2 values of all **CnTSS** crystals were enhanced at higher T and lower f conditions, suggesting slow molecular motions in solid or M1 phases were thermally activated due to the melting of alkoxy chains surrounding the π -stacking bowl columns. E Ferroelectric hysteresis in the P - E curves swere confirmed in S2 phase of **C6TSS**, **C8TSS**, and **C10TSS** (Fig. 3), whereas **C16TSS** also showed the ferroelectricity at liquid crystalline Col_h phase. The hysteresis loops of **C6TSS**, **C8TSS**, and **C10TSS** were clearly confirmed at f range from 100 to 200 Hz, whereas that of liquid crystalline **C16SS** was observed at much lower f range from 10 to 100 Hz.

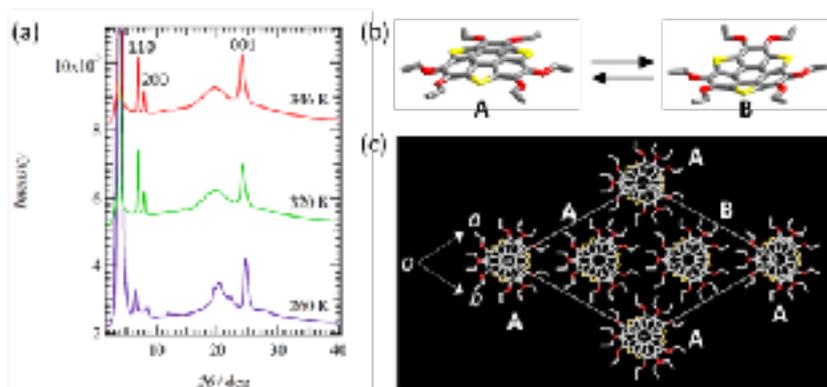


Fig.2 Molecular assembly structures of **CnTSS** derivative. (a) Temperatuer dependent PXRD patterns of **C10TSS**. (b) Bowl-to-bowl inversion from down **A** to up **B** conformation. (c) Unit cell of **C2TSS** viewed along the c axis.

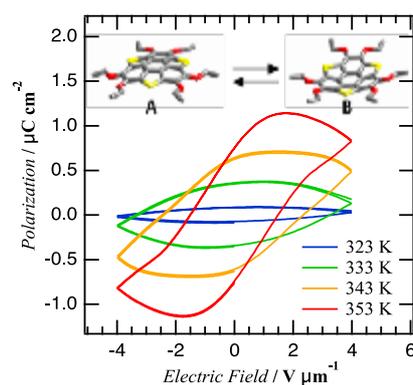


Fig.3 T -dependent P - E hysteresis curves of **C10TSS** at $f = 100$ Hz.

【References】

- [1] Akutagawa, T. *et al.*, *Nature Mater.* **8**, 342-347 (2009).
- [2] Xuexiang, L. *et al.*, *Angew. Chem. Int. Ed.* **53**, 535-538 (2014).