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Development of organic molecular crystals exhibiting both low and high dielectric properties by changing the crystallization solvent

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Abstract

We successfully developed a material that exhibits a dielectric constant modulation reaching up to 10^4 orders of magnitude using a single molecule through an extremely simple method: just changing the crystallization solvent. This achievement is based on a curved molecule, fluorosumanene, which exhibits a characteristic one-dimensional columnar structure derived from its bowl shape and in-plane vibrational motion in the solid state, as well as a behavior known as "bowl inversion motion" in solution.

Background & Results

In recent years, there has been growing interest in crystalline dielectric materials based on small organic molecules, in addition to the traditional inorganic and polymer materials that have dominated the development of dielectric materials. Organic compounds possess high potential to create flexible and printable materials by chemical control of their assembled structures and the various kinds of intermolecular interactions.

Monofluorosumanene (**FS**), a curved molecule derived from sumanene with a single fluorine atom introduction, exhibits bowl inversion dynamics in solution. This motion generates two isomers, **FS**$_{endo}$ and **FS**$_{exo}$, which differ in both the orientation and magnitude of their dipole moments depending on the geometry of the fluorine atom (Figure 1). In solution, **FS** exists as a diastereomeric mixture of **FS**$_{endo}$ and **FS**$_{exo}$, and resulting in an excess population of **FS**$_{endo}$ since **FS**$_{endo}$ is slightly more energetically stable. However, in the crystalline state, the composition ratio varies depending on the crystallization solvent used. For instance, when a polar solvent like DMF (dimethylformamide) is used, crystals with an excess of **FS**$_{exo}$ are obtained, in contrast to the solution-state equilibrium. On the other hand, using a less polar solvent like dichloromethane results in crystals with approximately a 1:1 ratio of **FS**$_{endo}$ to **FS**$_{exo}$. Dielectric spectroscopy revealed that the former exhibited Debye-type dielectric relaxation phenomena, while the latter showed an extraordinarily high dielectric constant (>10,000).

To elucidate the mechanisms underlying these properties induced by the crystallization solvent, quantum chemical calculations and molecular dynamics simulations were performed, revealing two key factors (Figure 2). The first is the difference in steric hindrance related to the position of the fluorine atom, which affects intermolecular interactions during crystal nucleation, making **FS**$_{exo}$ more easily incorporated into the crystal structure. The second factor is the contribution of solvation stabilization, which varies depending on the solvents. Solvation free energy analyses of solvation showed that **FS**$_{exo}$ is more stabilized than **FS**$_{endo}$ in DMF, while both isomers experience similar stabilization in dichloromethane.

Significance of the research and Future perspective

The realization of a dielectric constant reaching up to 10^4 orders is rare for purely organic materials. Furthermore, the ability to achieve both low-dielectric and high-dielectric properties from a single molecule by simply changing the crystallization solvent highlights the high potential of fluorosumanenes as energy-efficient dielectric organic crystal materials. Additionally, fluorosumanenes possess the unique characteristic of forming polar crystals. This feature, combined with the exceptional dielectric properties discovered in this study, is expected to enable their development as multifunctional materials.

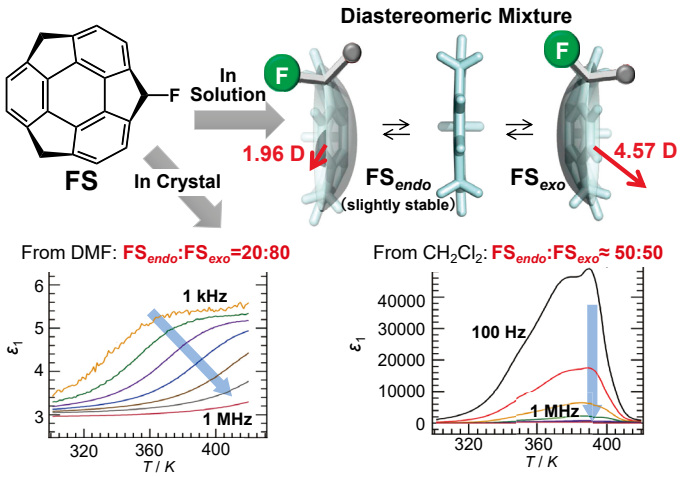

Figure 1

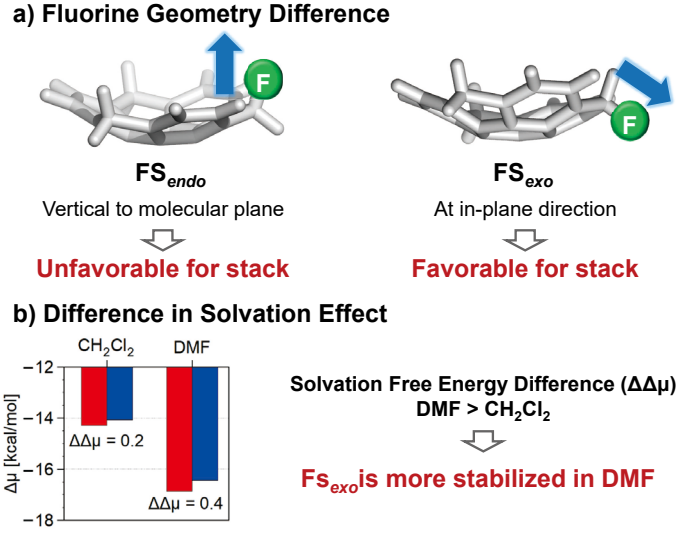

Figure 2

Patent

Treatise

Yakiyama, Yumi; Sakurai, Hidehiro et al. Biased bowl-direction of monofluorosumanene in the solid state. J. Am. Chem. Soc. 2024, 146 (8), 5224-5231. doi: 10.1021/jacs.3c11311

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Keyword organic crystal chemistry, curved-π conjugated system, dielectric property, fluorine, bowl inversion