Dielectric Response of Difluorinated Sumanene Caused by the In-plane Motion

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Organic molecule-based crystalline dielectric materials have attracted broad attention from chemists in recent years to develop new organic electronic devices. In their designing strategy, the molecular motion induced by the external dielectric field is required to maximize the polarization effect in the materials to realize a large dielectric constant. When we pay attention to the molecular motion in curved-π aromatics and their supramolecular complexes, especially to them containing C_{60}, it is found that they often show characteristic smoothness as exemplified by the molecular peapod.[1)] Such examples indicate that the "curve-to-curve" contact in the curved-π aromatics will afford the smooth molecular motion in the solid state. Sumanene (**1**) is one of the representative buckybowls and is known to show unique properties such as bowl inversion behaviour derived from its unique bowl shape.[2)] Especially **1** affords unidirectionally arraigned π-stacking columns in the solid state.[3)] However, this nature also makes the bowl inversion behaviour of **1** useless for the induction of dielectric response in the solid state. In this context, we instead focused on the in-plane motion of **2** in its columnar structure and attempted to utilize this motion to bring out the dielectric response (Fig. 1). In this work, we designed and synthesized a new curved π-conjugated molecule difluorosumanene (**2**), which possesses two fluorine atoms on the same benzylic carbon on pristine sumanene to possess a large dipole moment along the in-plane direction. Thermal analyses, variable temperature X-ray diffraction and IR measurements indicated the presence of in-plane motion of **1** although no clear phase transition was involved. Indeed, the dielectric measurement using its both powder and single crystal clearly showed that both real (ε_1) and imaginary (ε_2) parts of the dielectric constant were enhanced above ~360 K at 1 MHz with a Debye-type dielectric relaxation, confirming the in-plane motion of **1** induced by the external electric field.

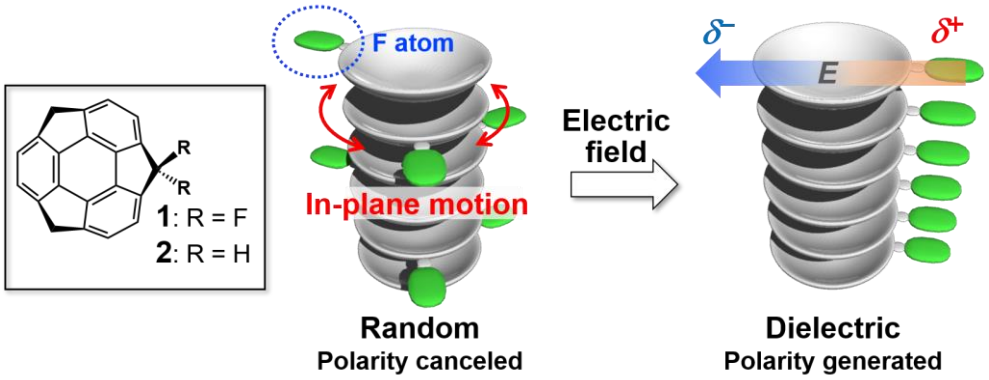

Fig. 1. Molecular structure of **1** and **2**, and Conceptual figure for this work.

References

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