Fluorosumanenes: Unique building blocks for dielectric materials

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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 arranged 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 sumanene skeleton 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 new fluorinated sumanene families and investigated their solid state dielectric properties. The representative one, difluorosumanene (2) possesses two fluorine atoms on the same benzylic carbon of pristine sumanene to have 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 2 although no clear phase transition was involved [4]-[16]. This thermal property of 2 realized an anisotropic dielectric response with a Debye-type dielectric relaxation in the single crystalline state. In addition, recently synthesized monofluorinated sumanene (3) was also investigated. Fluorine atom on the benzylic carbon of 3 has two different geometry, the outer (exo) and the inner (endo) sides of the bowl and therefore the two diastereomers show large difference in their dipole moments. We recently found that these diastereomers were convertible via bowl flipping motion in the solution state and that its exo-endo ratio in the crystalline state was controllable, showing significant difference in their dielectric responses.

Fig. 1. Molecular structure of 1, 2 and 3 as well as the conceptual figure for this work.