Bowl and Butterfly-like Shape Effects on the Formations and the Properties of Molecular Crystals

([1]*Graduate School of Engineering, Osaka University*, [2]*ICS-OTRI, Osaka University*) ○ Yumi Yakiyama[1,2]

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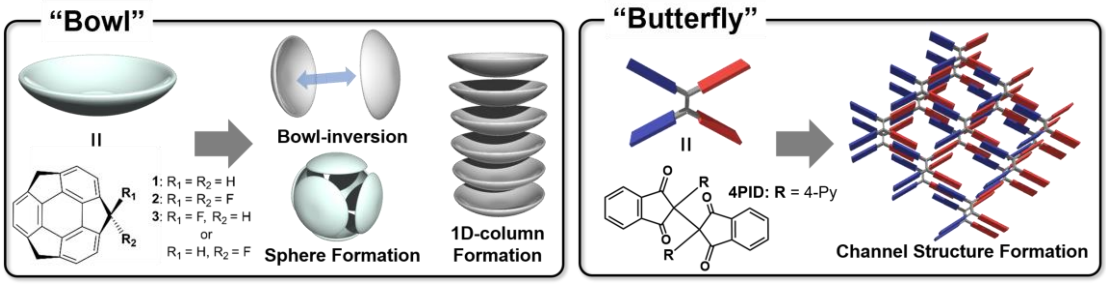
It is quite obvious that the molecular structure largely affects its aggregated structure as well as the resulting physical properties. Especially, some specific structural motifs generate characteristic packing patterns, which cannot be reached by the simple chemical functionalization. In this context, we focused on two types of non-planar molecular shapes, namely, bowl and butterfly-like structures, which possess clear structural features, showing 1D-column formation and 1D-channel construction, respectively, as the main building units of the functional molecular crystals (Figure). Here we show our recent works using bowl shaped sumanene derivative[1] and butterfly-shaped indanedione dimers[2] as well as their structural and physical properties.

"Bowl" shape molecule: Sumanene

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.[1] Especially **1** affords unidirectionally arraigned π-stacking columns in the solid state.[2] We focused on the possible in-plane motion of **1** in this 1D-stacking column structure and to confirm that we investigated the series of fluorinatedsumanenes via their 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 caused by the bowl flipping was involved.[3a] This thermal property of **2** realized an anisotropic dielectric response with a Debye-type dielectric relaxation in the single crystalline state. This dielectric property was further arranged by making solid solutions with pristine **1** and **2**.[3b]



Meanwhile, mono-substituted molecule, monofluorosumanene **3**, exhibited bowl inversion in the solution state, to be a diastereomeric mixture of the outer (*exo*)- and the inner (*endo*)-side F-substituted derivatives. The population ratio of the two conformers of monofluorinated derivatives in single crystals drastically changed depending on the crystallization solvents and the resulting *exo*/*endo* ratio emerged the significant change in the dielectric properties of the crystalline powder.[4]

"Butterfly" shape molecule: Indanedione dimers

4-pyridylindanedione dimer (**4PID**) is a distorted X-shape, in other words, "butterfly"-like molecule and affords high quality single crystals possessing 1D-channel structure with ca. 5 Å × 7 Å window size under the presence of less-polar solvent such as hexane as well as a tightly-packed structure by the recrystallization with polar solvent selectively. These two structures are interconvertible via guest molecule removal/insertion with keeping crystallinity.[5] The former 1D-channel structure was utilized for the incorporation of various kinds of molecules, such as chain, branched alkanes, simple aromatic compounds, etc. One useful example is the recognition of *p*-xylene from the xylene mixture which can be arranged by the number of N atoms in the hetero ring. This 1D-channel also worked as the space for emergence of unique physical properties such as second harmonic generation (SHG).

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