Design of molecular correlated motions in crystals by utilizing intermolecular cross-stacked packing manner of triaryltriazine derivates

Mingoo Jin

WPI-ICReDD, Hokkaido University
mingoo@icredd.hokudai.ac.jp

Keywords: Organic molecular crystal, Crystalline molecular rotor, Triaryltriazine

Design of correlated mechanical motion of molecules in crystals have been attracting significant interest for the development of molecular machines.1-3 In particular, gear-like molecular rotation via multiple rotary moieties has been noted as an attractive target because of the ability for transporting mechanical force at molecular-level as well as the alternation of the molecular geometry which can be related to the physical properties of solids.3 To achieve correlated motions in crystals, the crystal structure should provide (i) a local volume near the dynamic moiety, known as rotator, allowing molecular rotation to occur in the densely packed environment and (ii) a suitable intermolecular geometry between the neighbored rotators to exhibit correlated (geared) motion. However, the number of examples and mode of the correlated motions remains extremely limited due to the inherent difficulty to rationally design molecular crystal structures.

Here, we report the newly developed a crystalline molecular gear by utilizing inter-molecular packing manner of a 2,4,6-triaryl-1,3,5-triazine molecular rotors in crystal. The triazine multi-rotors possessing two different types of bulkiness of tri-alkyl silyl groups in stator as shown in below figure. Single crystal X-ray diffraction analysis revealed that the crystal of the molecular rotor 1 having TBS moiety clearly formed cross-stacked intermolecular packing in two molecules, and the dimer units were packed in separately. On the other hand, the rotor 2 possessing -O-TIPS moiety in stator constructed not only the cross-stacked gear geometry in dimer but also inter-dimer cross stacked packing mode of the gear units (Figure). Interestingly, the phenylene rotation of 1 and 2 occurred in correlated manner, observed by 2H and 13C-CPMAS solid-state NMR studies. Additionally, introduction of 2,3-difluorophenylene as the arylene rotators clearly states that the dipole-dipole interactions induced strong correlation of the geared motion in the solid-state. The precise correlation motions as well as the crystal structures will be described in the presentation.

Figure 1. Crystalline molecular gears by triaryltriazine possessing several types of bulky silyl derivates.