Controlling the arrangement of dipoles in the crystal by utilizing halogen bonding and bulky silyl moiety

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The design of dipole arrangement in a molecular crystal has attracted many interests in the crystal engineering field because integrated dipoles can play important roles in determining the electronic or photophysical properties in a solid state [1]. Generally, molecules bearing dipole prefer to arrange in antiparallel (nonpolar) alignment to cancel their polarity during the crystallization process (Fig. 1a, left). On the other hand, intermolecular interactions or effects between polar chains, such as halogen bonding, hydrogen bonding, steric effects, or chirality, enable the construction of polar crystals by compensation of the energetic disadvantage in the parallel alignment of the dipoles [2, 3] (Fig. 1a, right). Herein, we designed structurally asymmetric molecules 1-3 bearing polar 2,3-difluorophenyl group with a bulky silyl substituent on one side and a hydrogen (1) or a halogen substituent (2, 3) on the other side (Fig. 1b). Interestingly, in crystal 2 and 3, the halogen substituents formed triangle halogen supramolecular 3-synthon by halogen bonding among bromine or iodine substituents, resulting in helical parallel alignment of the dipoles, while antiparallel alignment in crystal 1 [4]. This quite simple modification of molecular structure allowed controlling the dipoles in the molecular crystal. In this presentation, we will deliver the detailed crystal structure and the arrangement of the dipoles.

Figure 1. (a) Antiparallel alignment (left) and parallel alignment (right) of polar chains. (b) This work; strategy for controlling the dipole arrangement in the crystal by utilizing halogen bonding and bulky substituent