The molecular perovskites with a general formula of ABX3, which mimic the cubic structure of the very well-known inorganic perovskites but has at least one molecular component (usually A-site cations and/or X bridges), have attracted growing attentions, as illustrated by the extensive studies on their phase transitions together with the relevant switching physical properties for possible applications such as dielectric switches, ferroelectrics, and multiferroics. Comparing with the well-studied perovskite oxides, the molecular perovskites with larger bridges as well as organic cations give rise to an increase of the complexity for structural variations as well as an opportunity to tailor the physical properties by taking advantage of the designable and tunable characteristics on the metal species, bridging ligands, and guest cation components.[1] This talk will present our recent works on the structural phase transitions of a series of new molecular perovskites and the relevant switching physical properties, such as the tunable dielectric switching behaviors caused by one-step or multi-step order-disorder transitions,[2] unusual temperature-sensitive dielectric response caused by the switchable molecular dynamics of polar guest cation in the variable confined space,[3] and a new multi-axial high-temperature ferroelectrics based on an unprecedented reconstructive ferroelectric transition achieved in a novel molecular perovskite.


**Keywords:** phase transition, ferroelectric, molecular dynamic