Effect of Guest Cations on the Ferroelectric Polarization Attributes of Supramolecular Metal-Organic Cavitand

Anant Kumar Srivastava, and Ramamoorthy Boomishankar*
Department of Chemistry, IISER Pune, Maharashtra, INDIA
(E-mail: aksrivastava@students.iiserpune.ac.in; boomi@iiserpune.ac.in)

Abstract:

Supramolecular metal-organic assemblies have gained recent attention as ferroelectric materials due to their synthetic simplicity, flexibility and ease in device fabrication.[1] Nevertheless, synthesis of such metal-organic based ferroelectrics is still challenging because of the strict requirement of a non-centrosymmetric polar packing arrangement. The noncentrosymmetric arrangement of dipoles in ferroelectric metal-organic and hybrid organic-inorganic materials can be easily induced by simple chemical modifications like nature of metal-ligand interactions, choice of cations and anions and the extra-framework molecules present in them. Noticeably, we have synthesized dipodal ligands based on phenyl phosphonic diamide backbone, $PhPO(NHPy)_2$ [Py = 2-pyridyl (L^1) or 3-pyridyl (L^2) or 4-pyridyl (L^3)], that can generate both centrosymmetric and noncentrosymmetric $\{M^{II}L_2\}_n$ based metal-organic assemblies.[2,3] Herein, I will discuss the synthesis and ferroelectric properties of two noncentrosymmetric cavitands $\{M^{II}L_2\}_4$ (M=Ni, Co) built on the phosphoramide ligand L^2, $PhPO(NH^3Py)_2$. The intrinsic cavity of the cavitands can encapsulate hydrated alkali metal cations, ranging from Li^+ to Cs^+ ions. Additionally, the guest-free and guest-encapsulated cavitands exhibit a well-saturated loop with high remnant polarization (P_r) ranging from 27 to 30 μCcm^{-2} with marginal variations in the coercive field (E_c) values. Interestingly, the ferroelectric fatigue measurements on all these systems show ample variation, as the cavitand with least polarizable Li^+ ion exhibits maximum (fatigue) tolerance whereas the most polarizable Cs^+ ions showing up to 35% loss in the P_r values, after 10^5 switching cycles. These observations highlight the importance of host-guest ferroelectric systems and effect of supramolecular interactions on the polarization attributes.

References and Notes:

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