Design of porous organic cage-cage cocrystals are extremely challenging, because there are no directional bonds like hydrogen bond, halogen bond and coordination covalent bonds (MOFs) associated with organic cages[1&2]. This work highlights the design and synthesis of multicomponent molecular cage-cage crystals without hydrogen bonds. A family of organic cages is identified later crystal engineering design principles[3] are applied and made design strategy robust by synthesizing, racemic and quasi racemic binary cage-cage cocrystals. Later, ternary and quaternary cage-cage cocrystals are synthesized. Cage-cage cocrystal design strategy hinges on concept of hetero chiral molecular recognition of organic cages which leads to widow-to-window and/or widow-to-arene crystal packing. 1,4-Dioxane played crucial role in switching crystal packing in quaternary (first quaternary in porous organic cage-cage cocrystal) cage-cage cocrystals and showed substantial gas sorption. In crystallographic point of view resultant quasi racemic binary cage-cage cocrystal retains crystal packing same as one of the native cage crystal packing and it shows more gas sorption.


Keywords: Porous Organic Cages, Crystal Engineering, Cocrystals