

Tuning the Packing Motifs of Contorted
Hexabenzocoronene Thin Films by Post-Deposition
Processing

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While the packing motifs of organic semiconductors have been shown to affect device performance, an understanding of why molecules crystallize into specific packing motifs, and how such packing motifs affect charge transport in devices remains lacking. Complicating such studies, accessing various polymorphs is difficult as the necessary conditions that appropriately balance the kinetics and thermodynamics of crystallization are highly materials system specific and must be experimentally determined. To this end, we have applied several post-deposition processing techniques to access different packing motifs in contorted hexabenzocoronene (HBC) thin films.

To tune the packing motif, we solvent-vapor anneal amorphous HBC films to induce crystallization. Using solvents with small hydrogen-bonding potentials and large molar volumes, we induce the formation of the commonly observed P21/c “slip-stack” packing motif that is also obtained on thermal annealing. Annealing with solvents having greater hydrogen-bonding potentials and smaller molar volumes, however, results in a previously-unpublished packing motif similar to that of the Pbcn “herringbone” structure of HBC.

To determine the relative stability of the two polymorphs, we subjected films of each polymorph to further processing. While HBC films with the herringbone packing motif showed no change in structure upon further thermal or solvent-vapor annealing, HBC films with the slip-stack motif readily converted to the herringbone motif upon solvent-vapor annealing with THF. Such an irreversible transition from the slip-stack structure to the herringbone structure suggests that the herringbone packing motif is thermodynamically favored.

To elucidate how chemical modifications affect the packing of molecules, we synthesized a series of four HBC derivatives having increasing fluorine substitutions on the peripheral aromatic rings and subjected them to the same post-deposition processing conditions. We found that we can access both packing motifs across the series of fluorinated molecules with the appropriate solvent choice. Unlike HBC, however, fluorinated HBC films having the slip-stack packing motif did not convert back to the herringbone packing motif upon solvent-vapor annealing with THF. Interestingly, fluorinated HBC films with the herringbone packing motif converted to the slip-stack packing upon thermal annealing, a transition not observed in films of the parent HBC compound. This transition indicates that the herringbone-packing motif is not the universally favored structure across the entire series of HBC derivatives explored. With the ability to access both packing motifs in hand, we are currently making HBC thin-film transistors to elucidate how the molecular packing affects charge transport.