The term ‘self-assembly’ describes the molecular processes of chemical organization which lead to nanostructured materials with emerging functions. The ability for humans to pre-program self-assembly through rational design of cooperative molecular components has changed the way scientists approach materials engineering, and has led to significant advances in medicine, electronics, and other areas of chemical science. In our recent work published in Angewandte Chemie International Edition, we directed the self-assembly between two organic semiconductors, one which can conduct positive charges (holes) and one which can conduct negative charges (electrons), using complementary hydrogen bonding interactions similar to those present in DNA. The self-assembled co-crystals displayed ambipolar charge transport in single-crystal field effect transistors with charge mobilities on the order of 0.1 cm$^2$V$^{-1}$s$^{-1}$, rivaling the highest reported charge mobilities of any co-crystal to date. The predictable intermolecular geometry of complementary hydrogen bonding provided a robust platform for self-assembly of these π-conjugated compounds, and enabled an unprecedented control of the solid state packing in organic semiconductors. This work, featured on the inside cover of Angewandte, represents a major advancement in solid-state structural control of organic electronic materials, and has implications for new ways of approaching morphology control in other thin-film organic semiconductor devices, such as organic photovoltaics.