A hybrid organic-inorganic two-dimensional layer structure with functional carboxylic acid (–COOH) groups protruding on both sides of zincophosphate sheets is prepared for the first time. The interior –COOH groups allow the hybrid sheets to stack tightly via strong hydrogen bonds to form a sturdy supramolecular network characteristic of extraordinary thermal stability. The supramolecular solid could exhibit tunable wettability via a facile mechano-chemical reaction, which is enabled by the –COOH groups exposed on the solid surface. We also observed an intriguing reversible lamella-to-nanorod transformation presumably initiated and prompted by surface and interior –COOH groups collectively. To investigate the reactivity of such a solid toward organic bases, we immersed the supramolecular network in solutions of bipyridyl alkanes and observed from the solutions two novel zinc coordination polymer compounds crystallized, demonstrating a unique disassembly-and-self-assembly process.