Brønsted acid doping of polythiophenes for dramatically improving electrical conductivities and thermoelectric properties

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Molecular doping is essential for organic thermoelectrics (TEs), but low solubilities of doped polymers hinder high quality film fabrication and complicate processing steps. Herein, we report particularly intriguing effects of molecular doping by a Brønsted acidic tris(pentafluoropheny)borane-water complex for poly(3-hexylthiophene) (P3HT). Notably, the doped P3HT films form a unique type Ⅱ polymorph with tightly interdigitated alkyl chains in ambient condition, which is known to be thermodynamically unfavorable. In addition, the doped P3HT shows conformational change to quinoid structure, leading to enhanced backbone planarity. As a result, the Brønsted acid-doped P3HT films exhibit superior electrical conductivities, TE power factors, figure-of-merits, and air stabilities, compared to those of P3HT films doped with conventional molecular or salt-type dopants. This doping strategy can also be expanded to other polythiophenes, guaranteeing its broad and practical applicability.