Doping polymer semiconductors is a central topic in plastic electronics and especially in the design of novel thermoelectric (TE) materials. In this contribution, it has been demonstrated that doping of oriented semicrystalline Poly(3-hexylthiophene-2,5-diyl) (P3HT) thin films with the dopant tris(4-bromophenyl) ammoniumyl hexachloroantimonate, known as magic blue (MB), helps reach charge conductivities of 3000 S cm\(^{-1}\) and TE power factors of 170 ± 30 μW mK\(^{-2}\) along the polymer chain direction. A combination of transmission electron microscopy polarized optical absorption spectroscopy, Rutherford backscattering, and TE property measurements helps clarify the conditions necessary to achieve such high charge conductivities. A comparative study with different dopants demonstrates that the doping mechanism is intimately related to the semicrystalline structure of the polymer and whether crystalline, amorphous or both phases are doped. The highest charge mobilities are observed when the dopant MB is preferentially located in the amorphous phase of P3HT, leaving the structure of P3HT nanocrystals almost unaltered. In this case, the P3HT nanocrystals are doped from their interface with the surrounding amorphous phase. These results indicate that doping preferentially the amorphous phase of semicrystalline polymer semiconductors is an effective strategy to reduce polaron localization, enhance charge mobilities, and improve TE power factors.

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