We investigated the influence of backbone regiochemistry on the conductivity, charge density, and polaron structure in the widely studied n-doped donor–acceptor polymer poly[N,N’-bis(2-octyldodecyl)-1,4,5,8-naphthalenediimide-2,6-diyl]-alt-5,5’-(2,2’-bithiophene) [P(NDI2OD-T2)]. In contrast to classic semicrystalline polymers such as poly(3-hexylthiophene) (P3HT), the regioirregular (RI) structure of the naphthalenediimide (NDI)-bithiophene (T2) backbone does not alter the intramolecular steric demand of the chain versus the regioregular (RR) polymer, yielding RI-P(NDI2OD-T2) with similar energetics and optical features as its RR counterpart. By combining the electrical, UV–vis/infrared, X-ray diffraction, and electron paramagnetic resonance data and density functional theory calculations, we quantitatively characterized the conductivity, aggregation, crystallinity, and charge density, and simulated the polaron structures, molecular vibrations, and spin density distribution of RR-/RI-P(NDI2OD-T2). Importantly, we observed that RI-P(NDI2OD-T2) can be doped to a greater extent compared to its RR counterpart. This finding is remarkable and contrasts benchmark P3HT, allowing us to uniquely study the role of regiochemistry on the charge-transport properties of n-doped donor–acceptor polymers.