Fusing bithiophene units with benzo moiety, benzo[2,1-b:3,4-b']dithiophene (BDT), was projected by theoretical calculations to lower the highest occupied molecular orbital (HOMO) energy level of resulting polymers compared with the bithiophene unit, which would enhance the open circuit voltage of bulk heterojunction photovoltaic cells fabricated from BDT-based polymers blended with PCBM. Furthermore, introducing the acceptor moiety (2,1,3-benzothiadiazole) should lower the optical bandgaps of the copolymers, which would improve the short circuit current. A series of new polymers were therefore synthesized, and bulk heterojunction photovoltaic devices were fabricated from blends of these structurally related polymers with PBCM to investigate the photovoltaic performances. Upon optimization of devices, total energy conversion efficiencies greater than 2% were achieved for two of these polymers. Further improvements are expected if the mobility and film morphology can be improved by the new materials design, together with low bandgap and low HOMO energy level.