Supporting Information



BDTT + SeDPP + TEGSeDPP (1.00:0.92:0.08) Pd(PPh₃)₄ Toluene/DMF

Synthesis of TEGSeDPP: The synthesis of **TEGSeDPP** followed the same route as the literature reported (*Adv. Energy Mater.* **2014**, *4*, 1300864), excepted the selenophene-substituted DPP was used.

Synthesis of PBSeDTEG8 (PBDSe3): **BDTT** (0.1809 g, 0.2000 mmol), **SeDPP** (0.1635 g, 0.1840 mmol) and **TEGSeDPP** (0.0135g, 0.0160 mmol) were dissolved into 10 mL toluene and 1 mL DMF in a flask protected by argon. The solution was flushed with argon for 10 minutes, then 10 mg of Pd(PPh₃)₄ was added into the flask. The solution was flushed with argon again for another 10 minutes. The oil bath was heated to 115 °C gradually, and the reaction mixture was stirred for 10 hours at 115 °C under argon atmosphere. Then, the mixture was cooled down to room temperature and the polymer was precipitated in ~100 ml methanol and the precipitated solid was collected and purified by silica gel chromatography using chloroform as eluent. The polymer was obtained as dark green-black solid, yield 30%. The polymer can be readily dissolved into chloroform, chlorobenzene or dichlorobenzene, etc.

Device layout



Fig. S1. The device layout and J-V measurement details for the actual devices.



Fig. S2. *J-V* measurement of the single junction devices simulating the subcells in the hybrid tandem structure. When measuring polymer front cell, we can coat a layer of back cell on the back of the ITO/Glass, thus part of incident is filtered before reaching the polymer absorber, *vice versa* for perovskite back subcell.