Supporting Information

Vapor-Phase Formation of a Hole-Transporting Thiophene Polymer Layer for Evaporated Perovskite Solar Cells

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KEY WORDS: in-situ polymerization, thiopehene, terthiophene polymer, hole-transporting polymer, co-evaporated perovskite, solar cell

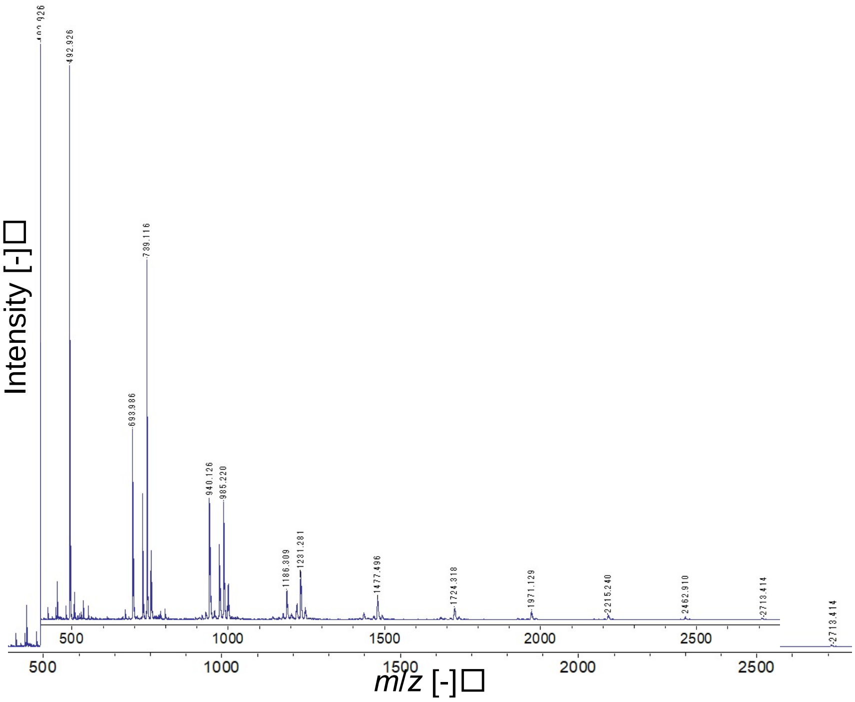


Figure S1. Molecular weight (relative molecular mass) of the in-situ vapor phase polymerized PTTh determined by a MALDI-TOFMS measurement using a ratio of the mass (*m*) and ionic charge (*z*).

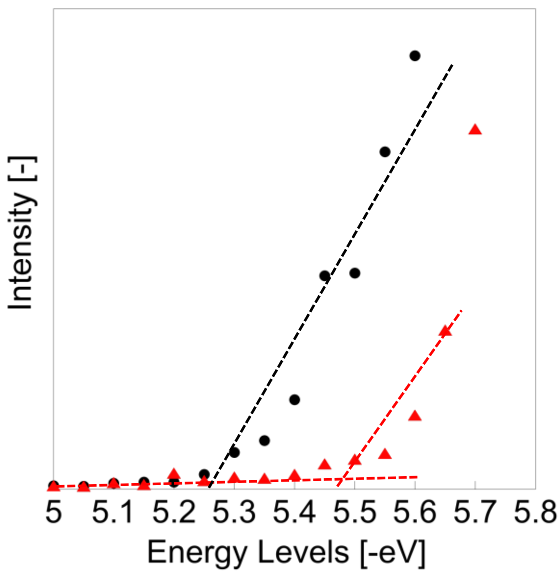


Figure S2. Photoelectron spectroscopy measured in air for estimating HOMO levels of PTTh (black dots) and TTh (red triangles).

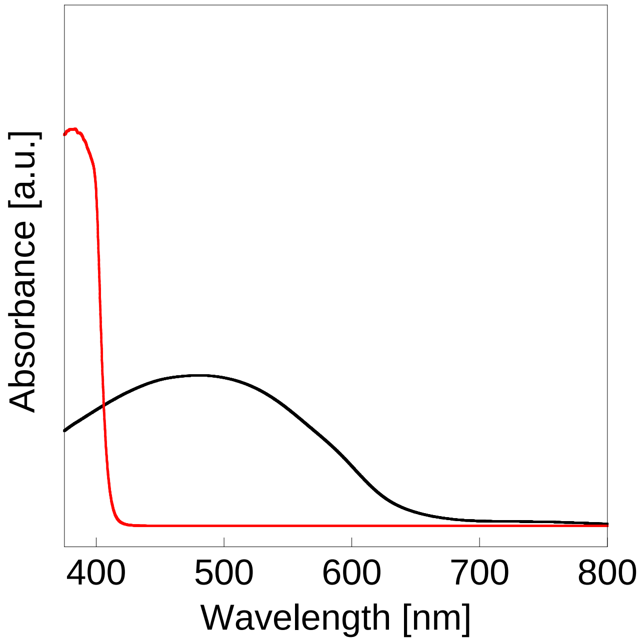


Figure S3. UV-Vis spectra of the thick PTTh (black) and TTh (red) layers of ca. 150 nm for determining the absorption edge.

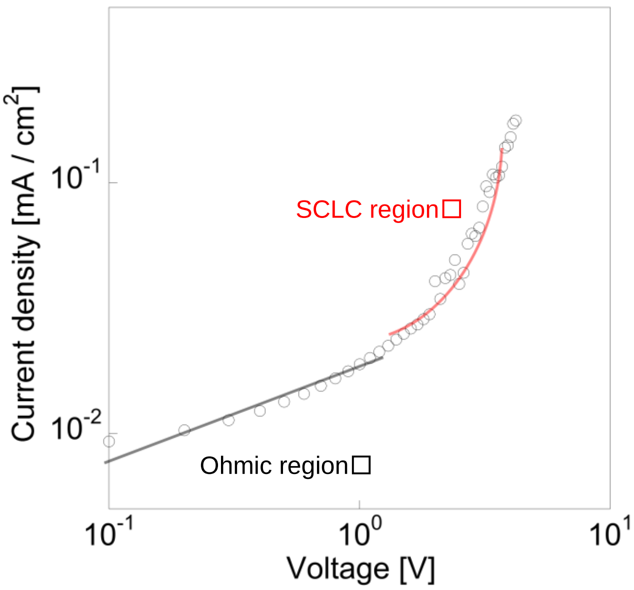


Figure S4. Space-charge-limited current (SCLC) result of PTTh using a hole-only device (FTO/PEDOT:PSS/PTTh/Au). At the SCLC region, hole mobility could be determined by Child-Langmuir equation of $\mu = 8JL^3/9\varepsilon V^2$ (μ: hole mobility, J: current density, L: film thickness, ε: electric constant, and V: voltage).

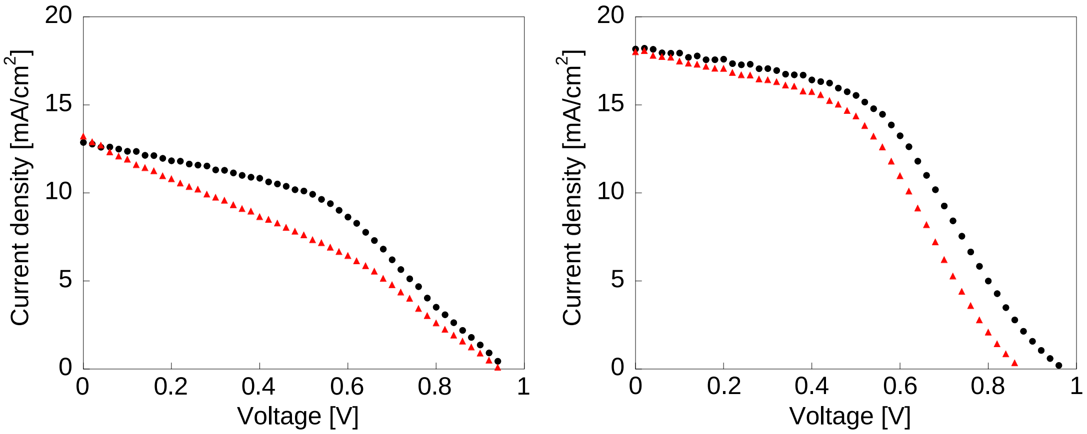


Figure S5. Hysteresis of the *I-V* curves fabricated with PTTh (left) and TaTm (right) (black dots: reverse scans and red triangles: forward scans).

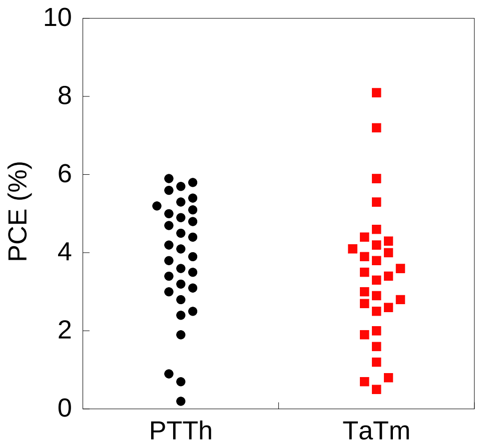


Figure S6. Statistics of PCEs of perovskite solar cells with (black cercles) PTTh and (red square) TaTm as hole transport materials.

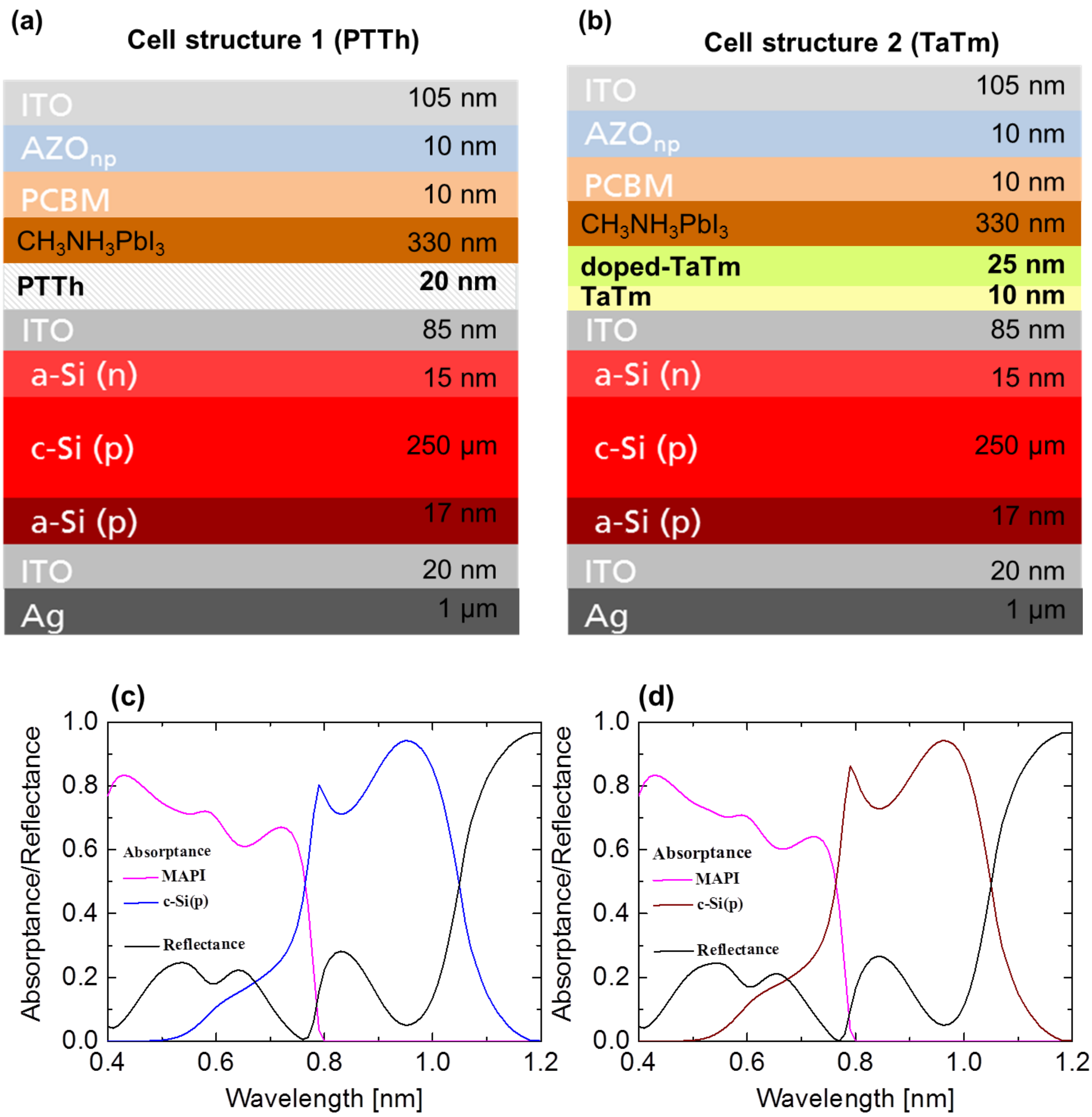


Figure S7. Simulated solar cell structures including cell structure 1 using PTTh (a) or the cell structure 2 using TaTm (b). The respective OPTOS simulation results display the absorptance in the perovskite and silicon *(planar rear side)*, as well as the reflectance for cell structure 1 (c) and cell structure 2 (d).

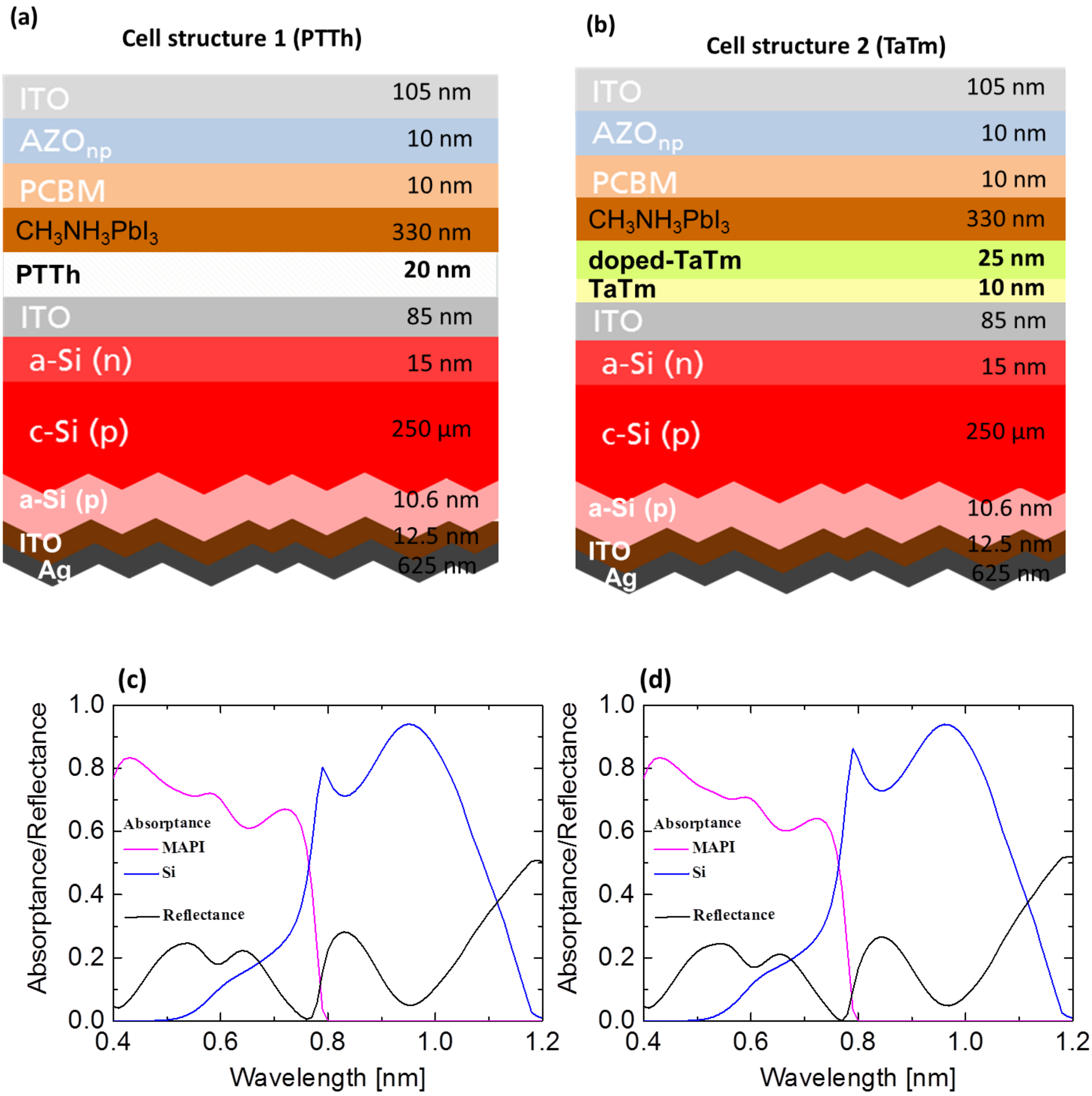
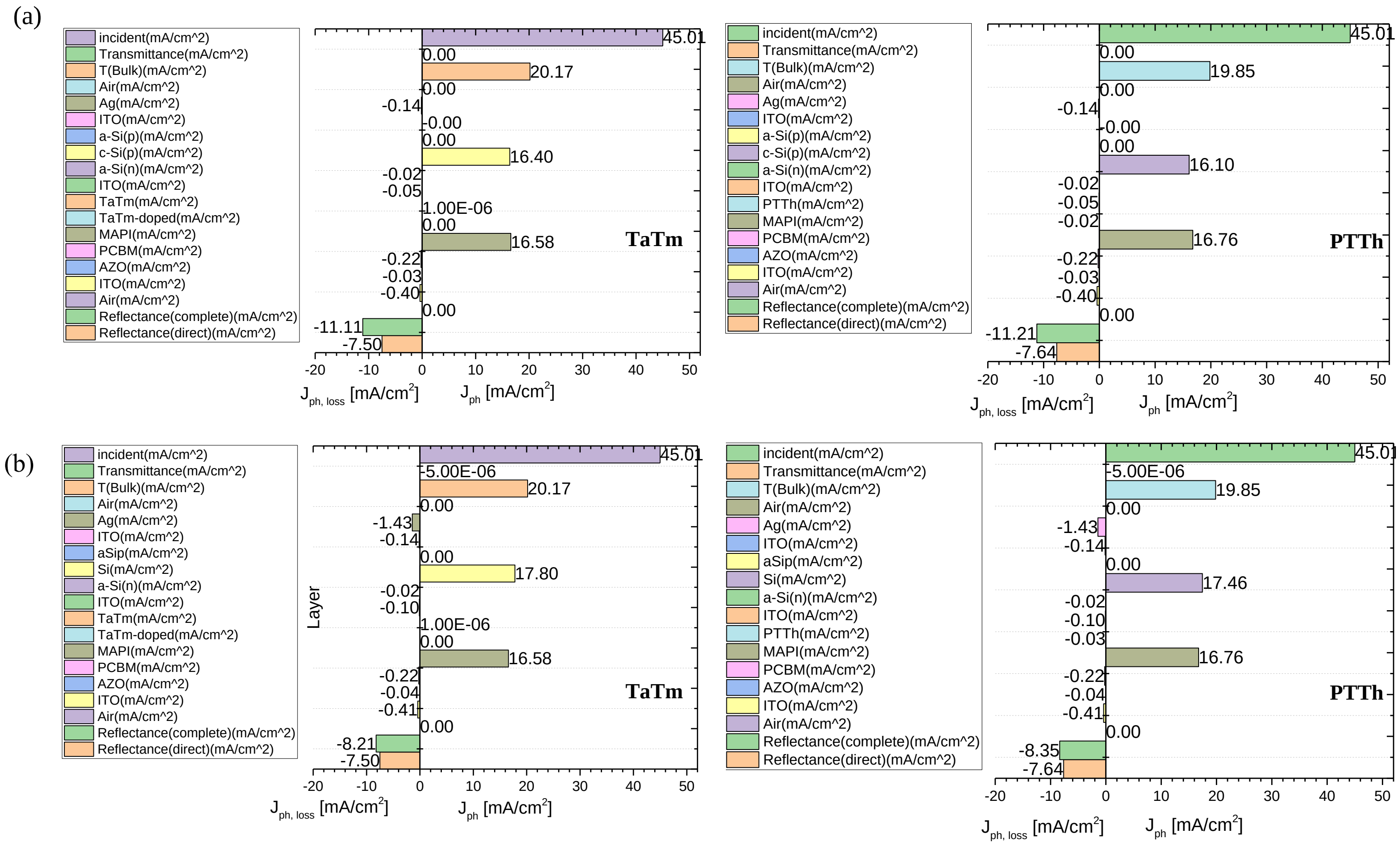


Figure S8. Cell structures including cell structure 1 using PTTh (a) or cell structure 2 using TaTm (b). The respective OPTOS simulation results display the absorptance in the perovskite and Silicon *(textured rear side)*, as well as the reflectance for cell structure 1 (c) and cell structure 2 (d).

Table S1. Current Extracted from OPTOS Simulation for Each Layer using (a) *Planar Rear Side* Silicon and (b) T*extured Rear Side* Silicon Substrates. *n-k* data has been taken from literature for PTTh[1], ITO[2], TaTm[2], doped-TaTm[2], co-evaporated perovskite[2], c-Si[3], a-Si[3], AZO[3], PCBM[4], and Ag[5].



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