Supplementary Information to

Polarization-enhanced Photoelectric Performance in Molecular

Ferroelectric Hexane-1,6-diammonium Pentaiodobismuth (HDA-Bil₅)-

based solar device

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Figure S1. Optical photograph of HDA-Bil_5 thin films with different thicknesses of 35 μ m (a), 25 μ m (b) and 10 μ m (c).



Figure S2. EDS spectra of HDA-Bil₅ (a) and TiO₂ (b) in HDA-Bil₅/TiO₂ composite film.



Figure S3. SEM images of HDA-Bil₅ single crystal (a) and HDA-Bil₅/TiO₂ films with different thicknesses of 10 μ m (b), 35 μ m (b), 45 μ m (c) and 70 μ m (e).



Figure S4. Optical photographs of TiO_2 thin-film before (a) and after (b) hydrothermal retreatment.



Figure S5. (a) *J*-t curves of the (HAD-Bil₅)-based solar device with a HAD-Bil₅ film thickness of 25 μ m before and after hydrothermal retreatment for TiO₂ ETL. (b) The evolution of the photocurrent density of the (HAD-Bil₅)-based solar device with different HAD-Bil₅ film thicknesses before and after hydrothermal retreatment for TiO₂ ETL. (c) *J*-t curves of the (HAD-Bil₅)-based solar device after exposing to air for different time at zero bias voltage under on-off sunlight simulator illumination.



Figure S6. Schematic and band diagram of (HDA-BiI₅)-based ferroelectric solar cells under different poling conditions: (a) without poling, (b) Positive poling, and (c) Negative poling .