Electronic Supplementary information (ESI)

Amorphous Electron Donors with Controllable Morphology for Non-fullerene Polymer Solar cells

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Figure S1. GPC chromatograms of PBDD-*CH* (a) and PBDD-*CH*-S (b) carried out in 1,2,4-trichlorobenzene at a column temperature of 150 $^{\circ}$ C.



Figure S2. UV–vis absorption spectra for PBDD-*CH* and PBDD-*CH*-S in their pristine films.



Figure S3. The ground-state geometries of BBDT-BDD repeated units (C: red, S: yellow, H: purple. To simplify the calculation, only one repeating unit of each polymer was subjected to the calculation, and 2-ethylhexyl was replaced by CH_3 groups).



Figure S4. J– $(V_{app}-V_{bi}-V_s)$ characteristics for PBDD-*CH*:ITIC and PBDD-*CH*-S:ITIC based devices.



Figure S5. 2D–GIWAXS patterns for PBDD-*CH*:ITIC and PBDD-*CH*-S:ITIC blending films.



Structure characterization of the monomers and polymers.

Figure S6. ¹HNMR spectra for BDD-CH.



Figure S7. ¹³CNMR spectra for BDD-*CH*.



Figure S8. ¹HNMR spectra for monomer DBrBDD-CH.



Figure S9. ¹³CNMR spectra for monomer DBrBDD-CH.



Figure S10. ¹HNMR spectra for PBDD-CH.



Figure S11. ¹HNMR spectra for PBDD-CH-S.



Figure S12. HRMS for monomer DBrBDD-*CH*.