Supporting Information

Chlorination of Low-Band-Gap Polymers: Toward High-Performance Polymer Solar Cells

Daize Mo,[†] Huan Wang,[†] Hui Chen,[†] Shiwei Qu,[†] Pengjie Chao,[†] Zhen Yang,[†] Leilei Tian,[‡] Yu-An Su,[§] Yu Gao,[⊥] Bing Yang,[⊥] Wei Chen,[*,§,∥] and Feng He[*,†]

[†]Department of Chemistry, South University of Science and Technology of China, Shenzhen, 518055, People's Republic of China

[‡]Department of Materials Science and Engineering, South University of Science and Technology of China, Shenzhen, 518055, People's Republic of China

[§]Materials Science Division, Argonne National Laboratory, 9700 Cass Avenue, Lemont, Illinois 60439, United States

[∥] Institute for Molecular Engineering, The University of Chicago, 5640 South Ellis Avenue, Chicago, Illinois 60637, United States

[⊥] State Key Laboratory of Supramolecular Structure and Materials College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

E-mail: hef@sustc.edu.cn; wchen@anl.gov

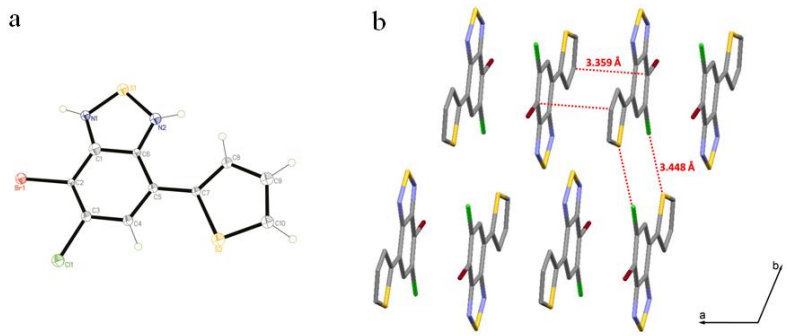

Figure S1. (a) X-ray crystal structure of compound **4**; (b) Molecular packing diagram of **4** viewed along the *ab* plane.

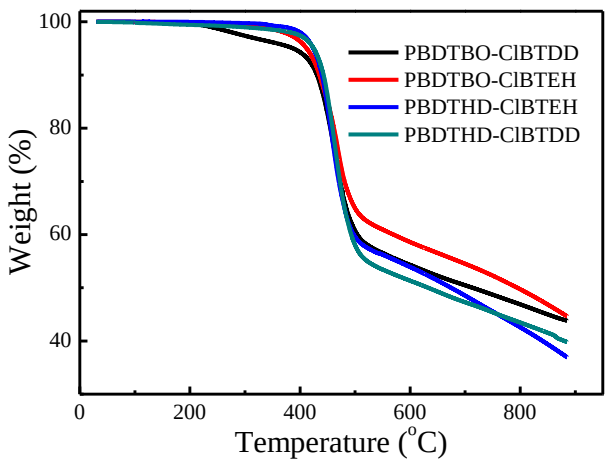

Figure S2. Thermogravimertic analysis (TGA) of **PBDTHD-ClBTDD**, **PBDTBO-ClBTDD**, **PBDTHD-ClBTEH**, and **PBDTBO-ClBTEH**.

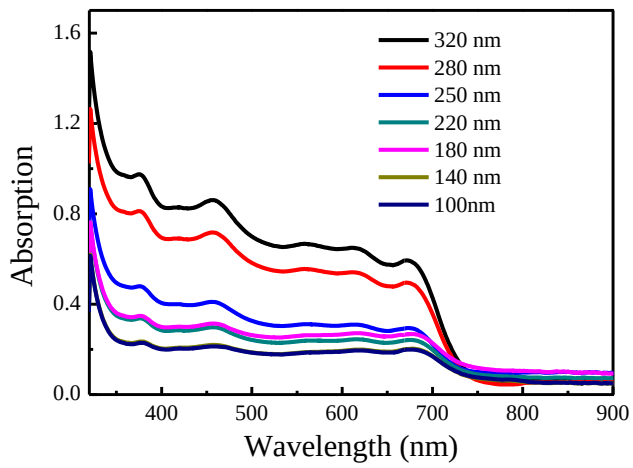

Figure S3. UV-vis absorption spectra of **PBDTHD-ClBTDD**/$PC_{71}BM$ blend films in the different thickness.

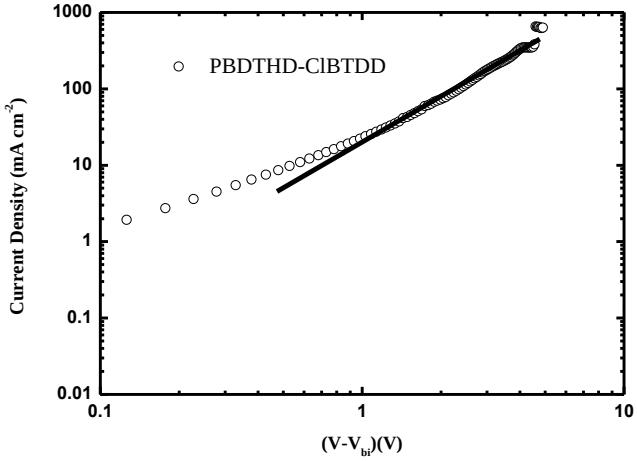

Figure S4. $J^{1/2}$~V characteristics of the **PBDTHD-ClBTDD** hole-only devices measured at ambient temperature.

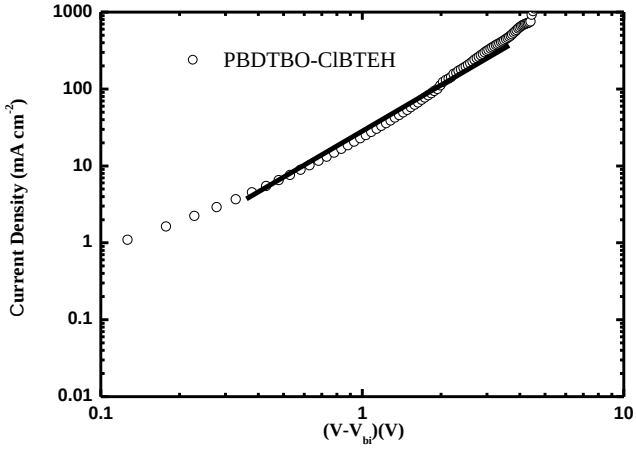

Figure S5. $J^{1/2}$~V characteristics of the **PBDTBO-ClBTEH** hole-only devices measured at ambient temperature.

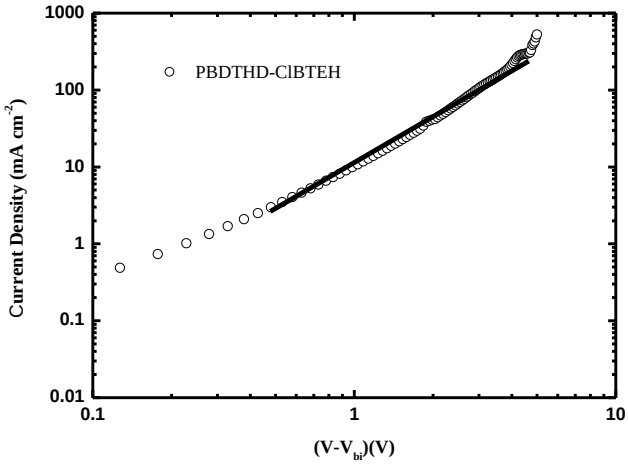

Figure S6. $J^{1/2}$~V characteristics of the **PBDTHD-ClBTEH** hole-only devices measured at ambient temperature.

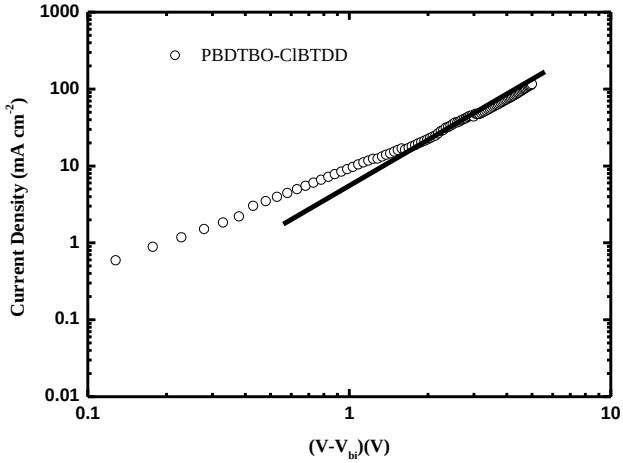

Figure S7. $J^{1/2}$~V characteristics of the **PBDTBO-ClBTDD** hole-only devices measured at ambient temperature.

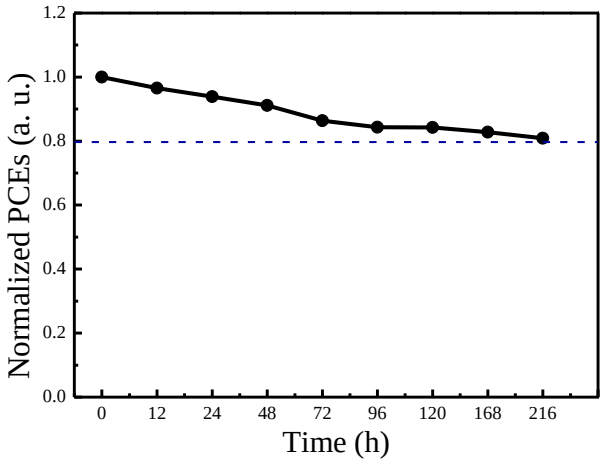

Figure S8. Normalized PCEs of ITO/ZnO/**PBDTHD-ClBTDD**:$PC_{71}BM$/MoO_3/Ag device as a function of storage time.

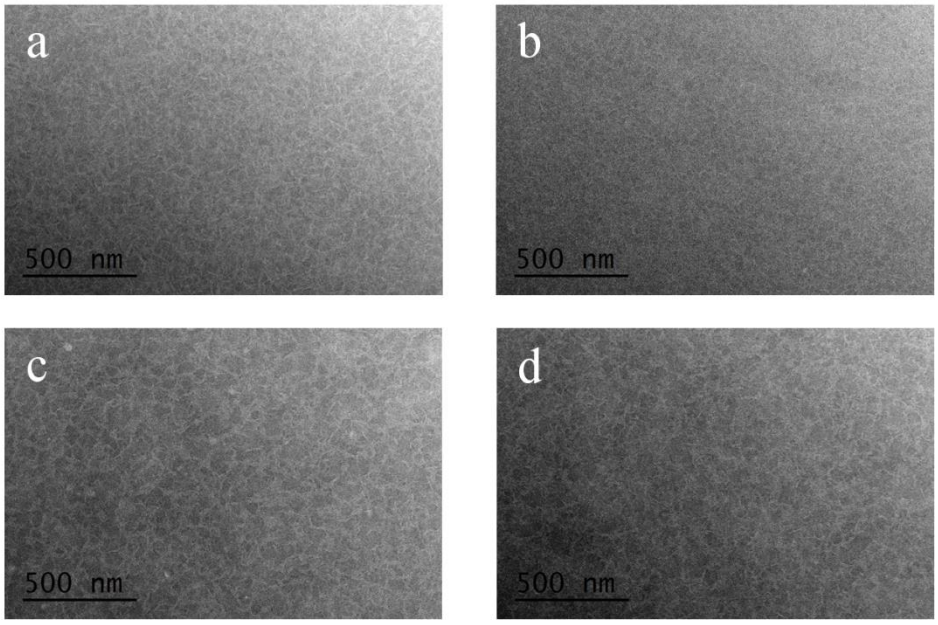

Figure S9. TEM images of the blend films of (a) **PBDTHD-ClBTDD**/$PC_{71}BM$, (b) **PBDTBO-ClBTEH**/$PC_{71}BM$, (c) **PBDTHD-ClBTEH**/$PC_{71}BM$, and (d) **PBDTBO-ClBTDD**/$PC_{71}BM$.

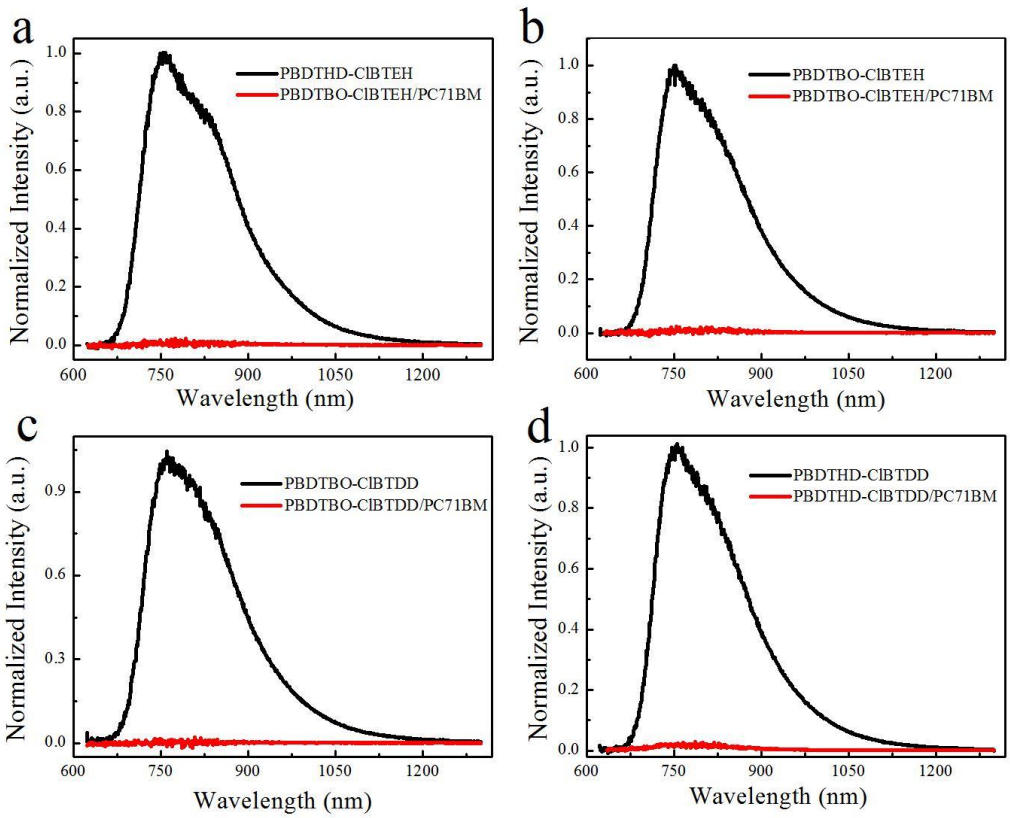

Figure S10. Photoluminescence of the polymer and their blend films. (a) **PBDTHD-ClBTEH** and **PBDTHD-ClBTEH**:PC71BM; (b) **PBDTBO-ClBTEH** and **PBDTBO-ClBTEH**:PC71BM; (c) **PBDTBO-ClBTDD** and **PBDTBO-ClBTDD**:PC71BM; (d) **PBDTHD-ClBTDD** and **PBDTHD-ClBTDD**:PC71BM

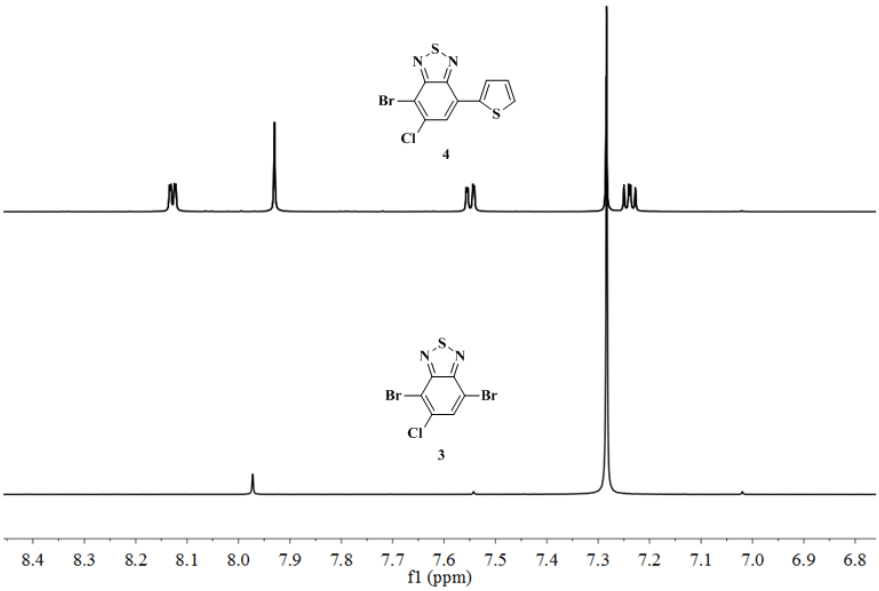

Figure S11. Comparison of ^{1}H NMR spectrum of compound **3** and **4**.

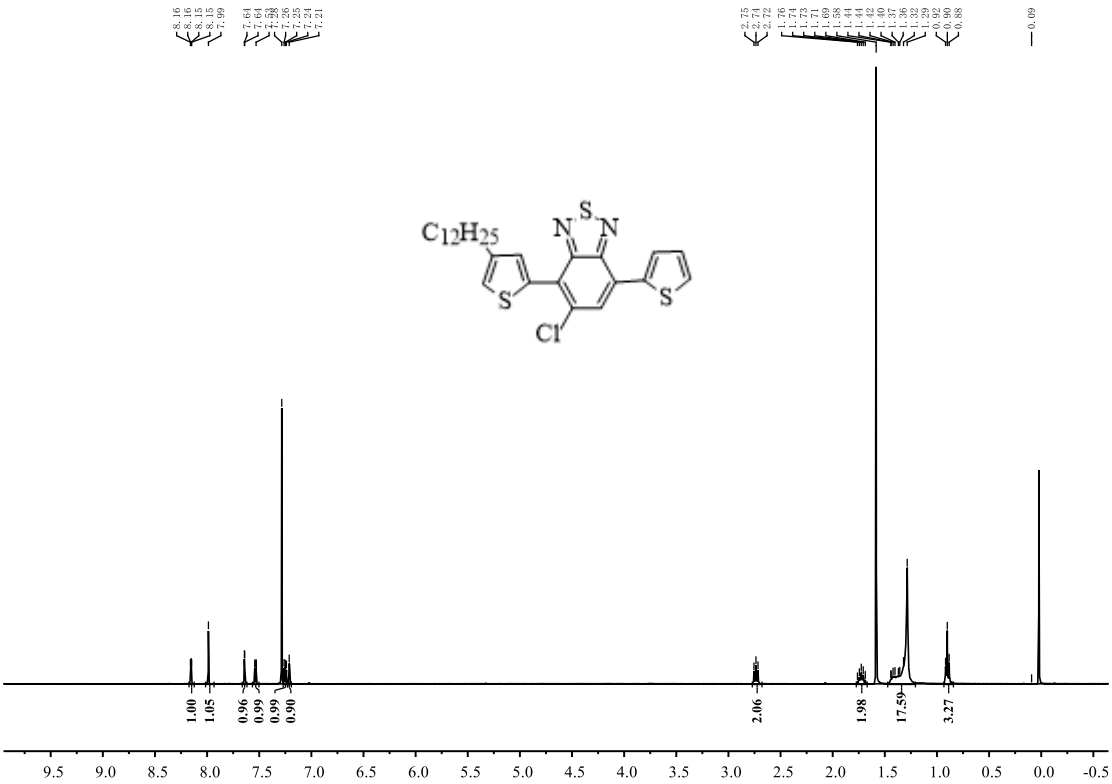

Figure S12. ^{1}H NMR spectrum of **5b**.

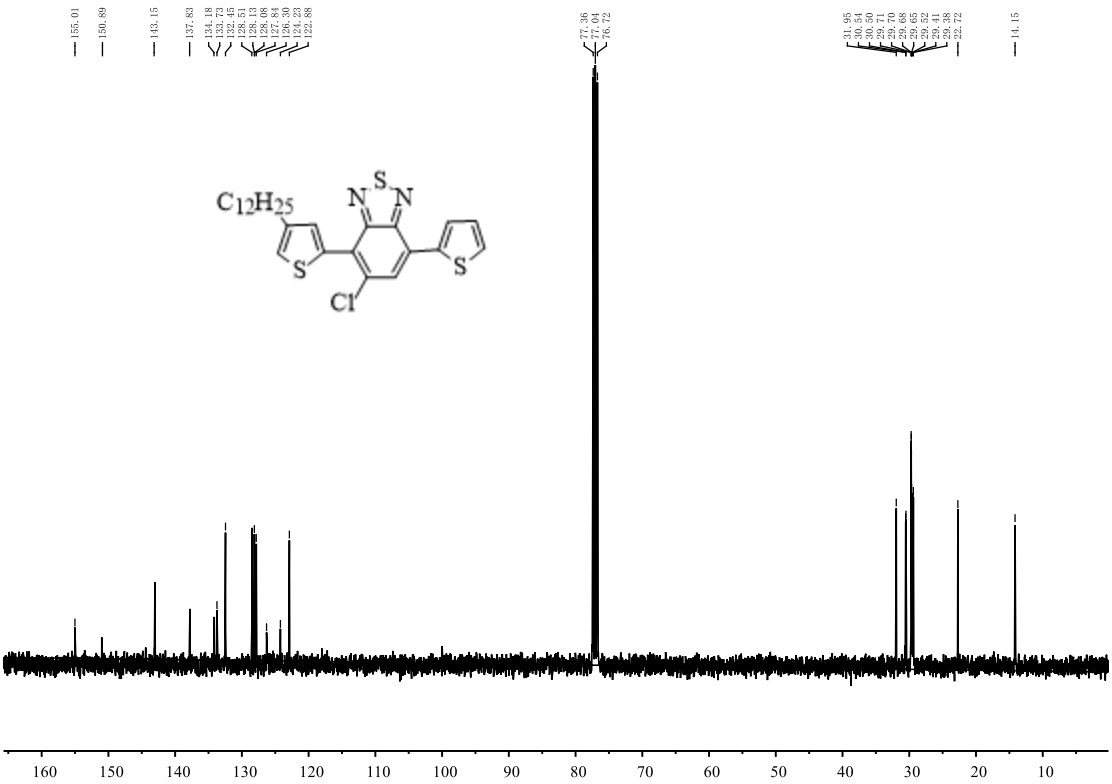

Figure S13. ^{13}C NMR spectrum of **5b**.

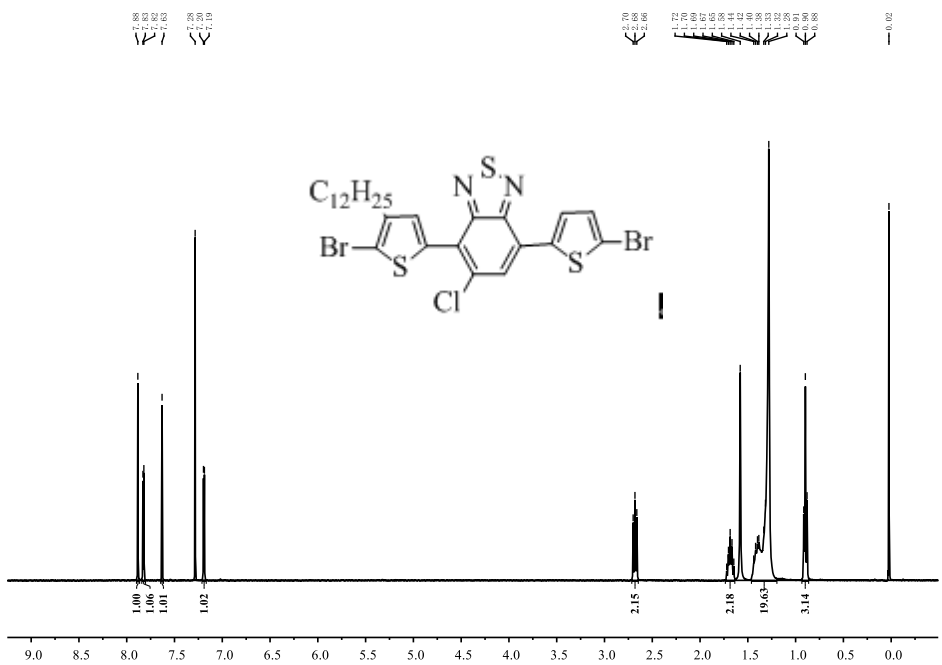

Figure S14. ^{1}H NMR spectrum of **6b**.

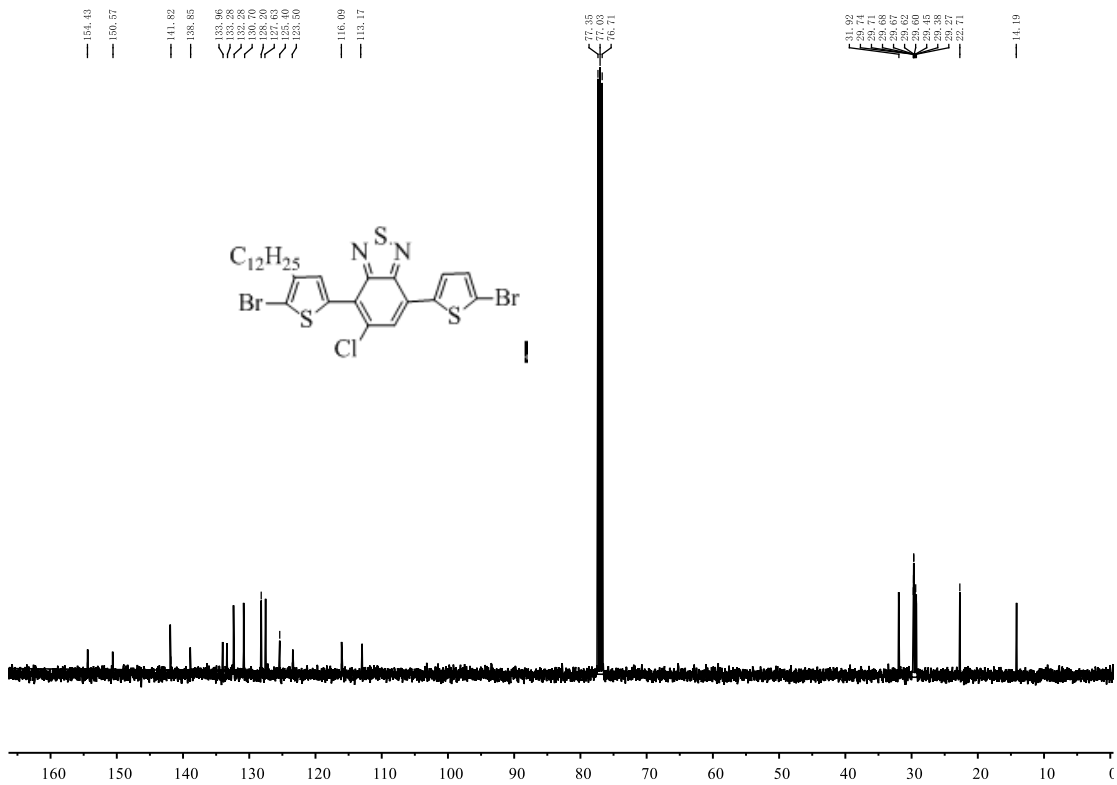

Figure S15. ^{13}C NMR spectrum of **6b**.

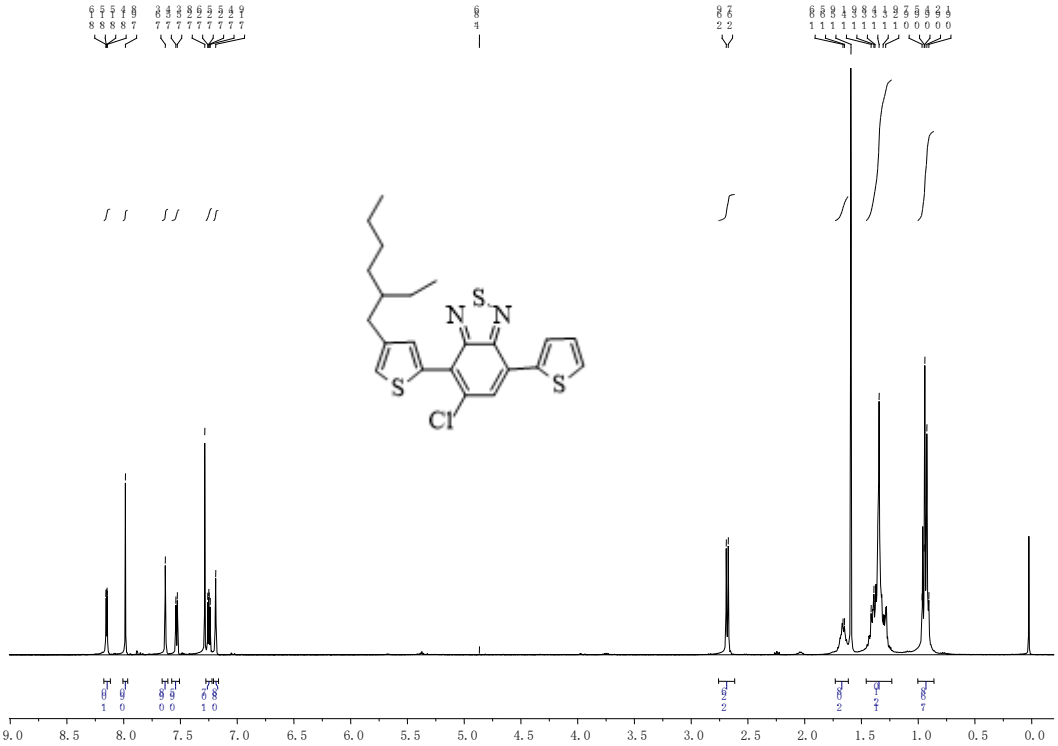

Figure S14. ^{1}H NMR spectrum of **5a**.

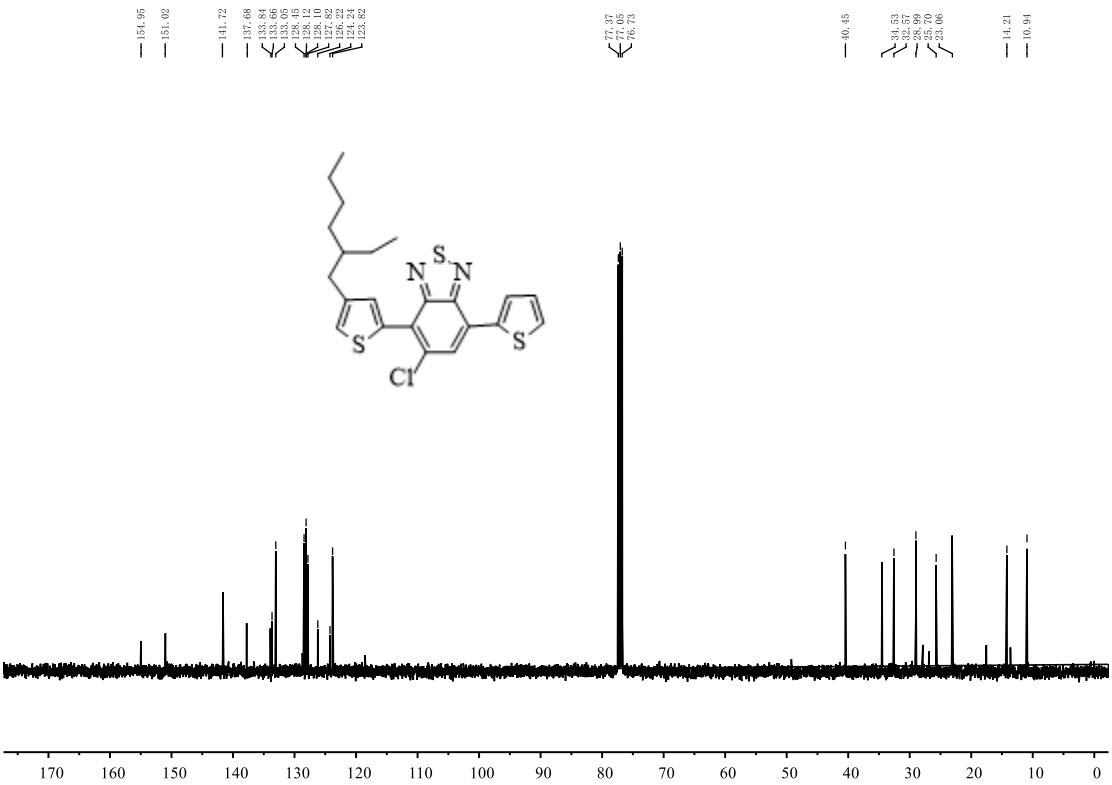

Figure S16. ^{13}C NMR spectrum of**5a**.

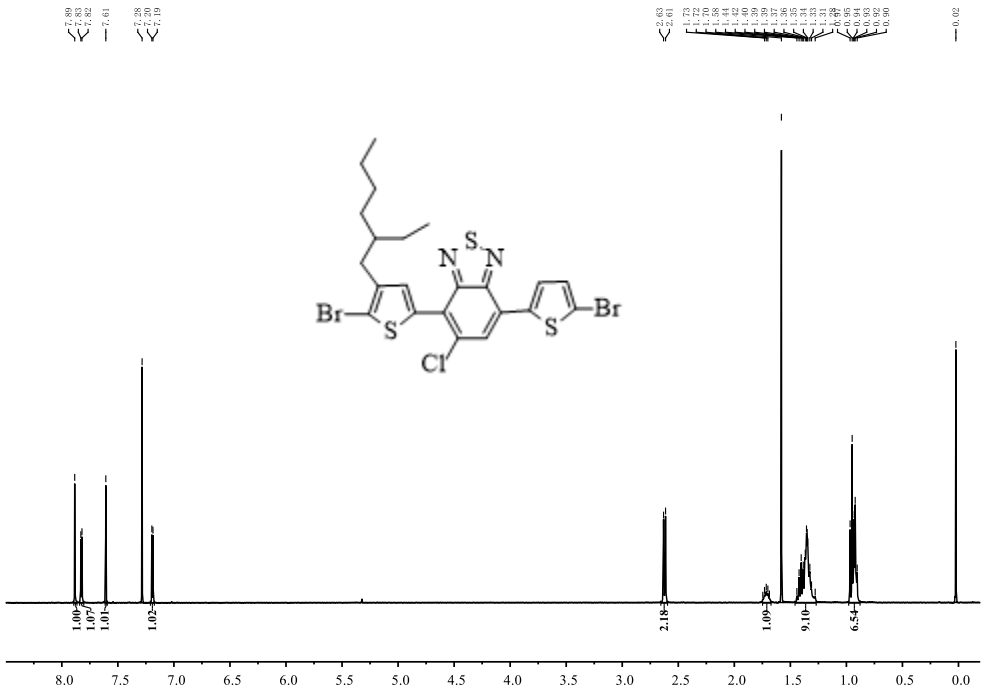

Figure S17. ^{1}H NMR spectrum of **6a**.

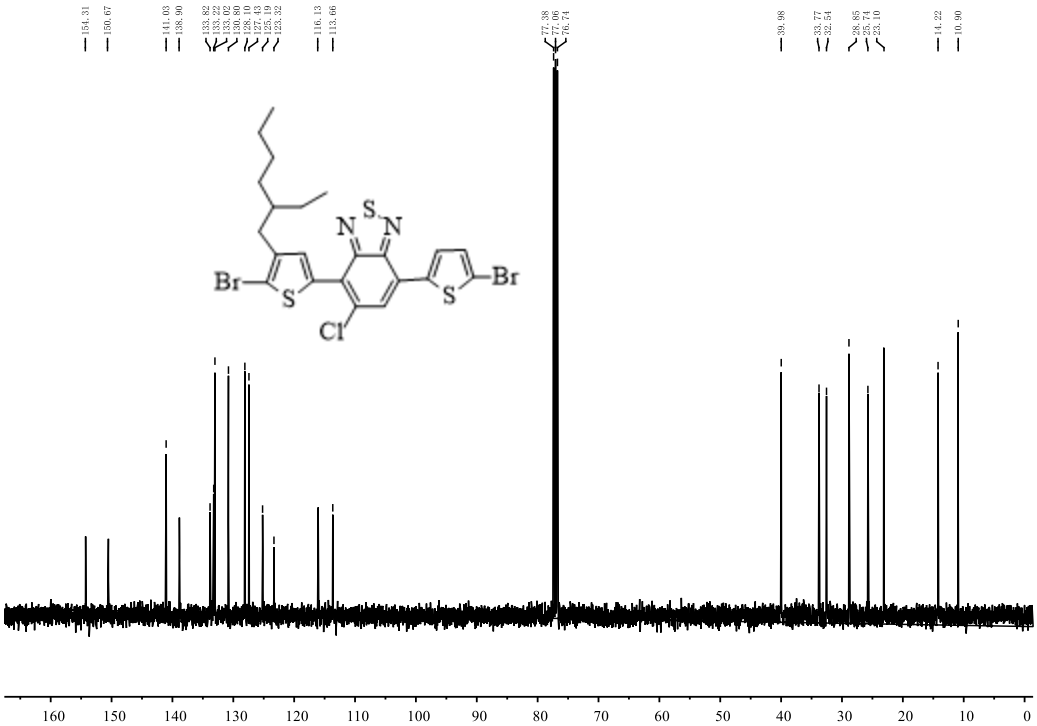

Figure S18. ^{13}C NMR spectrum of **6a**.