Supporting Information

for

Molecular Symmetry Effect on Morphology and Self-aggregation of Semiconducting Polymers

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Contents

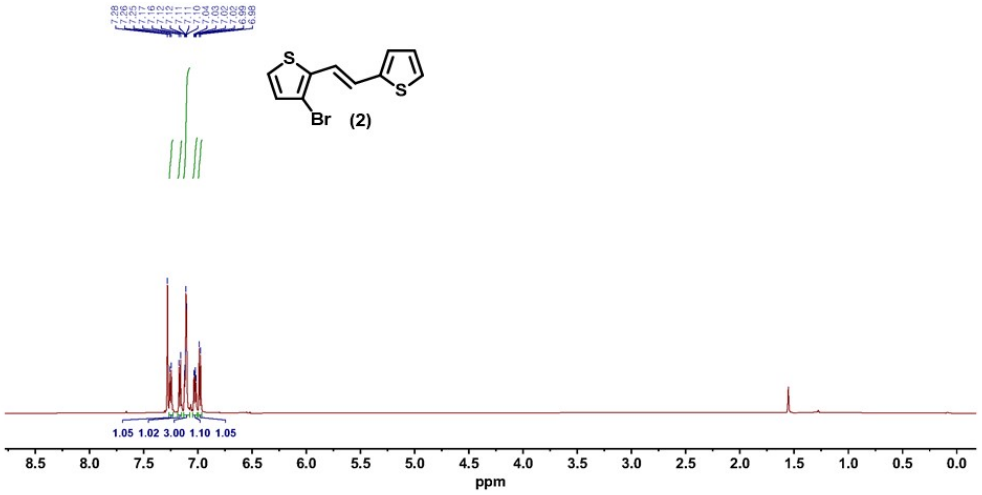
1. Experimental section

Materials

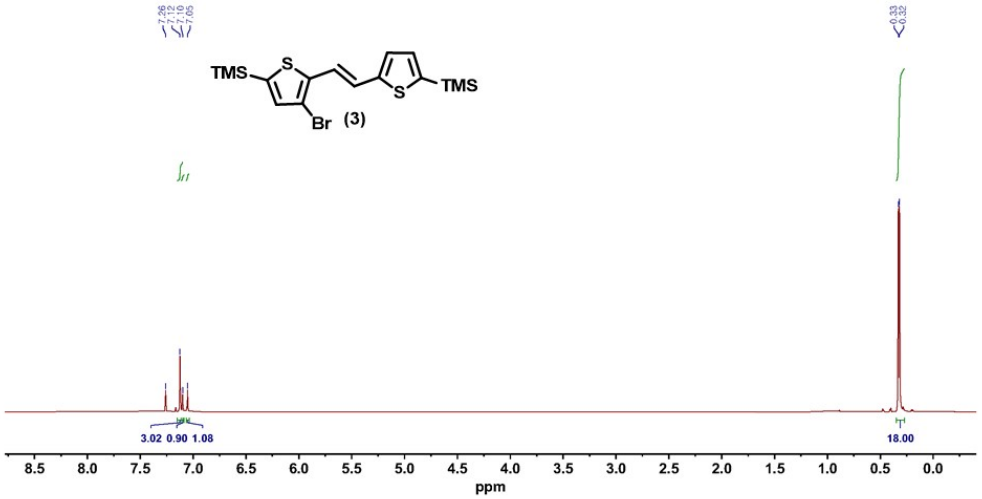
All reagents and chemicals were purchased from commercial sources Sigma-Aldrich and Suna Tech Inc. unless specified. (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (TVT), (*E*)-(4-fluoro-5-(2-(5-(trimethylstannyl)thiophen-2-yl)vinyl)thiophen-2-yl)trimethylstannane (asy-1FTVT), and (*E*)-1,2-bis(3-fluoro-5-(trimethylstannyl)thiophen-2-yl)ethane (2FTVT) are synthesized by following the methods and reported literatures.[1]

Device fabrication

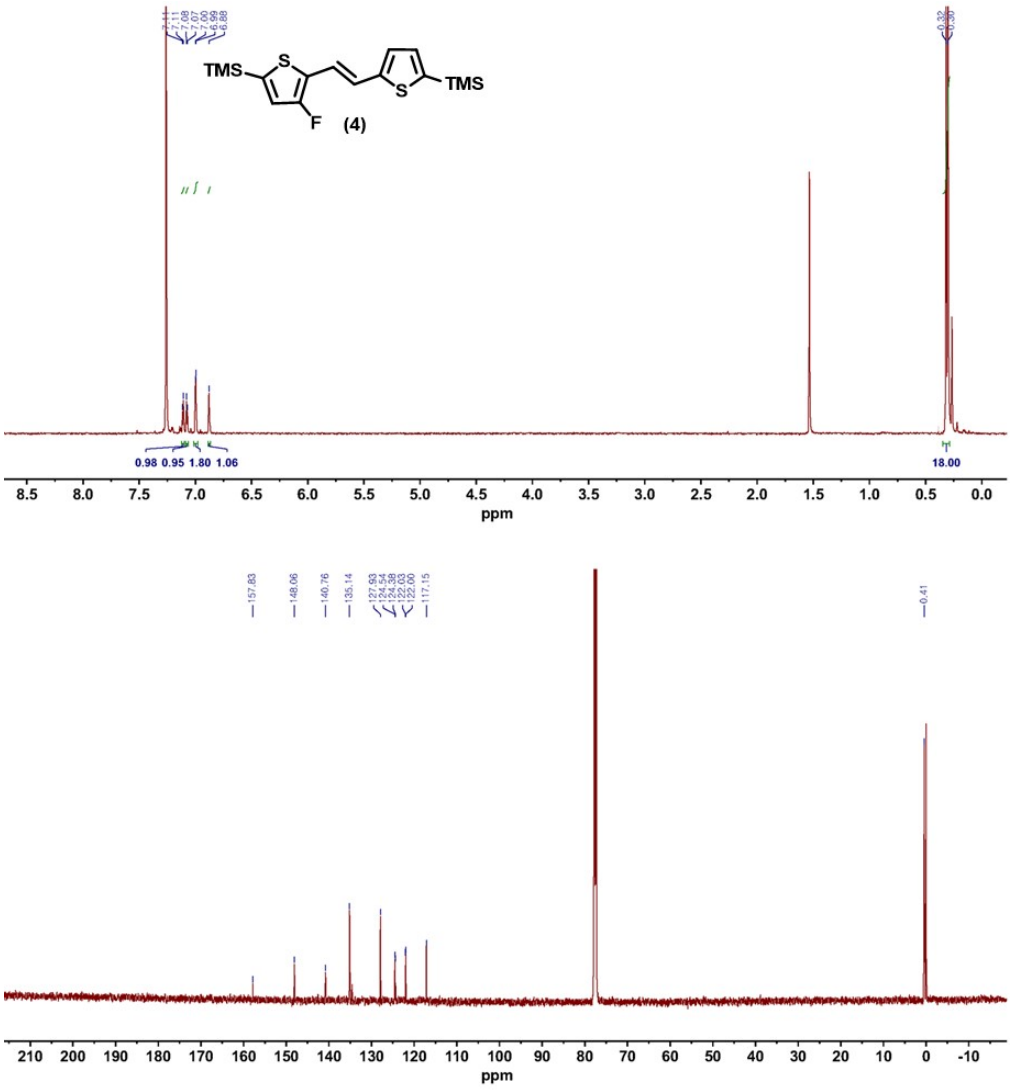
Organic solar cells were fabricated with inverted structure (ITO/ZnO/active layer/MoO_3/Ag). The ITO substrate was cleaned with ultra sonication with acetone and IPA for 10 min each and dried in a hot oven. Then, the cleaned ITO substrate was treated by UV ozone for 30 min. ZnO precursor was spin coated on ITO substrates and annealed at 200^{o}C for 10 min. A blend of PTB7-Th:NDI-based copolymers was dissolved in CF (1:1.5 w:w) with concentration of 18 mg/ml. Then, this blend solution with 0.5% CN was spin coated on ZnO layer in N_2-filled glove box. The MoO_3 and Ag was deposited by thermal evaporation on the active layer under $2*10^{-6}$ Torr.



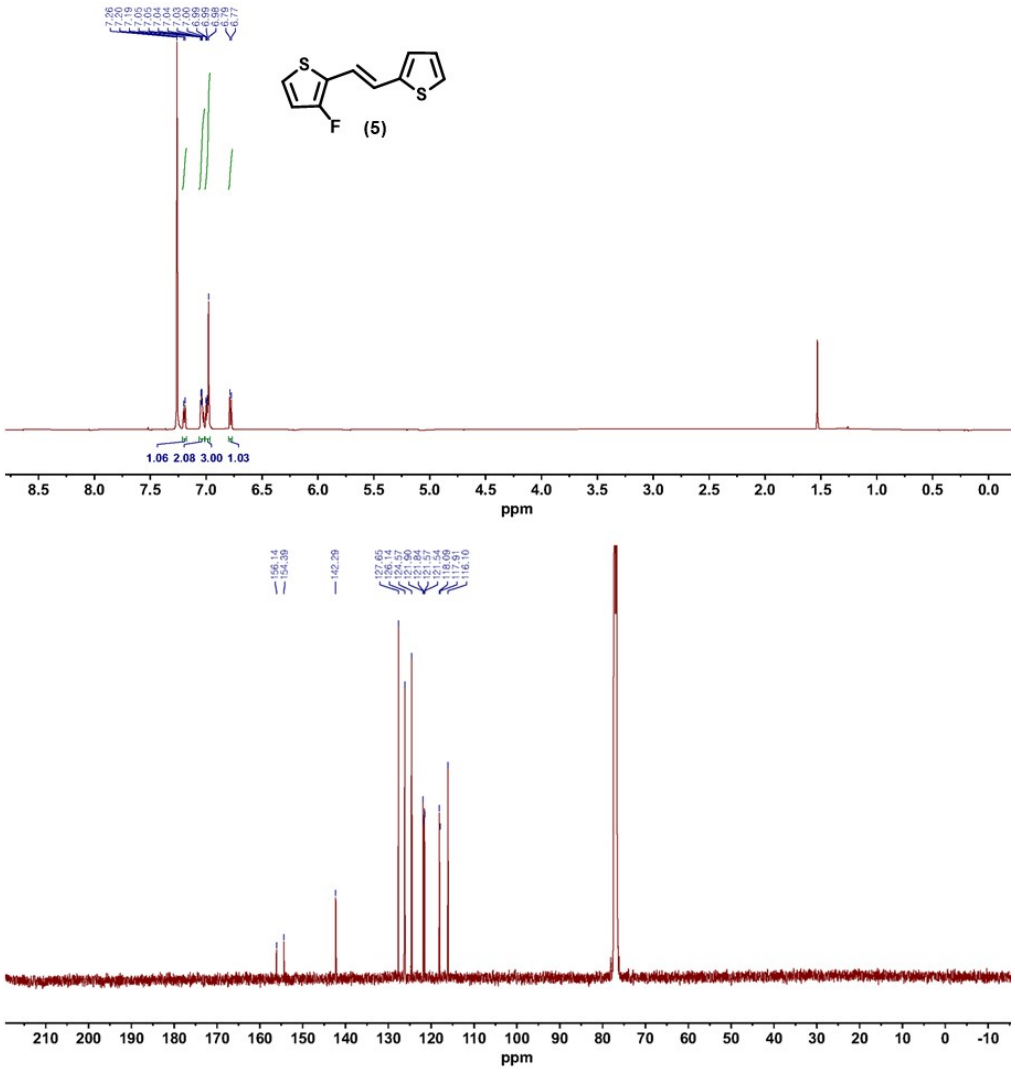
^{1}H-NMR spectrum of **(2)**



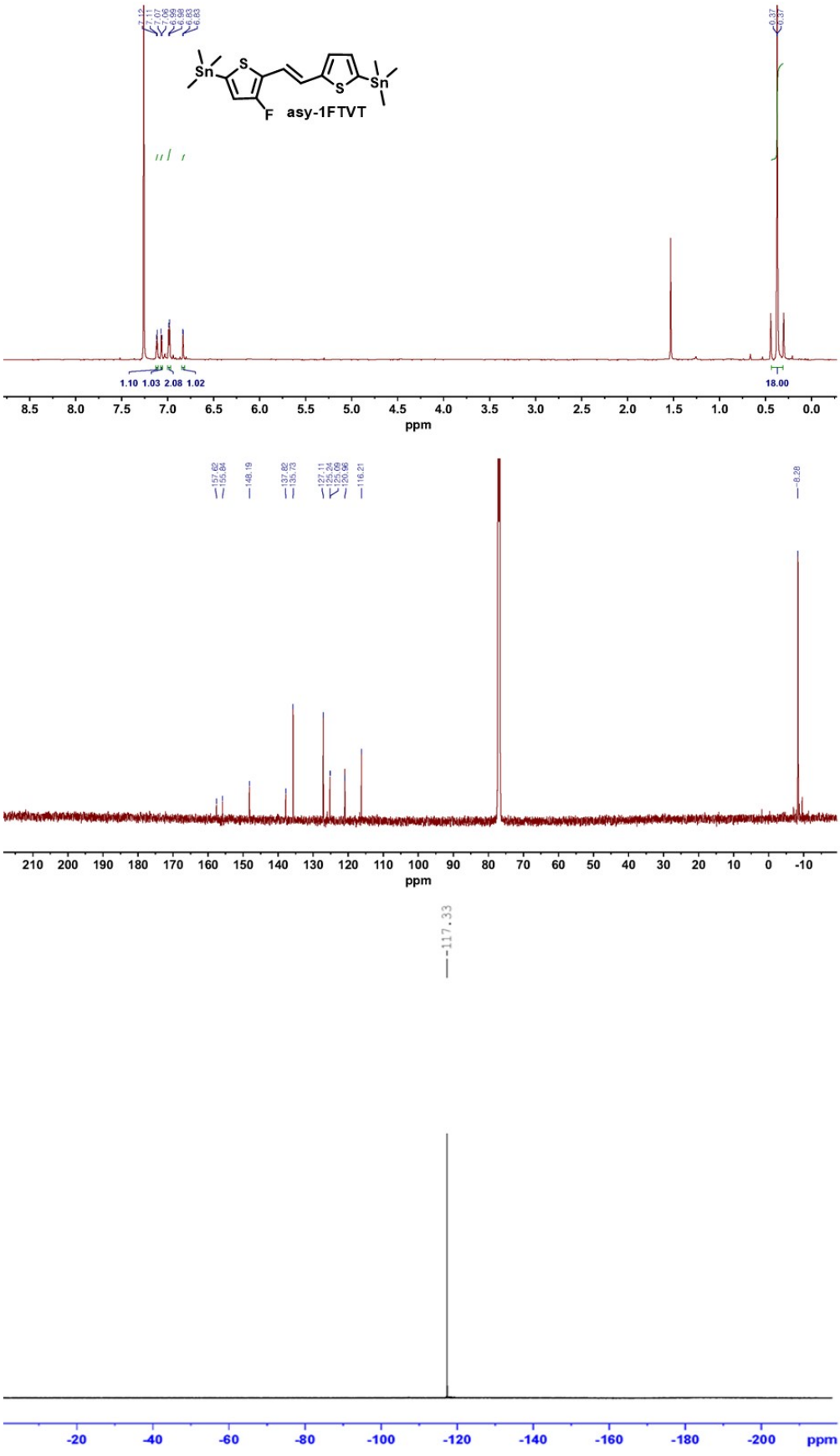
^{1}H-NMR spectrum of **(3)**



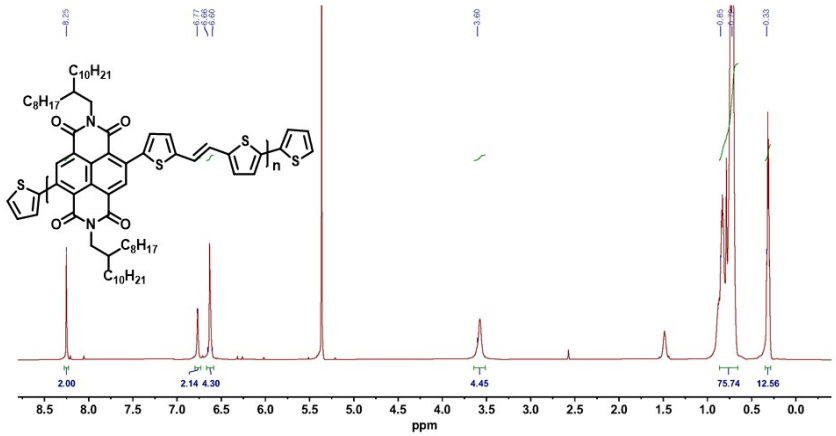
^{1}H and ^{13}C-NMR spectra of **(4)**



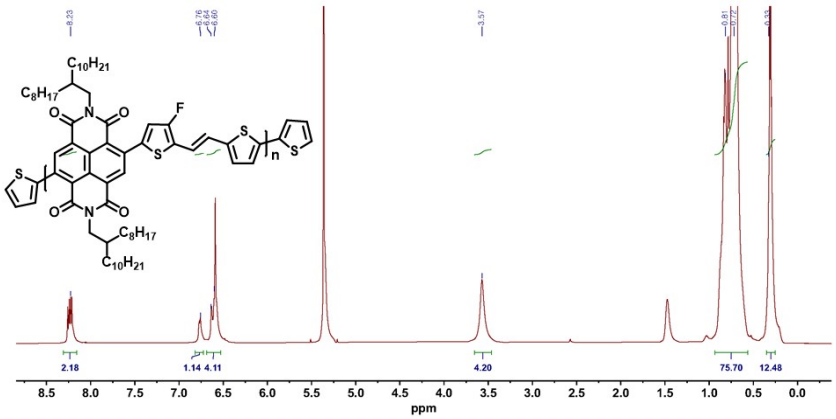
^{1}H and ^{13}C-NMR spectra of **(5)**



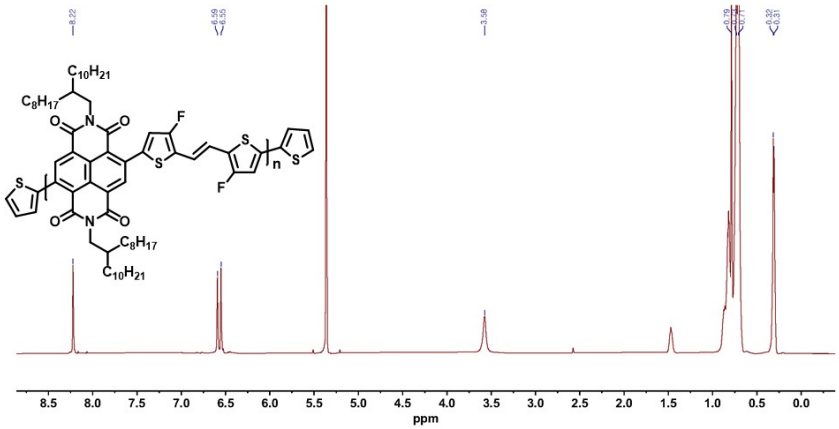
^{1}H, ^{13}C, and ^{19}F-NMR spectra of **asy-1FTVT**



^{1}H-NMR spectra of **PNDITVT**



^{1}H-NMR spectra of **asy-PNDI1FTVT**



^{1}H-NMR spectra of **PNDI2FTVT**

Figure S1. ^{1}H, ^{13}C, and ^{19}F nuclear magnetic resonance (NMR) spectroscopy of all the compounds.

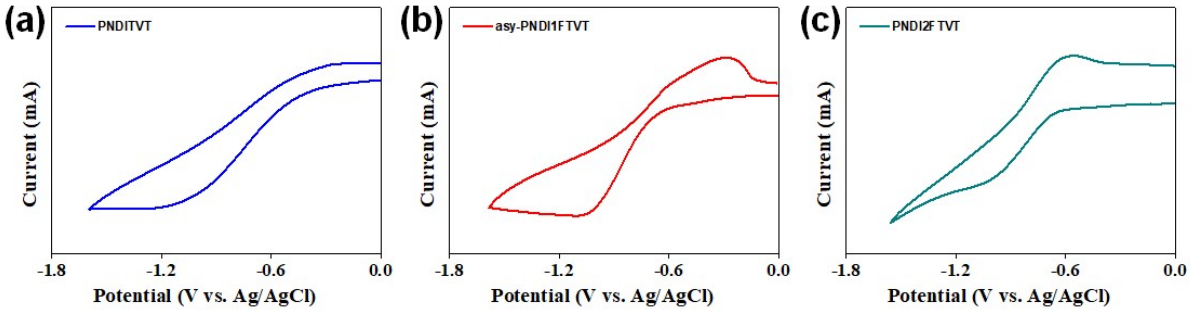


Figure S2. Cyclic voltammograms (CV) of the second reduction cycles of (a) **PNDI TVT,** (b) **asy-PNDI1FTVT**, and (c) **PNDI2FTVT**.

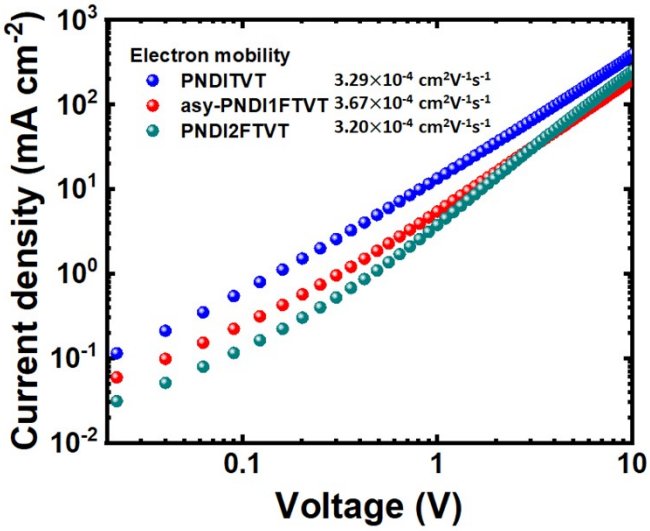


Figure S3. Space charge limited current (SCLC) mobility plots of three acceptor polymers.

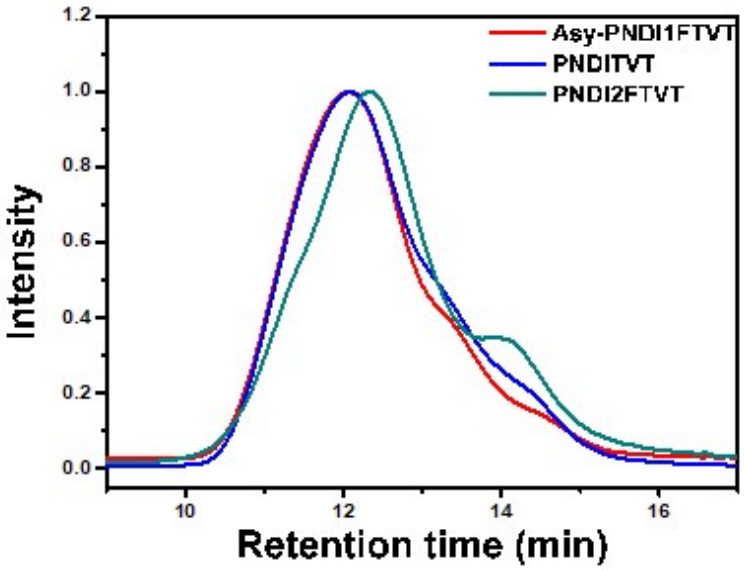


Figure S4. Gel permeation chromatographs of PNDITVT, asy-PNDI1FTVT and PNDI2FTVT.

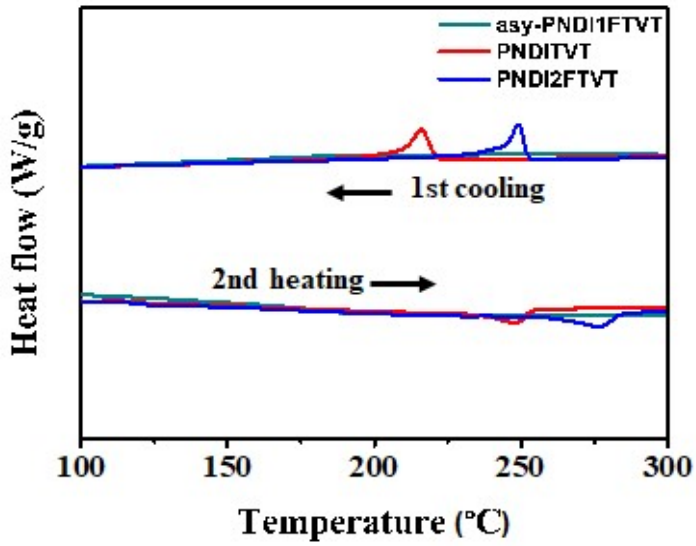


Figure S5. Differential Scanning Calorimeter thermograms of three copolymers.

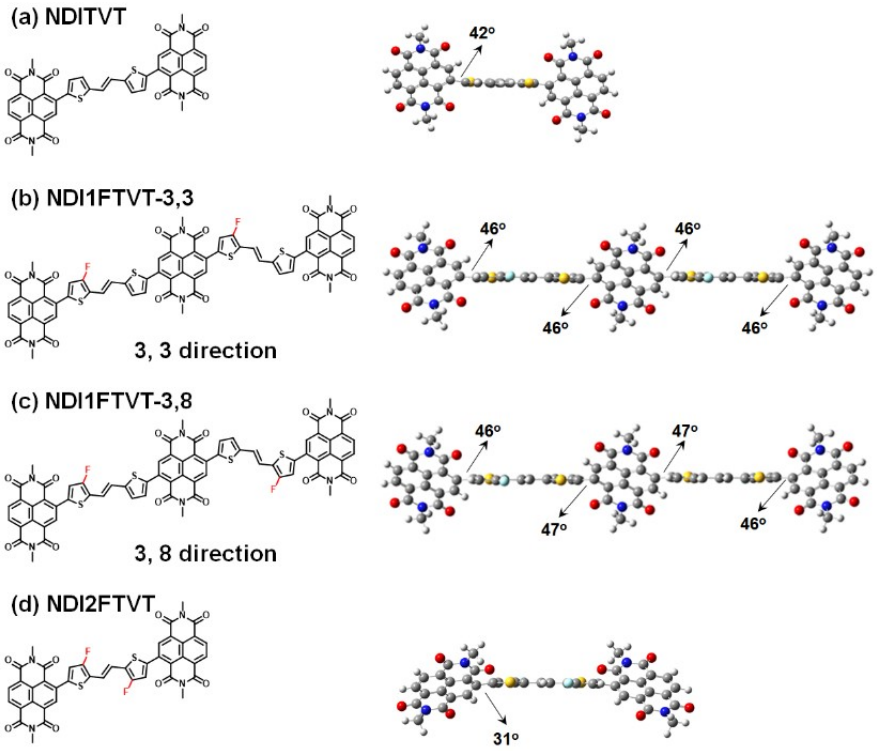


Figure S6. Optimized four model compounds (a) **NDITVT** (b) **NDI1FTVT-3,3** containing fluorine atoms at 3,3 positions, (c) **NDI1FTVT-3,8** containing fluorine atoms at 3,8 positions, and (d) **NDI2FTVT**.

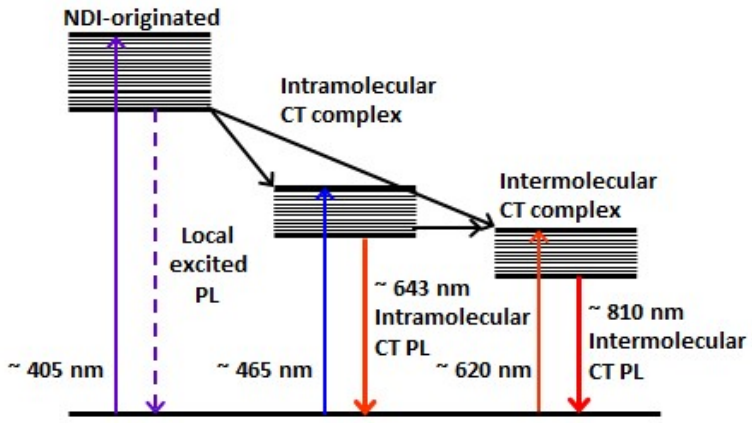


Figure S7. Jablonski diagram of **asy-PNDI1FTVT**.

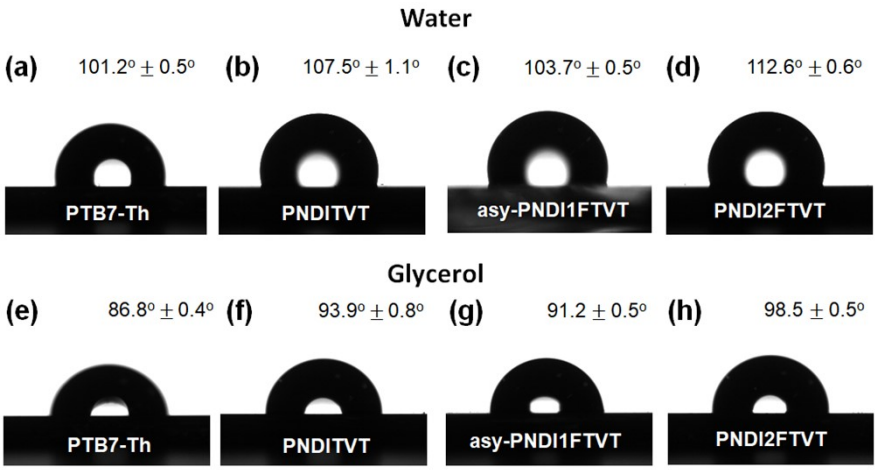


Figure S8. Contact angle measurement of PTB7-Th, **PNDITVT**, **asy-PNDI1FTVT**, and **PNDI2FTVT** (average value of 5 drops of each solvent).

References

1. M. Kim, W.-T. Park, S. U. Ryu, S. Y. Son, J. Lee, T. J. Shin, Y.-Y. Noh and T. Park, *Chem. Mater*., 2019, **31**, 4864-4872.