Supplementary Information (ESI) for

Comparison of thiophene- and selenophene-bridged donor-acceptor low band-gap copolymers used in bulk-heterojunction organic photovoltaics

Hung-Yang Chen,[a,b,c] Shih-Chieh Yeh[a], Chin-Ti Chen*[a] and Chao-Tsen Chen*[c]

[a]*Institute of Chemistry, Academia Sinica, Taipei, Taiwan 11529, Republic of China. Fax:+886 2 27831237; Tel:+886 2 27898542; E-mail: cchen@chem.sinica.edu.tw*
[b]*Nano Science and Technology Program, TIGP, Academia Sinica, Taipei, Taiwan 11529.*
[c]*Department of Chemistry, National Taiwan University,Taipei, Taiwan 11617.*

S1. The current-voltage output and transfer curves of four copolymer OFETs.

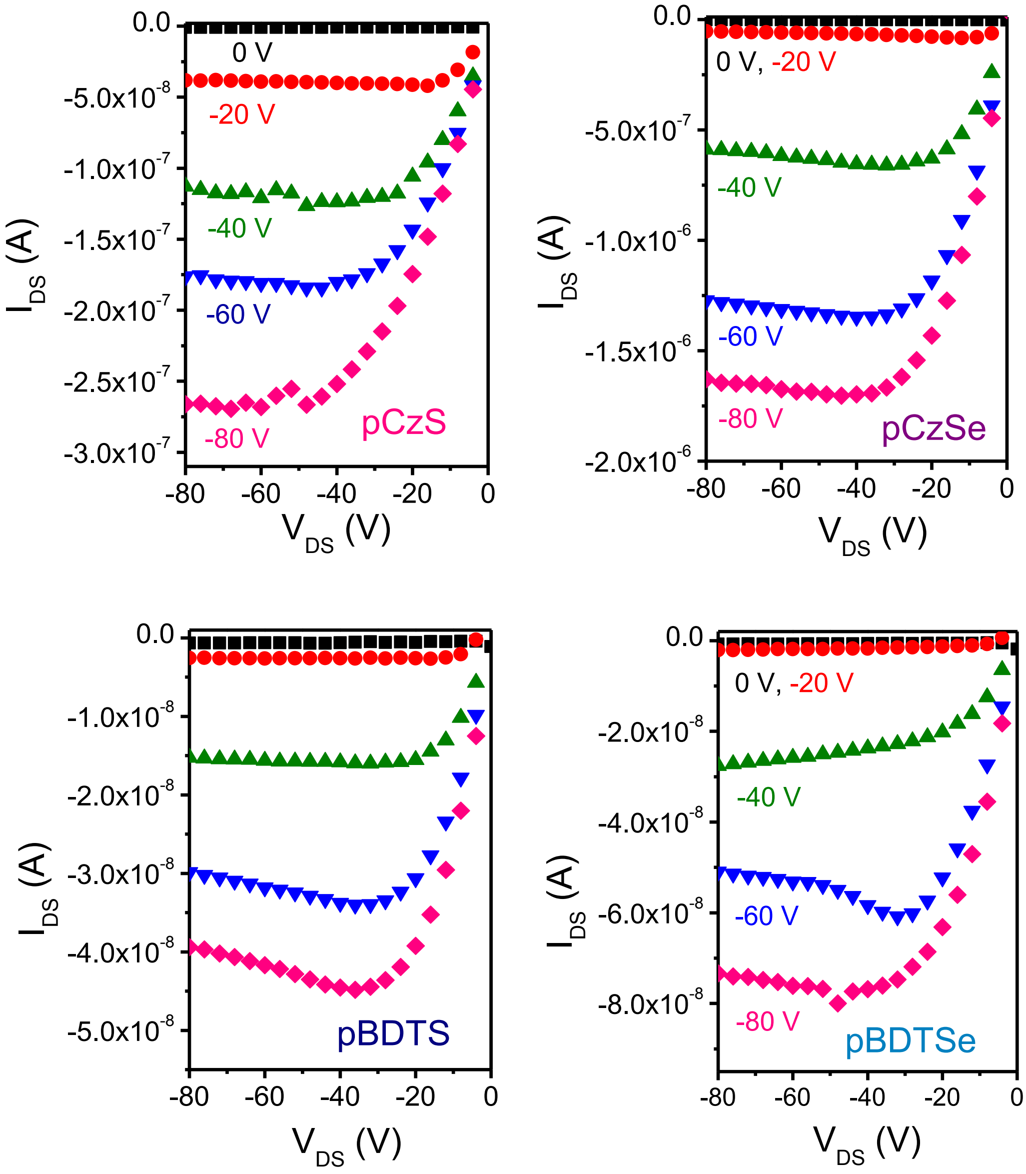

Figure S1. OFET output curves at various gate voltages V_G (0 ~ -80V).

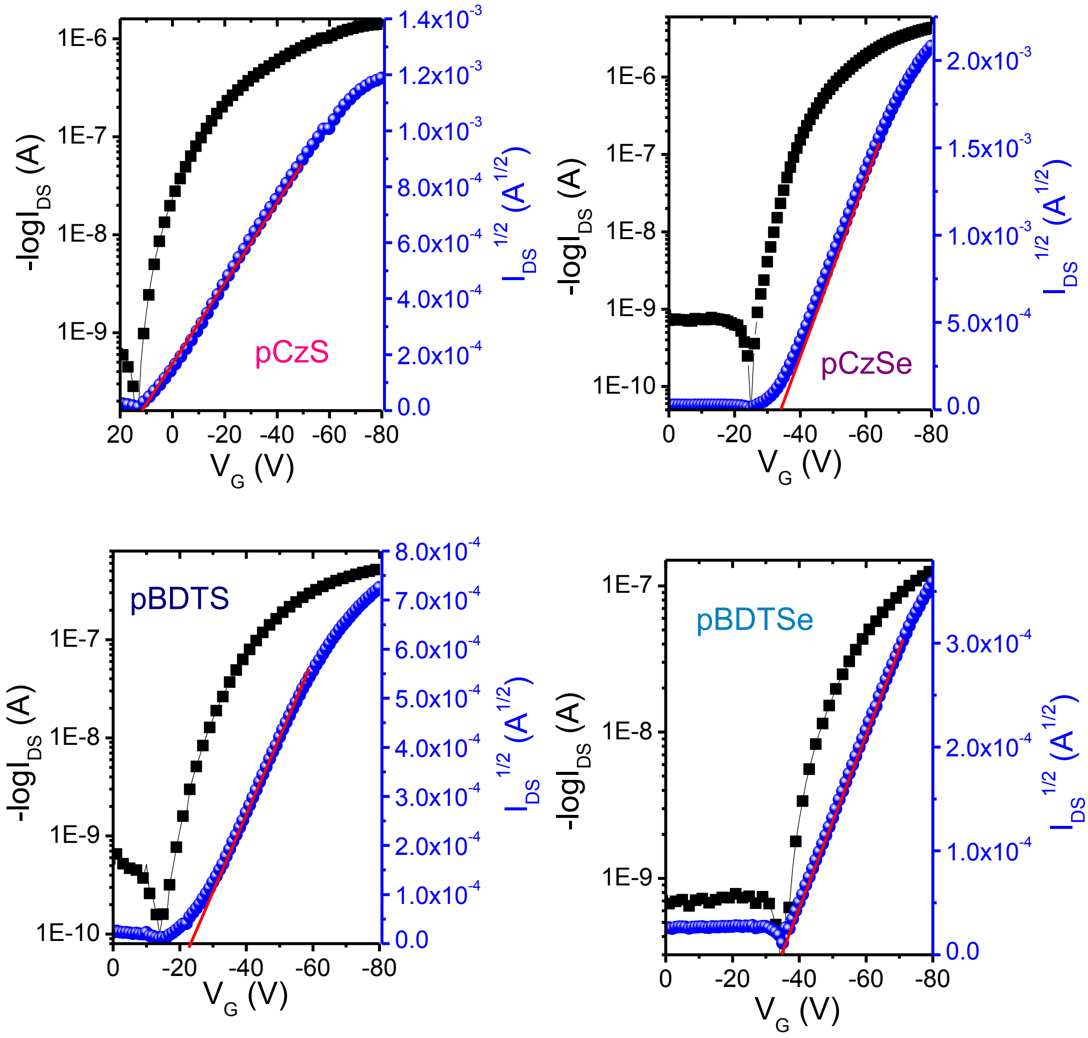

Figure S2. OFET transfer curves at drain-source voltage V_{DS} at -40 V.

S2. The experimental details of the theoretical calculation.

Four theoretical model D-π-A-π-D-π-A-π, a dimer-like (D-π-A-π)$_2$ segment of **pCzS**, **pCzSe**, **pBDTS**, and **pBDTSe**, respectively, were optimized by applying density functional theory (DFT) with the hybrid B3LYP functional and 6-31G* basis set. With the optimized structure, calculations on the electronic ground states of each model were processed using DFT with the hybrid B3LYP functional and 6-31G* basis set.[1] The singlet excited states of the three molecules were studied with time-dependent density functional theory (TDDFT) by using the hybrid B3LYP functional.[2] All calculations were preformed with a developmental version of Q-Chem.[3]

Reference

1. A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
2. M. E. Casida, In *Recent Advances in Density Functional Methods*, *Part 1*; D. P. Chong, Ed.; World Scientific: Singapore, 1995; p 155.
3. J. Kong, C. A. White, A. I. Krylov, C. D. Sherrill, R. D. Adamson, T. R. Furlani, M. S. Lee, A. M. Lee, S. R. Gwaltney, T. R. Adams, C. Ochsenfeld, A. T. B. Gilbert, G. S. Kedziora, V. A. Rassolov, D. R. Maurice, N. Nair, Y. Shao, N. A. Besley, P. E. Maslen, J. P. Dombroski, H. Daschel, W. Zhang, P. P. Korambath, J. Baker, E. F. C. Byrd, T. Van Voorhis, M. Oumi, S. Hirata, C.-P. Hsu, N. Ishikawa, J. Florian, A. Warshel, B. G. Johnson, P. M. W. Gill, M. Head-Gordon and J. A. Pople, *J. Comput. Chem.* **2000**, *21*, 1532.

S3. ^{1}H NMR spectra and proposed peak assignment of four copolymers.

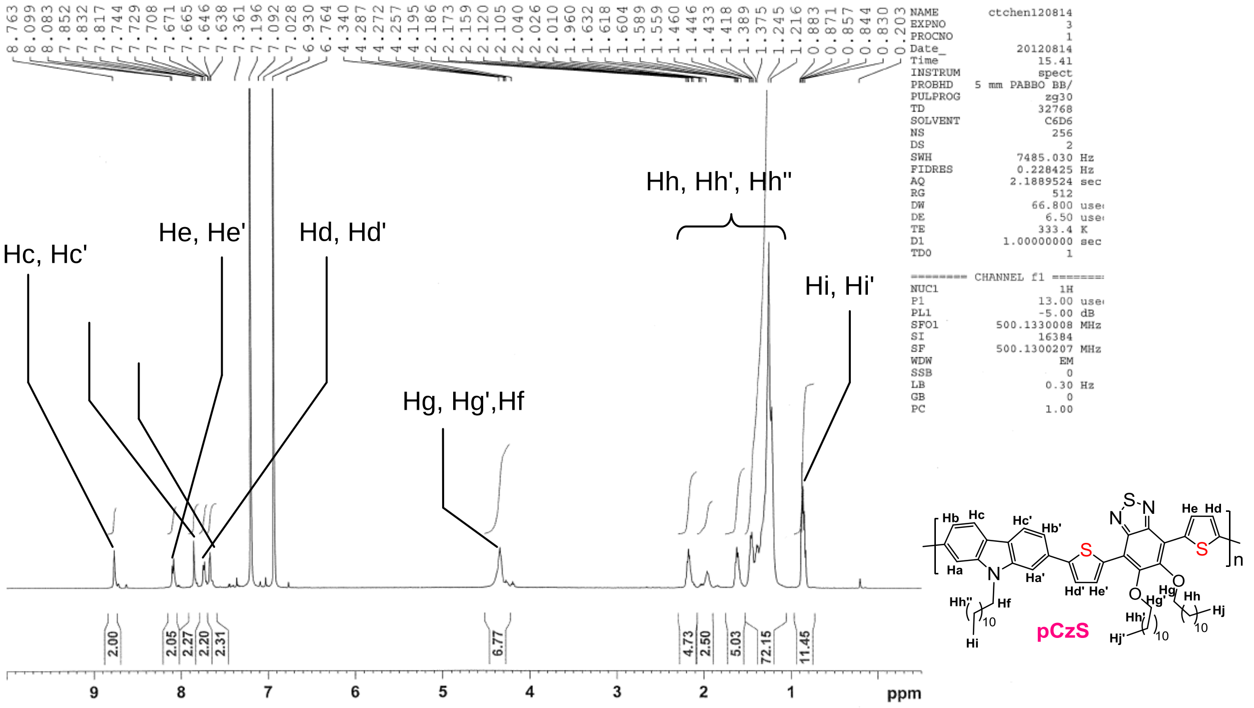

Figure S3. ^{1}H NMR spectrum (500 MHz, 1,2-dichlorobenzene-d_4, 60 ^{o}C) of **pCzS**.

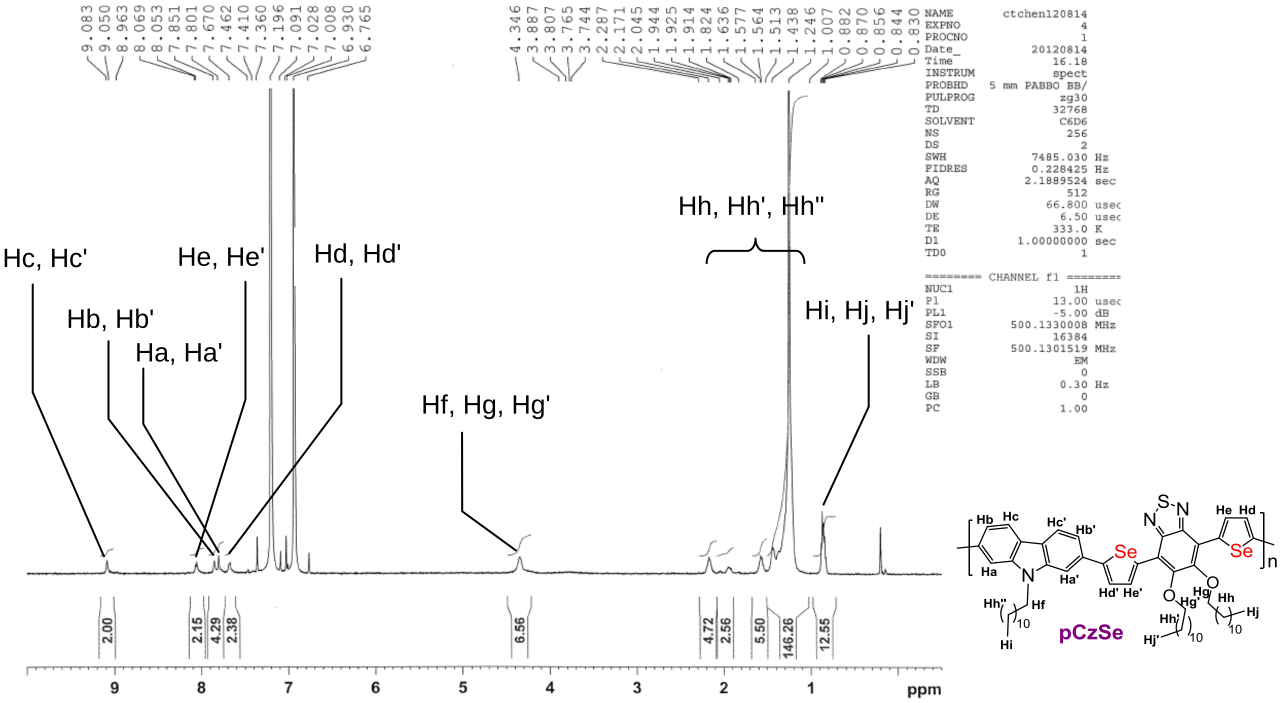

Figure S4. ^{1}H NMR spectrum (500 MHz, 1,2-dichlorobenzene-d_4, 60 ^{o}C) of **pCzSe**.

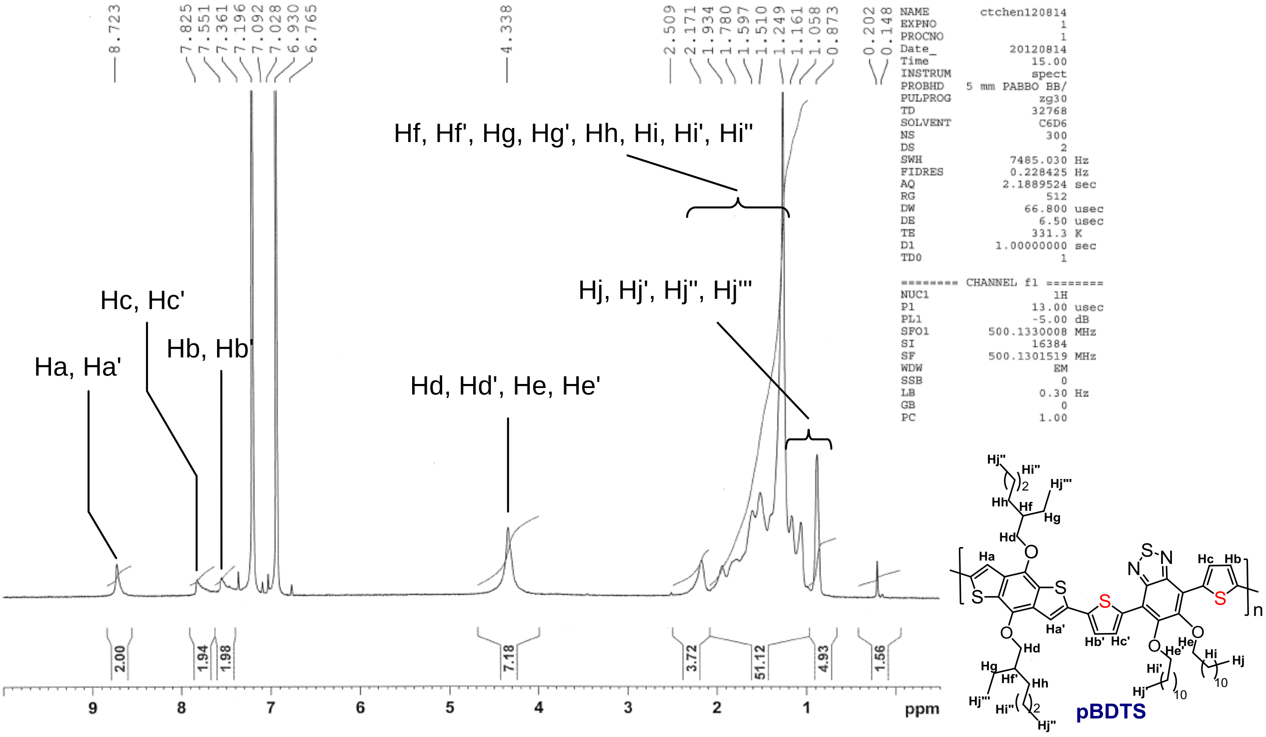

Figure S5. ^{1}H NMR spectrum (500 MHz, 1,2-dichlorobenzene-d_4, 60 °C) of **pBDTS**.

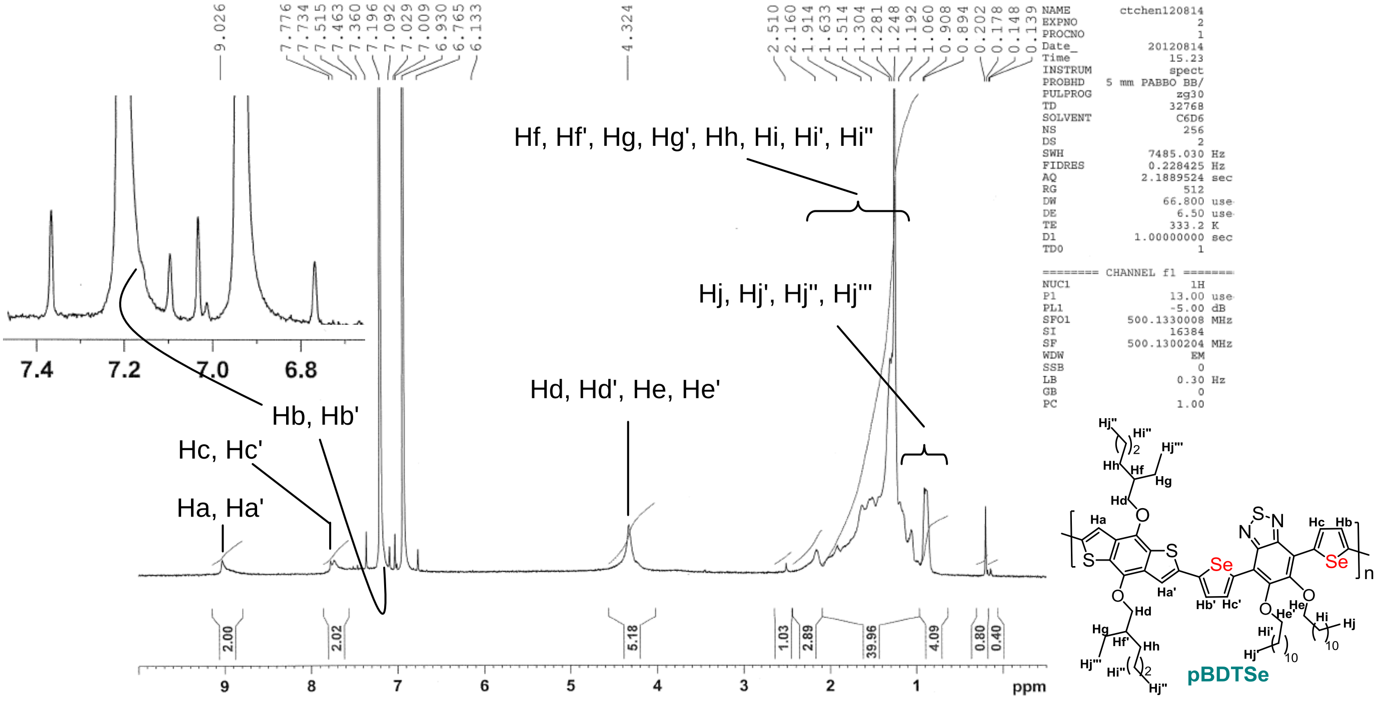

Figure S6. ^{1}H NMR spectrum (500 MHz, 1,2-dichlorobenzene-d_4, 60 °C) of **pBDTSe**.