Supporting Information for:

Improved operational lifetime of deep-red phosphorescent organic light-emitting diodes using a benzothienobenzothiophene (BTBT)-based p-type host material

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General Considerations:

Quantum chemical calculations were performed using the hybrid density functional theory (DFT), functional Becke and Hartree-Fock exchange, and Lee Yang and Parr correlation (B3LYP) as implemented in the Gaussian 09 program packages.[1] Electrons were described by the Pople 6-31G(d,p) and 6-311+G(d,p) basis sets for molecular structure optimization and single-point energy calculations, respectively. The BDEs of the anion states were calculated at the URB3LYP 6-31G(d) level of theory according to the enthalpy change in the corresponding reaction of homolytic cleavage of a single bond in the gas phase at 298 K and 1 atm.[2] ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL 400 spectrometer. Mass spectra were obtained using a JEOL JMS-K9 mass spectrometer and a Waters SQD2 mass spectrometer with atmospheric pressure solid analysis probe (ASAP). Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Diamond DSC Pyris instrument under nitrogen atmosphere at a heating rate of 10°C min^{-1}. Thermogravimetric analysis (TGA) was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10°C min^{-1}. UV-Vis spectra were measured using a Shimadzu UV-3150 UV-vis-NIR spectrophotometer. Photoluminescence spectra were measured using a FluroMax-2 (Jobin-Yvon-Spex) luminescence spectrometer. The ionization potential (I_p) was determined using a photoelectron yield spectroscopy (PYS) in vacuum (~10^{-3} Pa).[3] The phosphorescent spectra were measured using a streak camera (C4334 from Hamamatsu Photonics) at 5K.

[1] *Gaussian 09*, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[2] (a) N. Lin, J. Qiao, L. Duan, L. Wang, Y. Qiu, *J. Phys. Chem. C.* **2014**, 118, 7569. M. Hong, M. K. Ravva, R. Winget, J.-L. Bredas, *Chem. Mater.* **2016**, 28, 5791.

[3] H. Ishii, D. Tsunami, T. Suenaga, N. Sato, Y. Kimura, M. Niwano, *J. Surf. Sci. Soc. Jpn.* **2007**, *28*, 264.

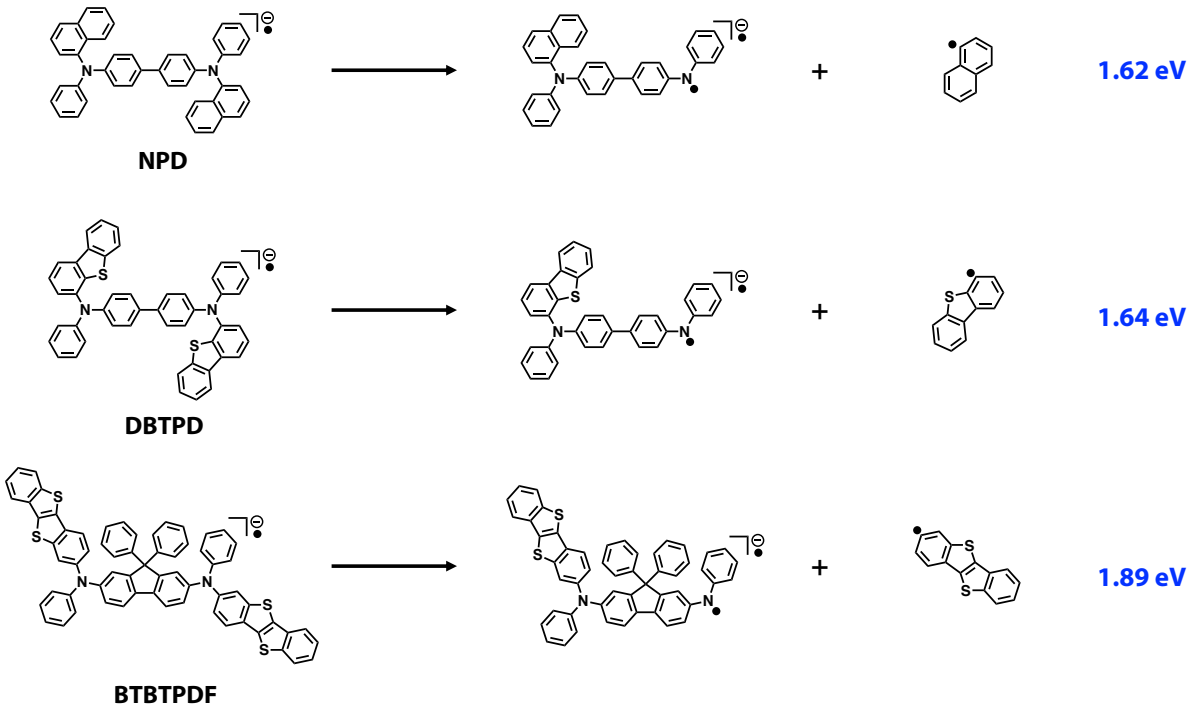

Figure S1. Calculated bond dissociation energy of p-type host materials at B3LYP 6-31G(d) level.

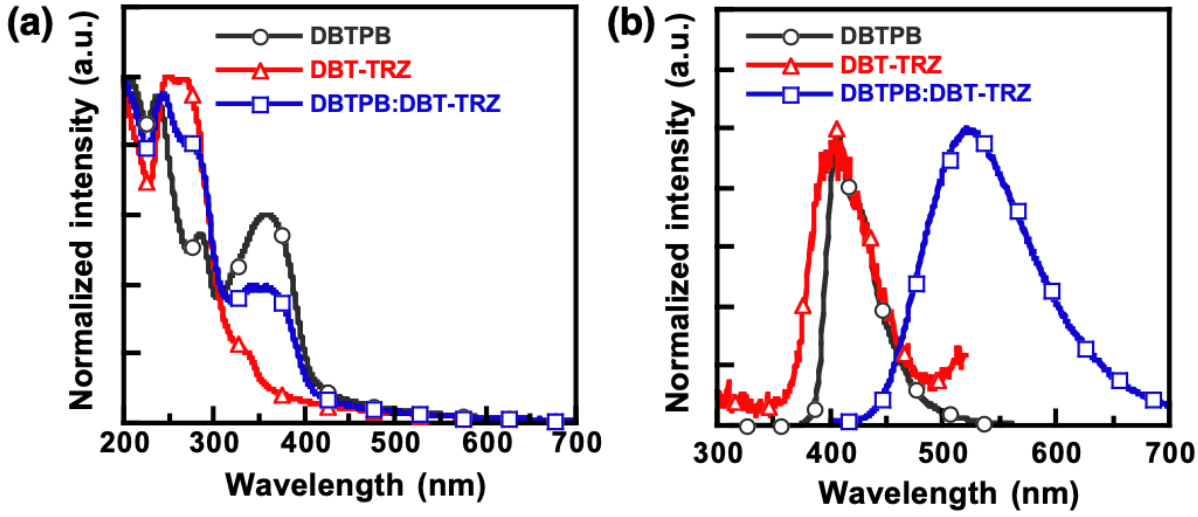

Figure S2. (a) Normalized UV-vis absorption spectra and (b) normalized PL spectra of the **DBTPB** and **DBT-TRZ** films, and **DBTPB:DBT-TRZ** (1:1, molar ratio) co-deposited film.

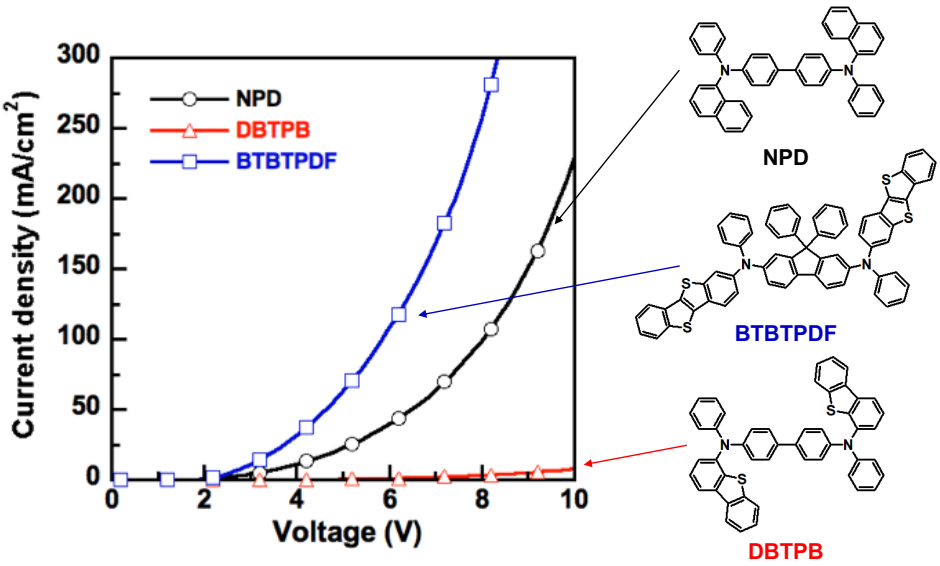

Figure S3. *J–V* characteristics of hole-only devices (HODs).

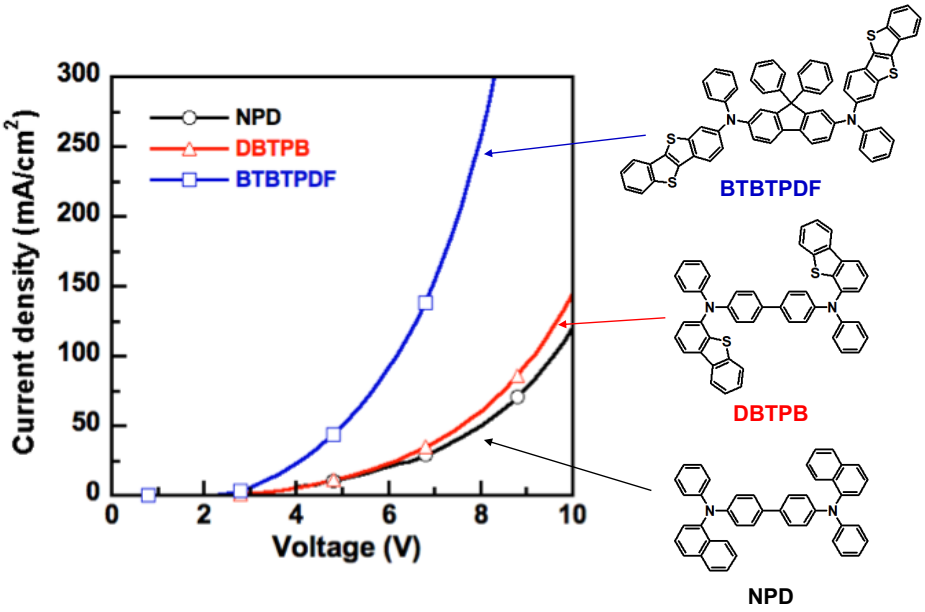

Figure S4. *J–V* characteristics of emitter-doped hole-only devices (doped-HODs).

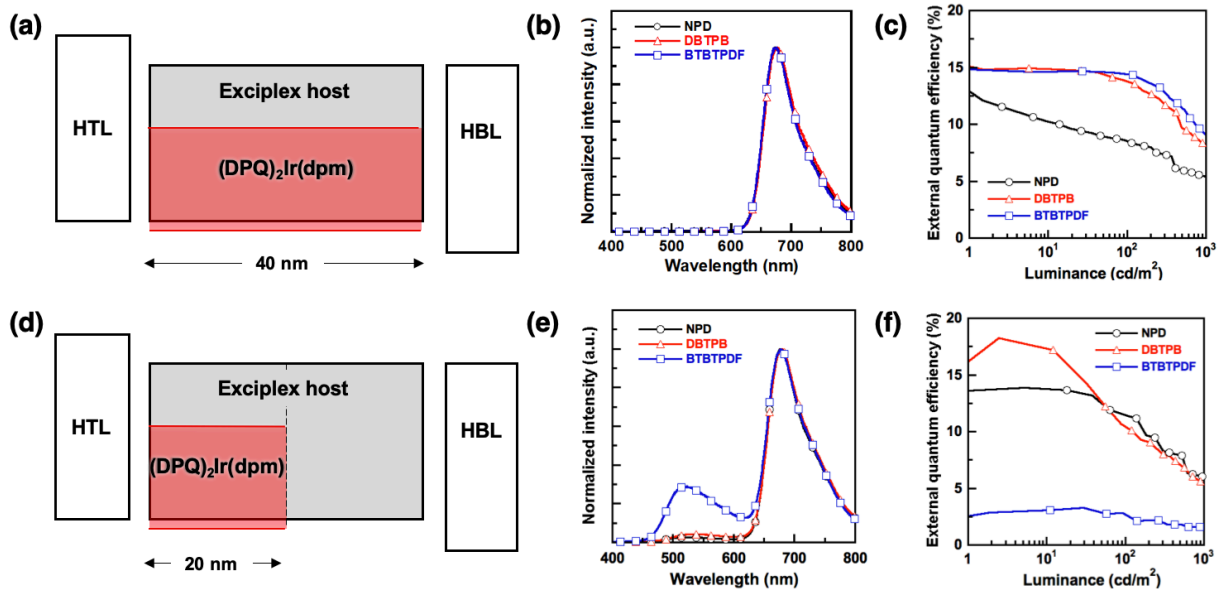

Figure S5. Performances of devices fully doped with 3 wt.% of the emitter: (a) the device structure, (b) EL spectra, (c) η_{ext}–L characteristics. Performances of devices partially doped with 3 wt.% of the emitter: (d) the device structure, (e) EL spectra, (f) η_{ext}–L characteristics.

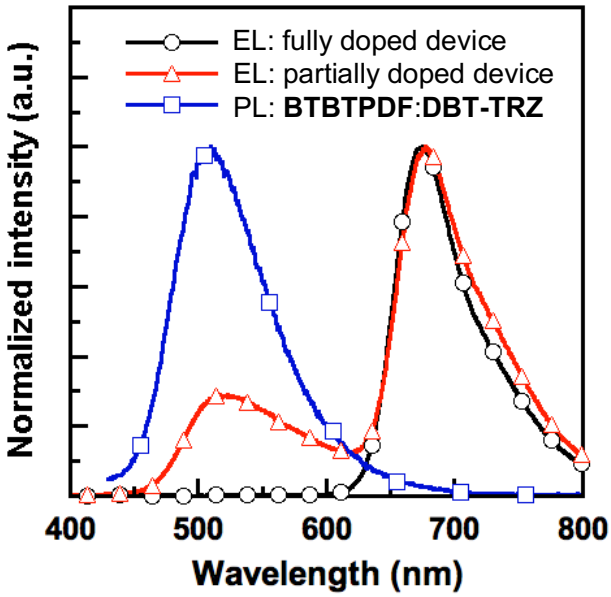

Figure S6. Comparisons of EL and PL spectra of the **BTBTPDF** : **DBT-TRZ** based exciplex host.