Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis of Donor-Acceptor Conjugated Copolymers Based on Benzo[1,2-*b*:4,5-*b′*]dithiophene and 2,1,3-Benzothiadiazole via Direct Arylation Polycondensation: Toward Efficient C-H Activation in Nonpolar Solvents

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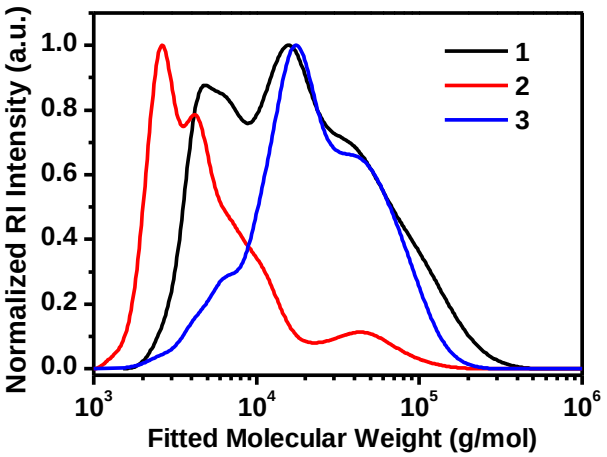

Figure S1. GPC curves of **PBDTBTs** polymerized in different catalyst systems. Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h, at the condition of **line 1**: $Pd(OAc)_2$ (5 mol %)/ PCy_3·HBF_4 (10 mol %), K_2CO_3 (0.6 mmol), PivOH (0.06 mmol) in DMAc (1 mL); **line 2**: Herrmann Catalyst (5 mol %)/ (*o*-MeOPh)$_3$P (10 mol %), Cs_2CO_3 (0.6 mmol), PivOH (0.06 mmol) in THF (1 mL); **line 3**: Pd_2dba_3 (5 mol %)/(*o*-MeOPh)$_3$P (10 mol %), Cs_2CO_3 (0.6 mmol), PivOH (0.06 mmol) in THF (1 mL).

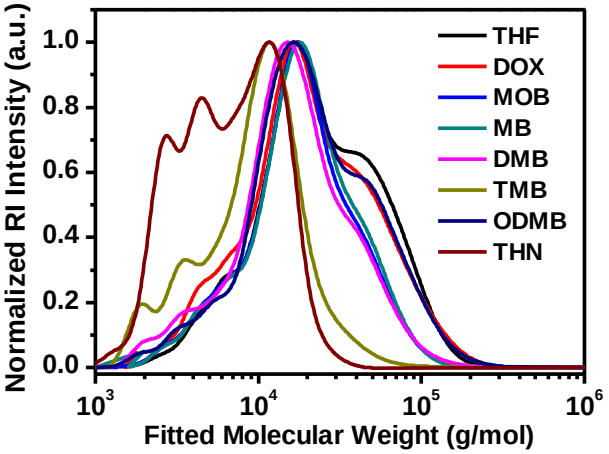

Figure S2. GPC curves of **PBDTBTs** polymerized in different solvents. Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in solvent (1 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), Cs_2CO_3 (0.6 mmol) and PivOH (0.06 mmol).

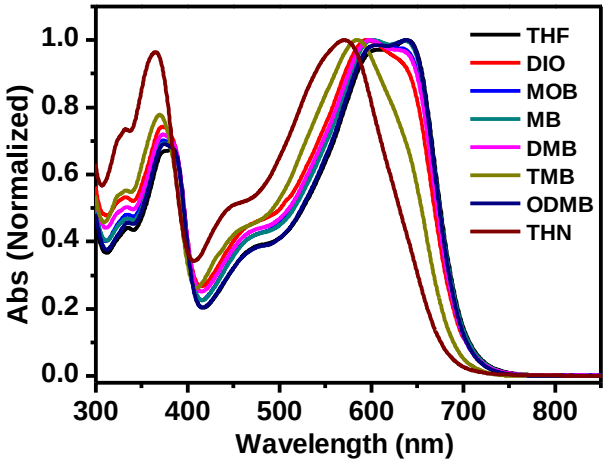

Figure S3. UV-vis absorption spectra of chloroform solutions of **PBDTBTs** polymerized in different solvents. Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in solvent (1 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), Cs_2CO_3 (0.6 mmol) and PivOH (0.06 mmol).

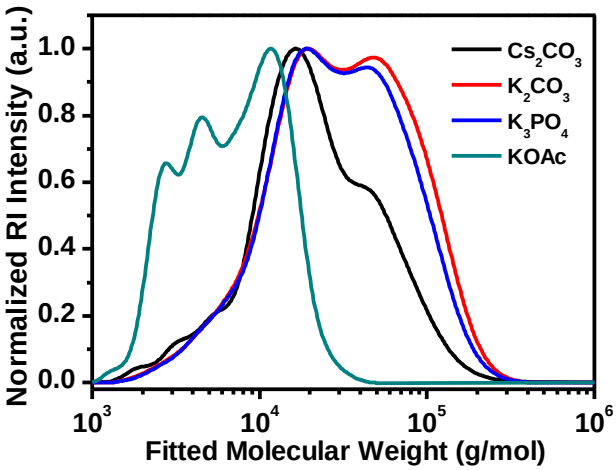

Figure S4. GPC curves of **PBDTBTs** polymerized with different base. Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in ODMB (1 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), base (0.6 mmol) and PivOH (0.06 mmol).

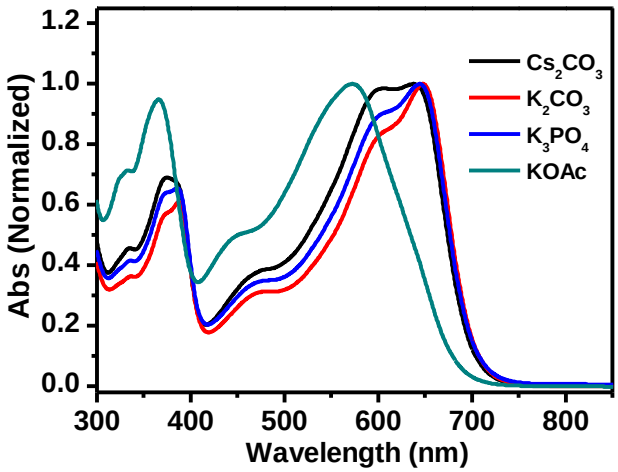

Figure S5. UV-vis absorption spectra of chloroform solutions of **PBDTBTs** polymerized with different base. Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in ODMB (1 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), base (0.6 mmol) and PivOH (0.06 mmol).

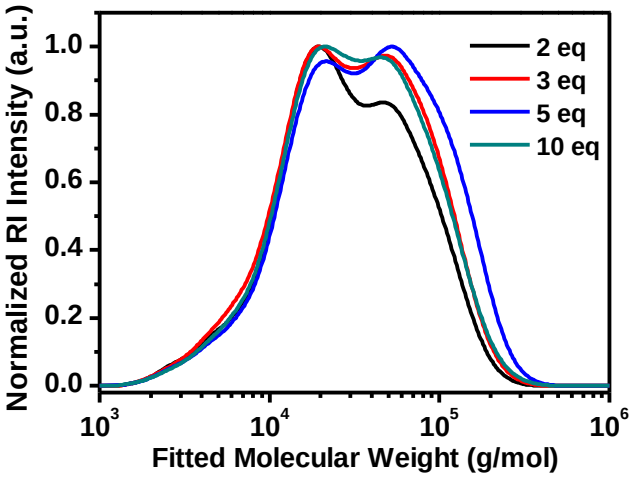

Figure S6. GPC curves of **PBDTBTs** polymerized with different equivalent of K_2CO_3. Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in ODMB (1 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 and PivOH (0.06 mmol).

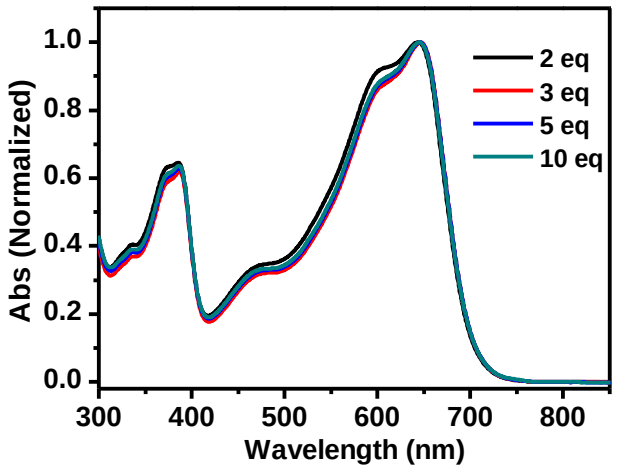

Figure S7. UV-vis absorption spectra of chloroform solutions of **PBDTBTs** polymerized with different equivalent of K_2CO_3. Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in ODMB (1 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 and PivOH (0.06 mmol).

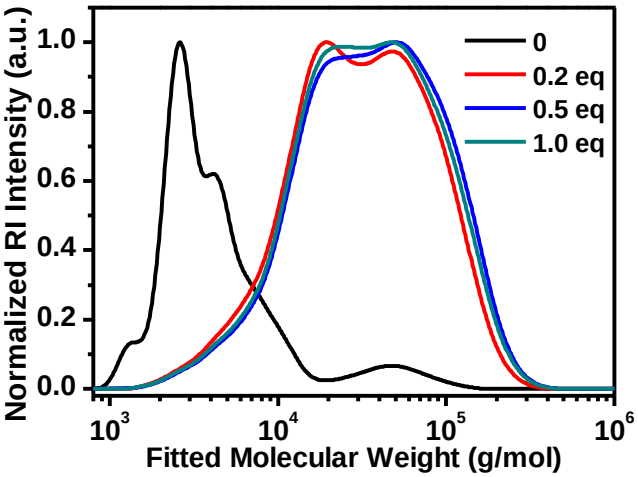

Figure S8. GPC curves of **PBDTBTs** polymerized with different equivalent of PivOH. Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in ODMB (1 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (0.6 mmol) and PivOH.

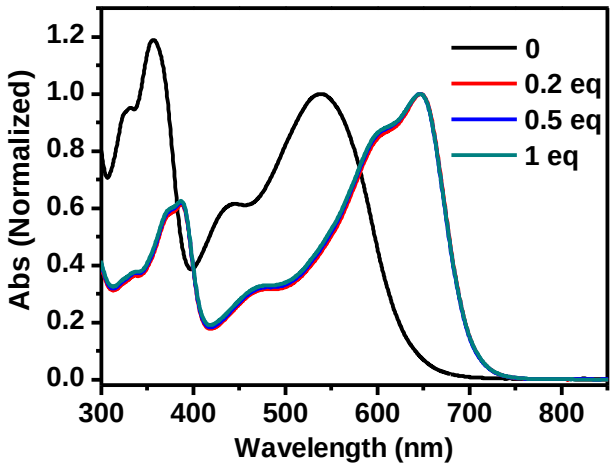

Figure S9. UV-vis absorption spectra of chloroform solutions of **PBDTBTs** polymerized with different equivalent of PivOH. Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in ODMB (1 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (0.6 mmol) and PivOH.

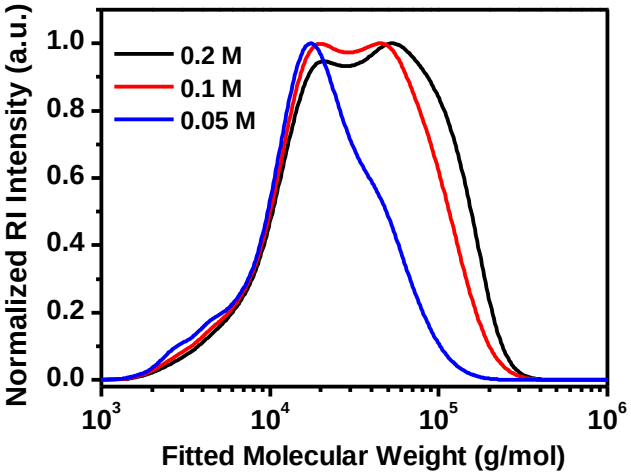

Figure S10. GPC curves of **PBDTBTs** polymerized at different concentration. Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in ODMB (1, 2 or 4 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (1 mmol) and PivOH (0.06 mmol).

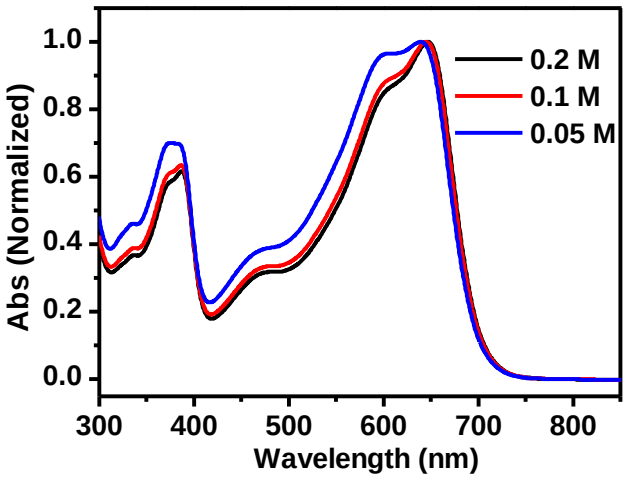

Figure S11. UV-vis absorption spectra of chloroform solutions of **PBDTBTs** polymerized at different concentration. Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in ODMB (1, 2 or 4 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (1 mmol) and PivOH (0.06 mmol).

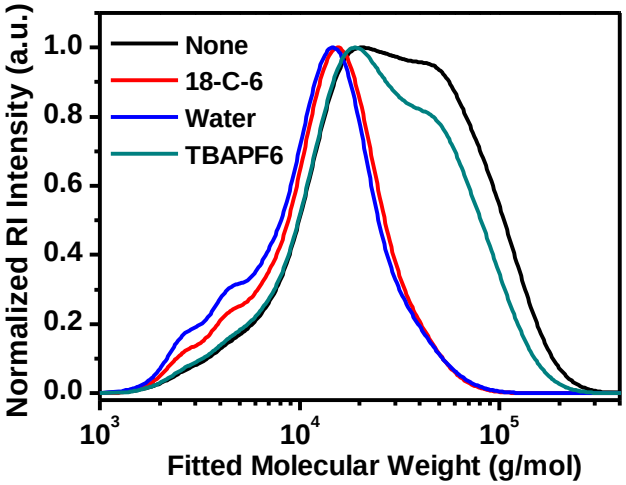

Figure S12. GPC curves of **PBDTBTs** polymerized with different phase transfer agents (PTA). Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in ODMB (2 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (1 mmol), PivOH (0.06 mmol) and PTA (0.06 mmol).

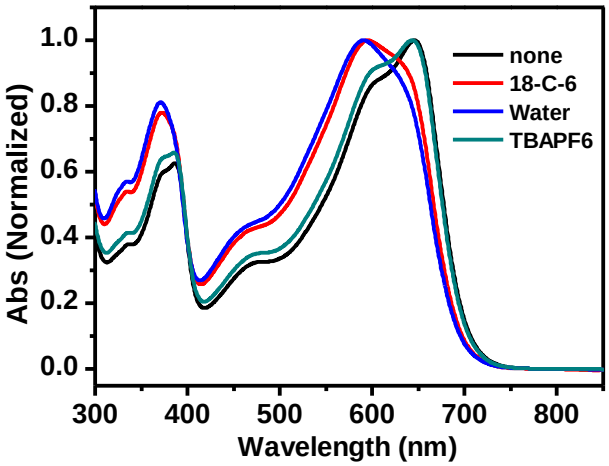

Figure S13. UV-vis absorption spectra of chloroform solutions of **PBDTBTs** polymerized with different phase transfer agents (PTA). Polymerizations of **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were run at 100 ℃ for 24 h in ODMB (2 mL), with Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (1 mmol), PivOH (0.06 mmol) and PTA (0.06 mmol).

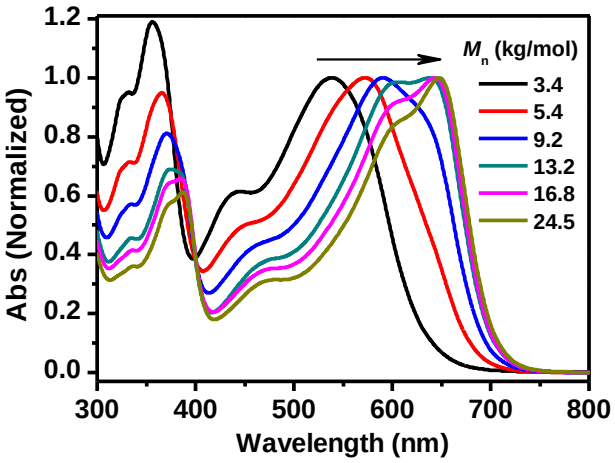

Figure S14. UV-vis absorption spectra of chloroform solutions of **PBDTBTs** with different molecular weight synthesized in ODMB under different conditions: lines corresponding to the polymers with M_n/M_w of 3.4/7.7, 5.4/8.5, 9.2/15.7, 13.2/23.7, 16.8/35.9 and 24.5/60.1 (kg/mol), respectively.