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

Xiaocheng Wang, Mingfeng Wang*  
School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore
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 °C for 24 h, at the condition of line 1: Pd(OAc)$_2$ (5 mol %)/PCy$_3$·HBF$_4$ (10 mol %), K$_2$CO$_3$ (0.6 mmol), PivOH (0.06 mmol) in DMAc (1 mL); line 2: Herrmann Catalyst (5 mol %)/(o-MeOPh)$_3$P (10 mol %), Cs$_2$CO$_3$ (0.6 mmol), PivOH (0.06 mmol) in THF (1 mL); line 3: Pd$_2$dba$_3$ (5 mol %)/(o-MeOPh)$_3$P (10 mol %), Cs$_2$CO$_3$ (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 °C for 24 h in solvent (1 mL), with Pd$_2$dba$_3$ (5 mol %), (o-MeOPh)$_3$P (10 mol %), Cs$_2$CO$_3$ (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 °C for 24 h in solvent (1 mL), with Pd_{2}dba\text{3} (5 mol %), (o-MeOPh)\text{3}P (10 mol %), Cs\text{2}CO\text{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 °C for 24 h in ODMB (1 mL), with Pd_{2}dba\text{3} (5 mol %), (o-MeOPh)\text{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 °C for 24 h in ODMB (1 mL), with Pd2dba3 (5 mol %), (o-MeOPh)3P (10 mol %), base (0.6 mmol) and PivOH (0.06 mmol).

Figure S6. GPC curves of PBDTBTs polymerized with different equivalent of K2CO3. Polymerizations of HDBDT (0.2 mmol) and BrBT (0.2 mmol) were run at 100 °C for 24 h in ODMB (1 mL), with Pd2dba3 (5 mol %), (o-MeOPh)3P (10 mol %), K2CO3 and PivOH (0.06 mmol).
**Figure S7.** UV-vis absorption spectra of chloroform solutions of PBDTBTs polymerized with different equivalent of K$_2$CO$_3$. Polymerizations of HDBDT (0.2 mmol) and BrBT (0.2 mmol) were run at 100 °C for 24 h in ODMB (1 mL), with Pd$_2$dba$_3$ (5 mol %), (o-MeOPh)$_3$P (10 mol %), K$_2$CO$_3$ 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 °C for 24 h in ODMB (1 mL), with Pd$_2$dba$_3$ (5 mol %), (o-MeOPh)$_3$P (10 mol %), K$_2$CO$_3$ (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 °C for 24 h in ODMB (1 mL), with Pd$_2$dba$_3$ (5 mol %), (o-MeOPh)$_3$P (10 mol %), K$_2$CO$_3$ (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 °C for 24 h in ODMB (1, 2 or 4 mL), with Pd$_2$dba$_3$ (5 mol %), (o-MeOPh)$_3$P (10 mol %), K$_2$CO$_3$ (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 °C for 24 h in ODMB (1, 2 or 4 mL), with Pd$_2$dba$_3$ (5 mol %), (o-MeOPh)$_3$P (10 mol %), K$_2$CO$_3$ (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 °C for 24 h in ODMB (2 mL), with Pd$_2$dba$_3$ (5 mol %), (o-MeOPh)$_3$P (10 mol %), K$_2$CO$_3$ (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 °C for 24 h in ODMB (2 mL), with Pd$_2$dba$_3$ (5 mol %), (o-MeOPh)$_3$P (10 mol %), K$_2$CO$_3$ (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.