

Supporting Information for

Solvent-Resistant Azide-Based Hole Injection/Transporting Conjugated Polymer for Fluorescent and Phosphorescent Light- Emitting Diodes

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Experimental Section

4-Butyl-*N,N*-bis(4-bromophenyl)aniline (1)

4-Butylaniline (4.00 g, 26.8 mmol), 1-bromo-4-iodobenzene (16.7 g, 59.0 mmol), KOH (13.7 g, 243 mmol), 1,10-phenanthroline (0.176 g, 0.970 mmol), CuCl (0.100 g, 0.950 mmol), and toluene (50 mL) were added sequentially to a two-neck reaction flask equipped with a condenser. The contents of the reaction vessel were heated under reflux for 30 min and then kept stirring for 12 h under a N₂ atmosphere. The reaction mixture was filtered then extracted with toluene (100 mL) and brine (100 mL). The organic phase was dried (MgSO₄), filtered, and concentrated under vacuum. The residue was subjected to column chromatography (SiO₂; hexane) to give a colorless wax (7.9 g, 64 %). ¹H NMR (Figure S1, CDCl₃, δ): 7.30 (dd, 4H; ArH), 7.07 (d, 2H; ArH), 6.96 (d, 2H; ArH), 6.90 (dd, 4H; ArH), 2.56 (t, 2H; CH₂), 1.63–1.52 (m, 2H; CH₂), 1.41–1.29 (m, 2H; CH₂), 0.93 (t, 3H; CH₃).

4-Butyl-*N,N*-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-4-phenyl)aniline (2)

n-Butyllithium (2.5 M in hexane; 6.59 mL, 16.5 mmol) was added to a solution of 4-butyl-*N,N*-bis(4-bromophenyl)aniline (1; 3.00 g, 6.53 mmol) in anhydrous THF (65 mL) at –78 °C and then the mixture was stirred at that temperature for 45 min. The solvent was evaporated in vacuo and then the residue was taken up into CHCl₃ and washed with brine. The organic phase was dried (MgSO₄) and concentrated; the residue was recrystallized from MeOH to give colorless crystals (2.3 g, 77%) ¹H NMR (Figure S1, CDCl₃, δ): 7.64 (d, 4H; ArH), 7.03 (m, 8H; ArH), 2.56 (t, 2H; CH₂), 1.63–1.53 (m, 2H; CH₂), 1.38–1.31 (m, 26H; CH₂ and C₈H₂₄), 0.92 (t, 3H; CH₃). ¹³C NMR (125 MHz, CDCl₃, δ):

150.5, 145.2, 139.6, 136.5, 130.1, 126.5, 122.9, 84.1, 35.3, 33.8, 24.9, 22.5, 14.0.

6-Bromobutyl-9(3,6-carbazole) (4)

3,6-Dibromo-9*H*-carbazole (3.50 g, 10.7 mmol), powdered anhydrous K₂CO₃ (2.98 g, 21.5 mmol), 1,6-dibromohexane (26.3 g, 0.107 mol), and dry MeCN (45 mL) were placed in a condenser-equipped reaction flask and then stirred with heating at 95 °C for 36 h. After cooling to room temperature, the mixture was filtered and the solvent evaporated. The residue was recrystallized from petroleum ether to give colorless crystals (3.9 g, 75%). ¹H NMR (Figure S3, CDCl₃, δ): 8.10 (d, 2H; ArH), 7.54 (dd, 2H; ArH), 7.25 (d, 2H; ArH), 4.25 (t, 2H; CH₂), 3.35 (t, 2H; CH₂), 1.90–1.75 (m, 4H; CH₂), 1.51–1.28 (m, 4H; CH₂).

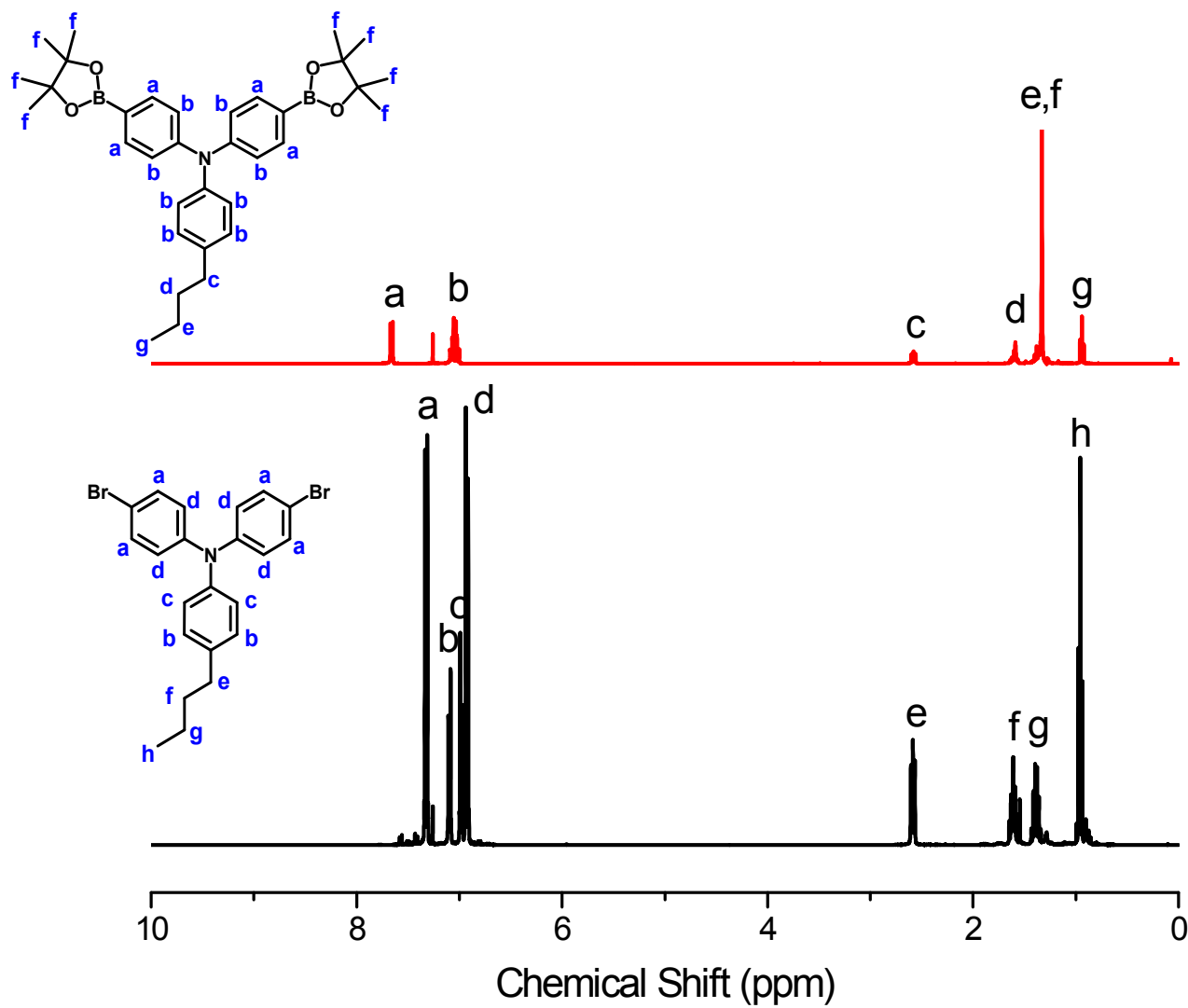


Figure S1: ¹H NMR spectra of the monomers 1 and 2.

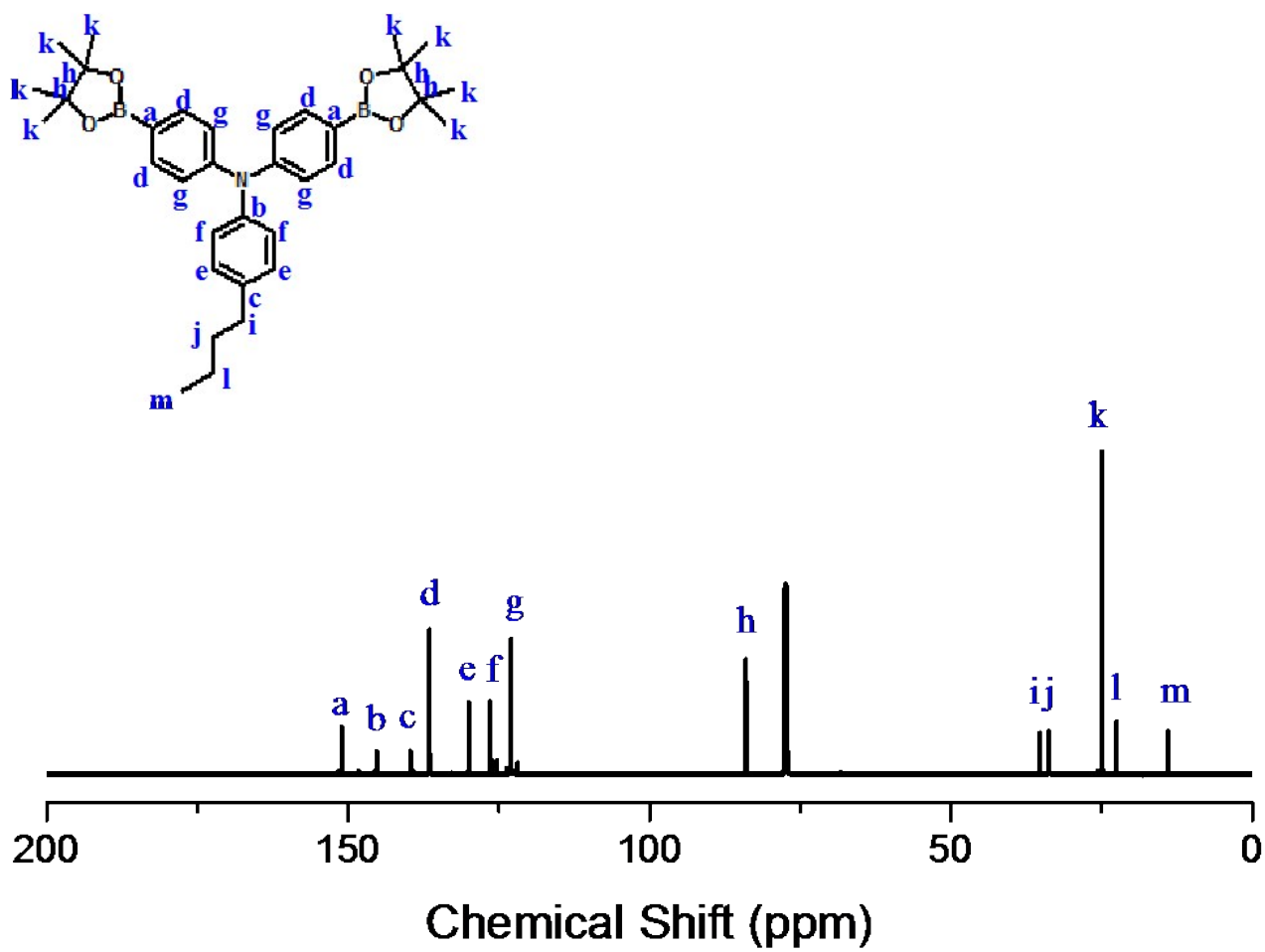


Figure S2: ¹³C NMR spectrum of the monomer 2.

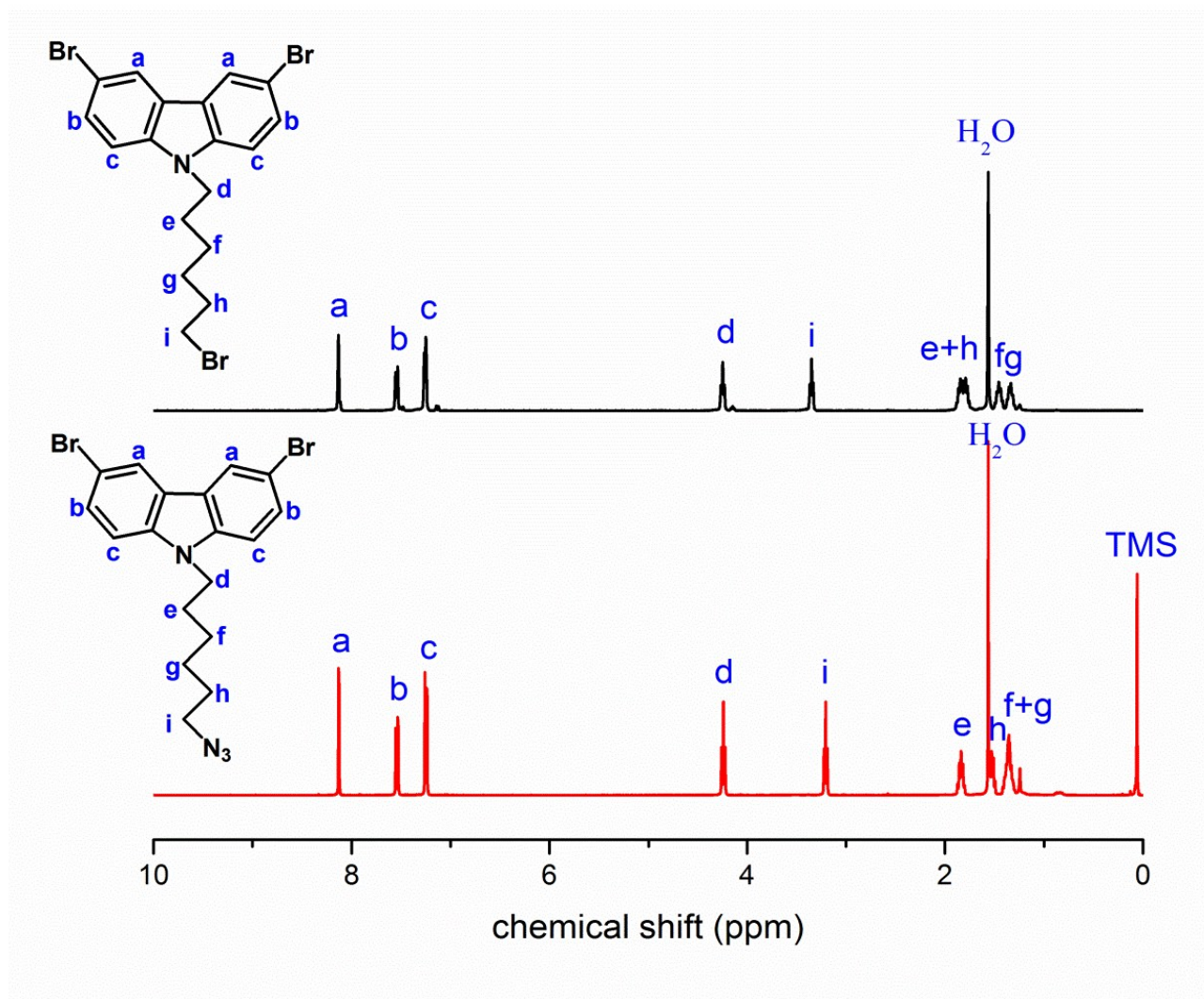


Figure S3: ¹H NMR spectra of the monomers 4 and 5.

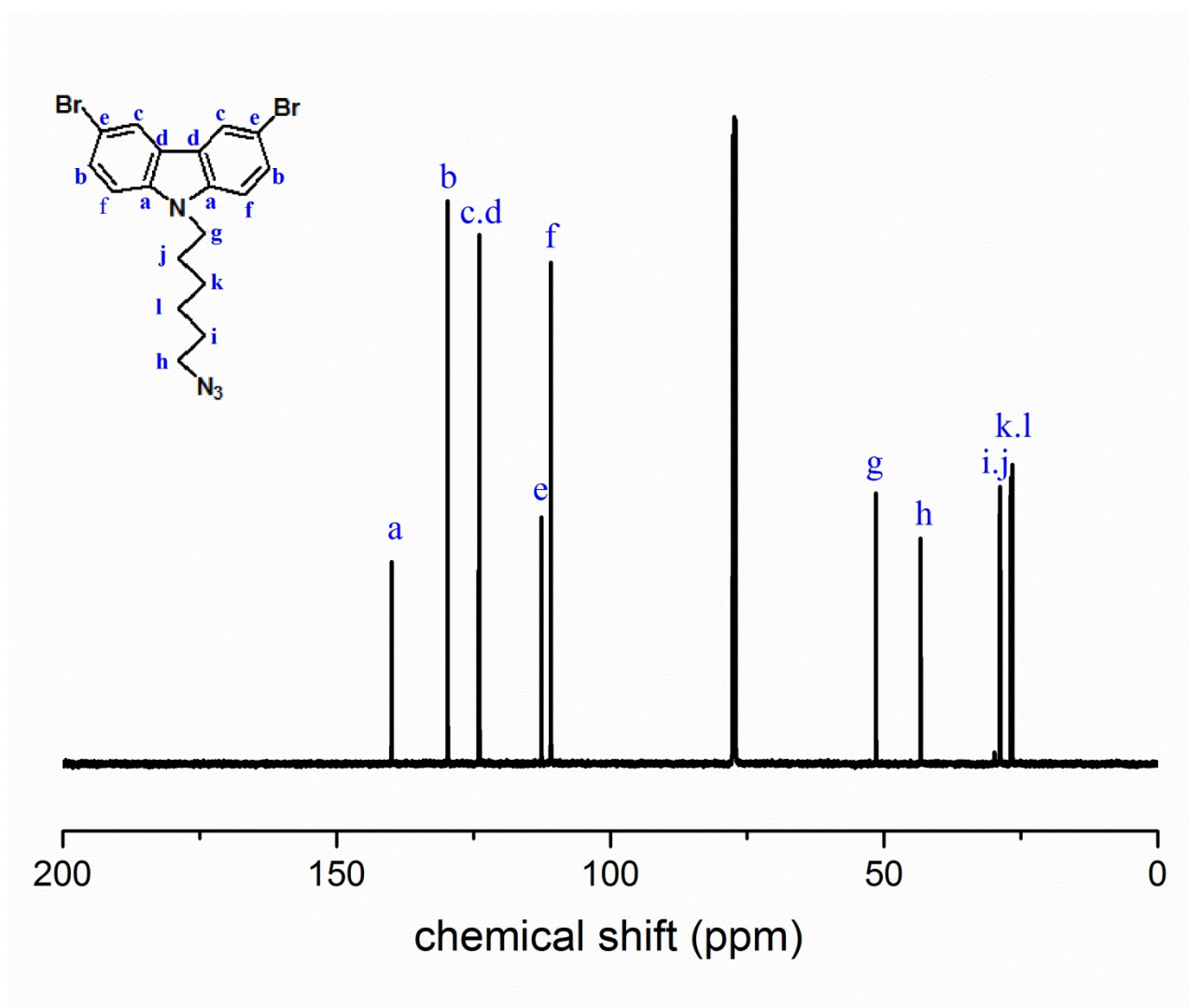


Figure S4: ^{13}C NMR spectrum of the monomer 5.

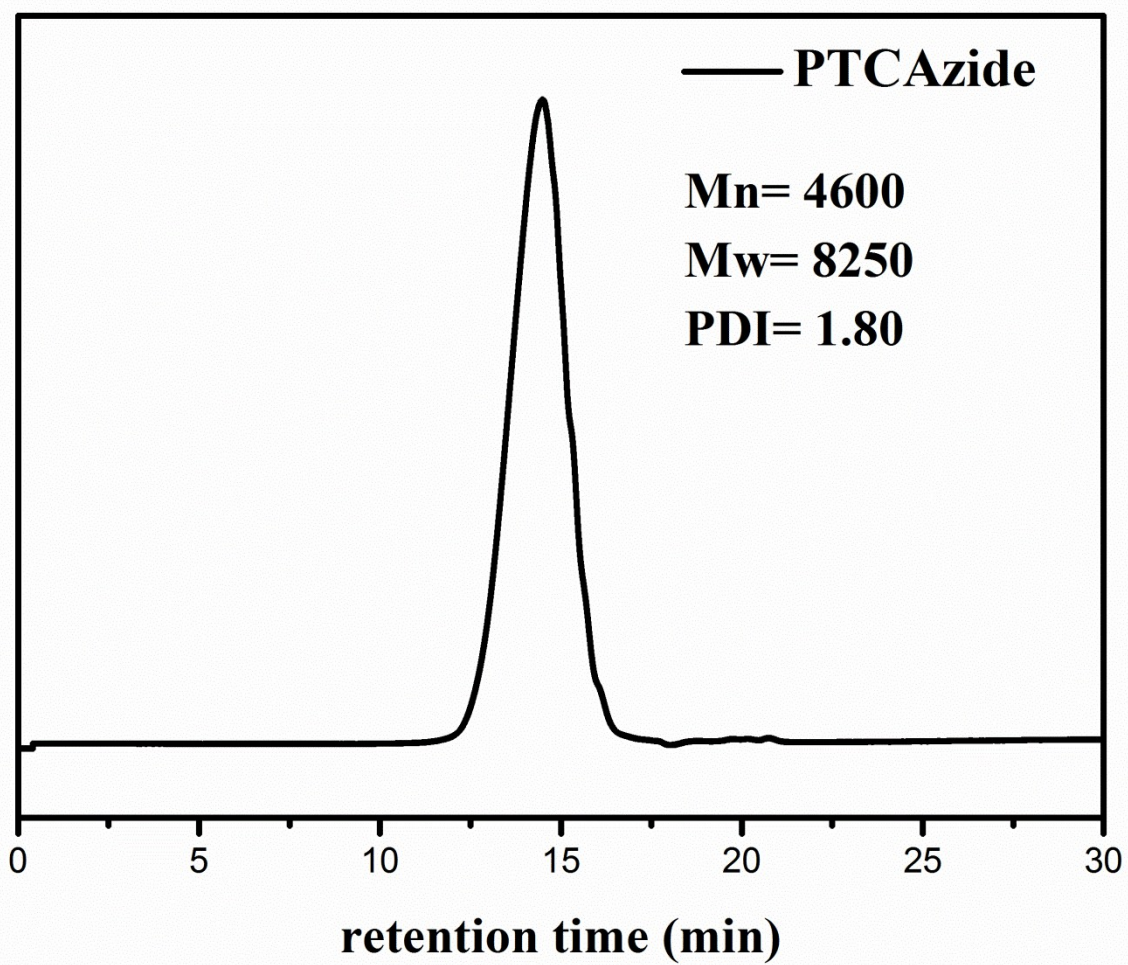


Figure S5: GPC trace of the copolymer PTCAzide.

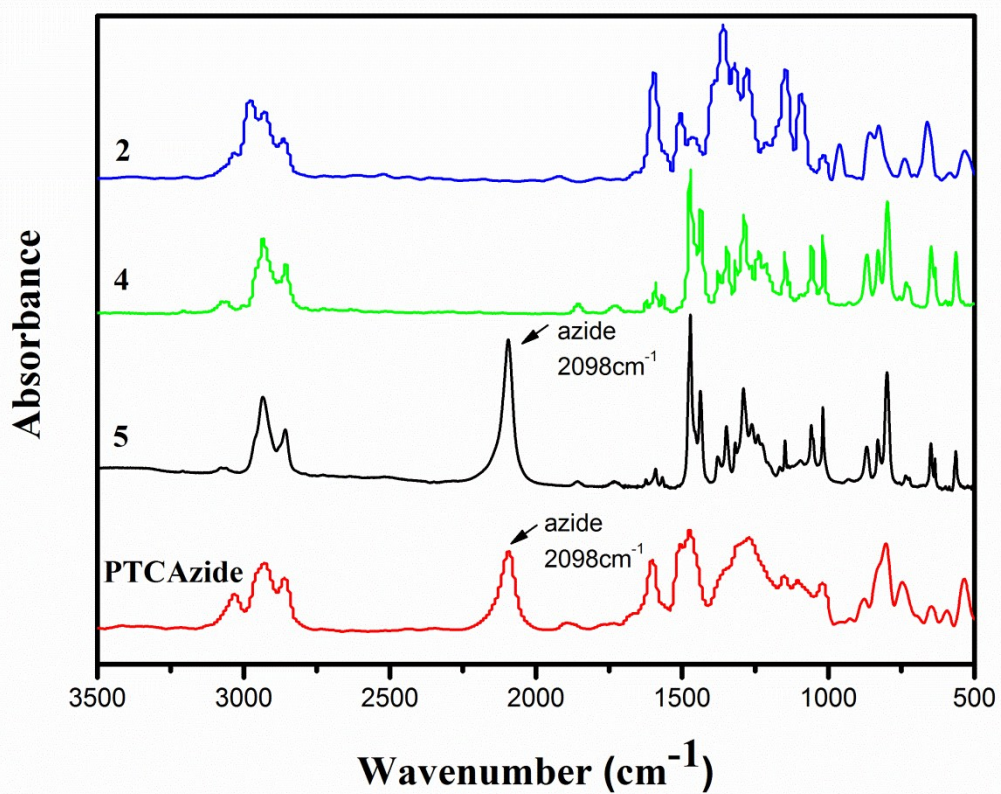


Figure S6: FTIR spectra of the copolymer PTCAzide and the corresponding monomers used in this study.

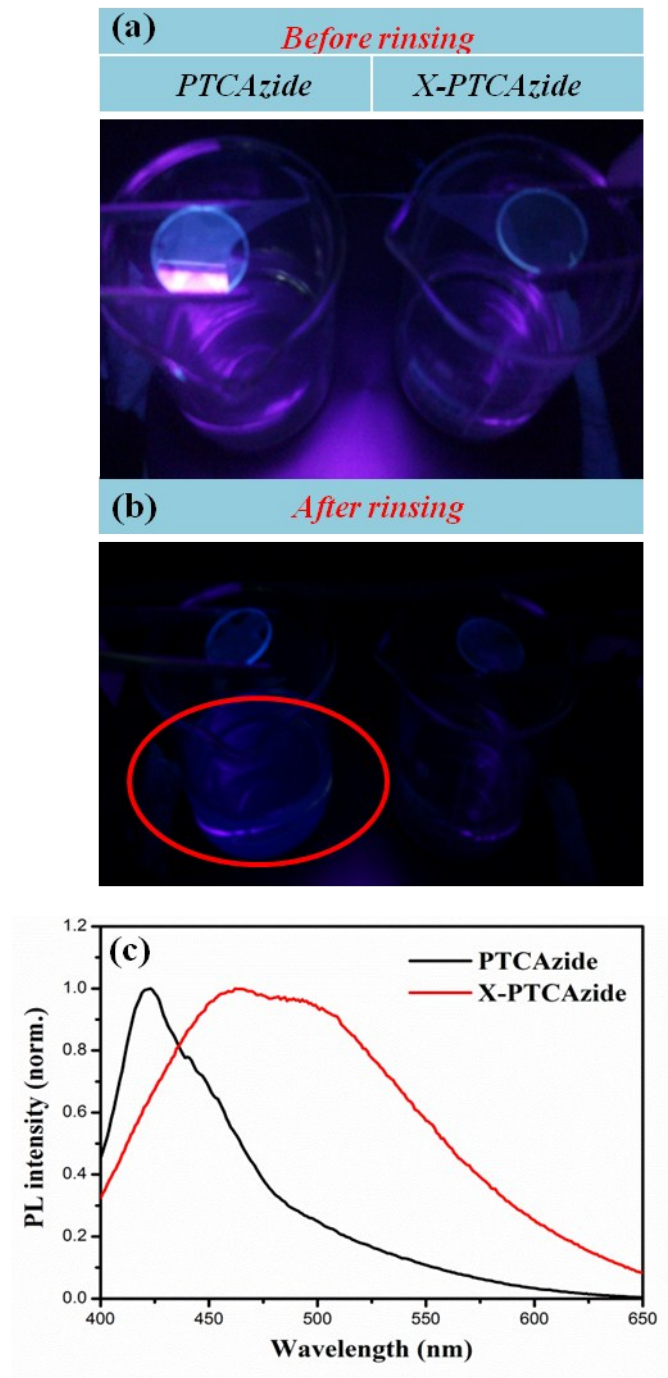


Figure S7: Image for polymer thin film (a) before and (b) after chlorobenzene rinsing (Left: PTCAzide, Right: X-PTCAzide). PL spectra of PTCAzide and X-PTCAzide has been in (c) in normalized scale.

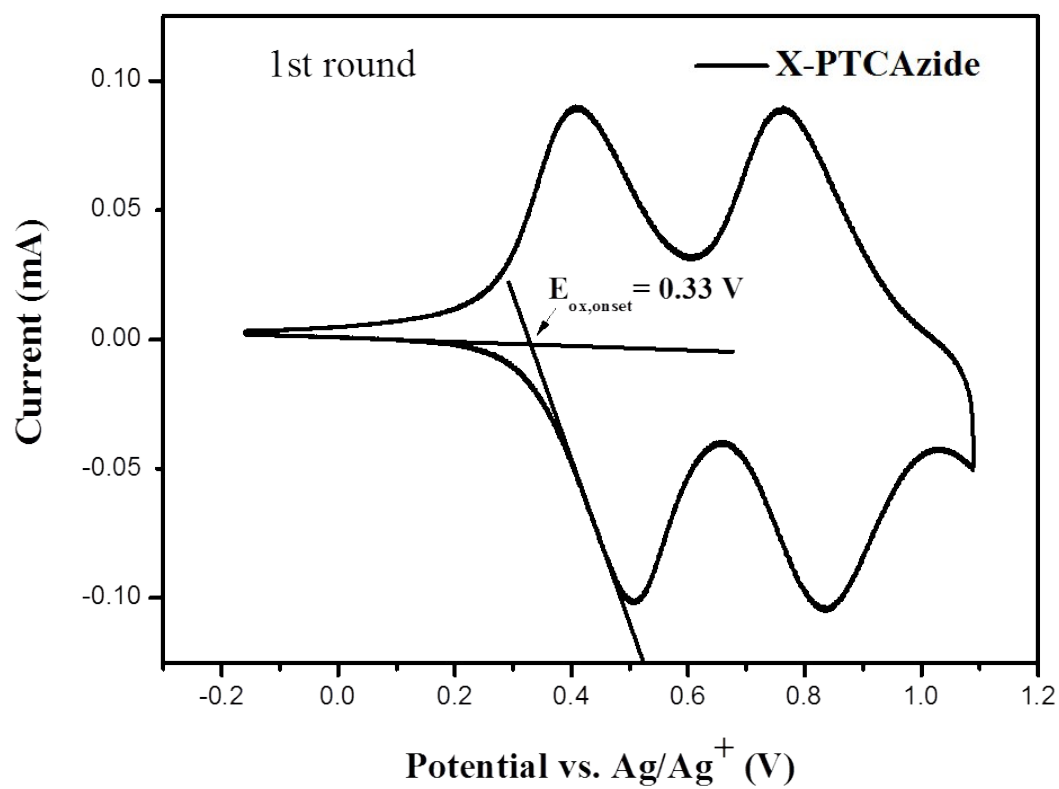


Figure S8: First-round cyclic voltammogram of X-PTCAzide.

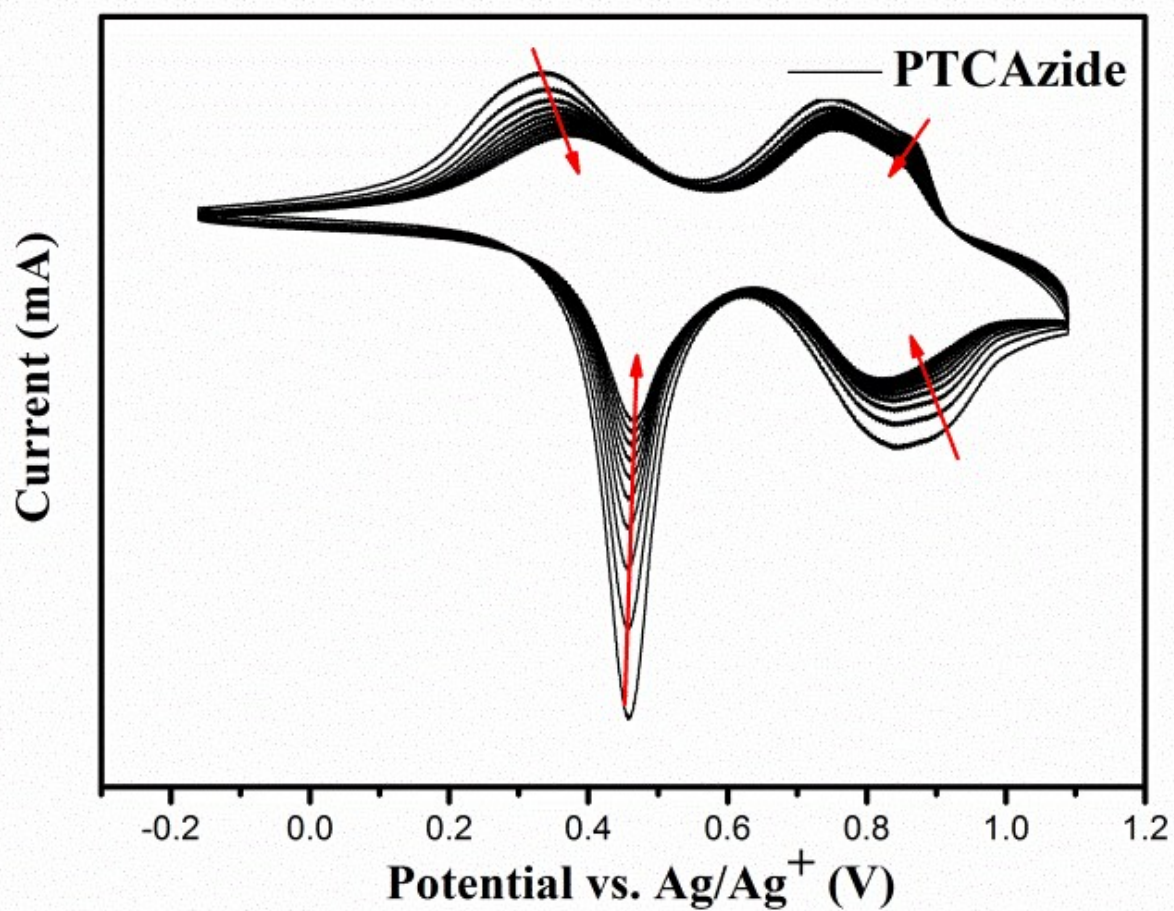


Figure S9: 10 cycle Cyclic voltammograms of PTCAzide on ITO substrates at a scan rate of 100 mV s⁻¹.

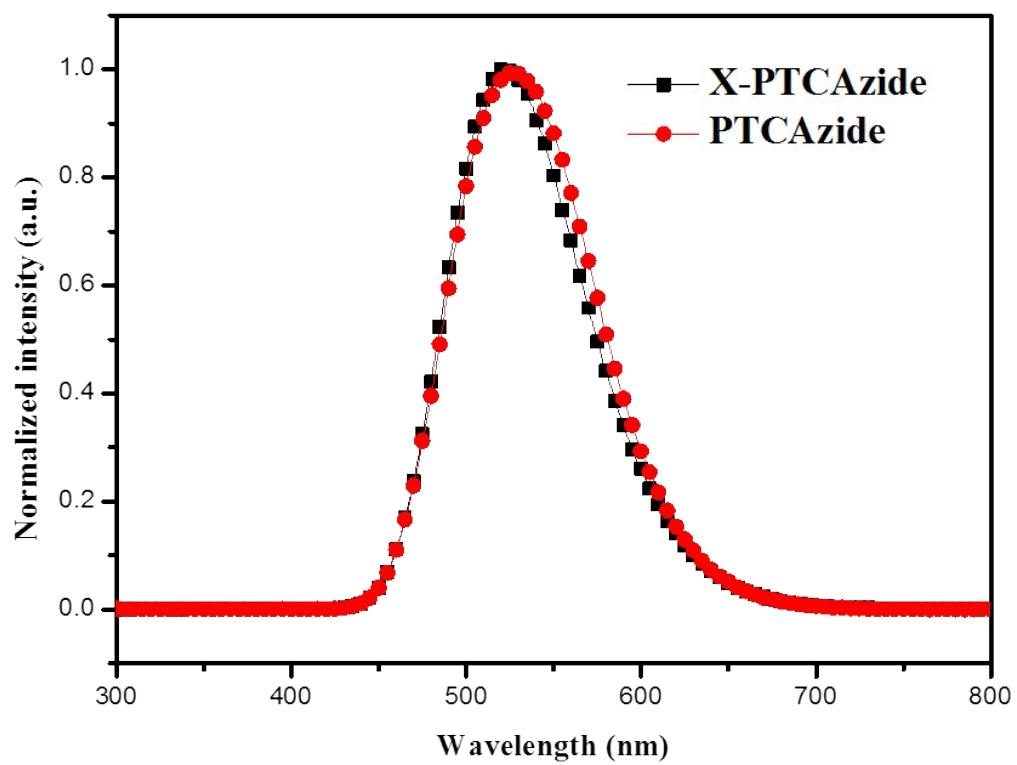


Figure S10: Electroluminescence from devices having the structure ITO/HITL/NPB/Alq₃/LiF/Al.

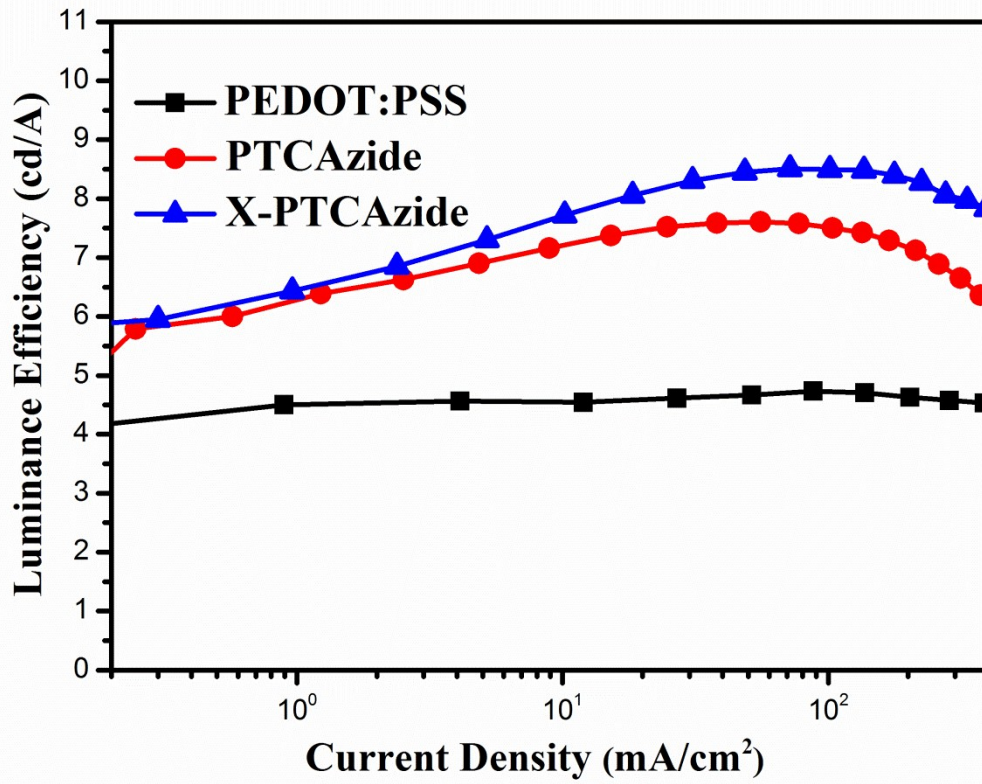


Figure S11: LE-J of device characteristic with structure ITO/HITL/NPB/Alq₃/LiF/Al.

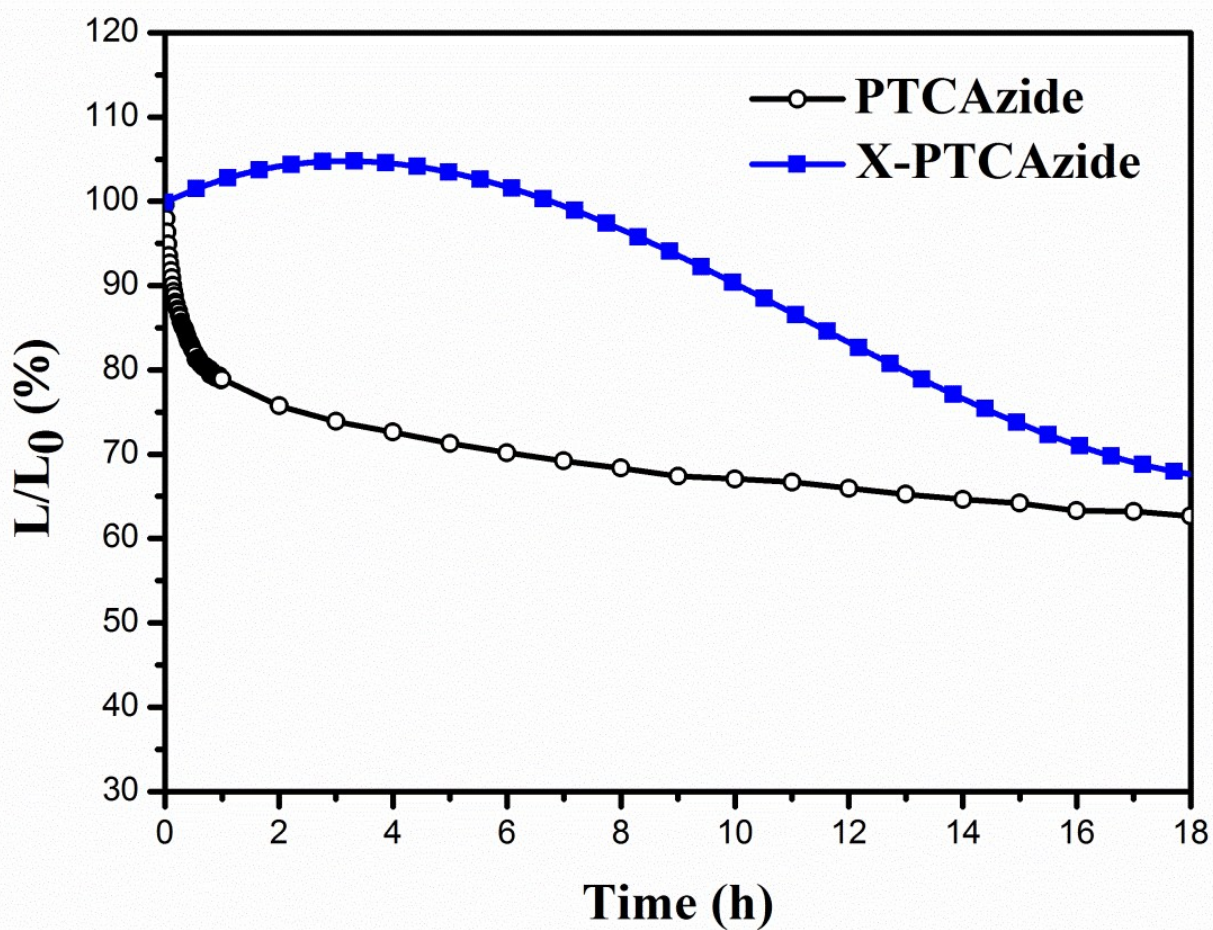


Figure S12: Comparison of device operational stability of ITO/HITL/NPB/Alq₃/LiF/Al device at a constant operating current density of 13.6 mA cm⁻² for PTCAzide device, 12.7 mA cm⁻² for X-PTCAzide device. The initial brightness was 1000 cd m⁻² for both devices. The measurement was conducted under a nitrogen atmosphere in a glove box.

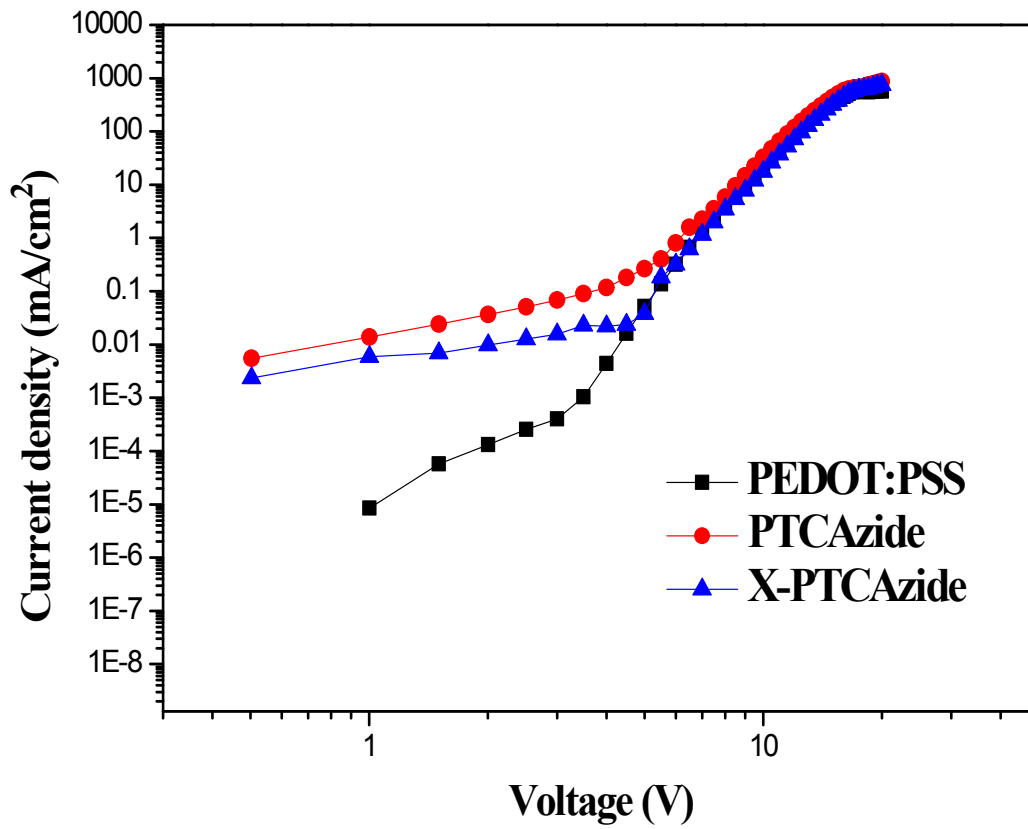


Figure S13: Leakage current of devices having the structure ITO/HITL/Ir(ppy)₃:PVK/BCP/Alq₃/LiF/Al.