

**Synthesis and Characterization of Fully Conjugated Donor-Acceptor-Donor
Triblock Copolymers**

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S-1. Synthesis and spectral characterization of 3b, 4b, 7 and 8

5,10-Diethyltetradecane-7,8-dione, 3b. Prepared a solution of 2-ethylhexylmagnesium bromide by adding 2-ethylhexyl bromide (17.3 mL, mol) dropwise to a solution of Mg (2.61 g, mol) in THF (250 mL) and let stir for 1 h at room temperature. In a separate flask, added LiBr (17 g, mol) in THF (100 mL) to a solution of CuBr (14 g, mol) in THF (150 mL) by syringe. Cooled the mixture to -96 °C by a pentane/liquid nitrogen slurry. Added 2-ethylhexylmagnesium bromide solution to the mixture dropwise over 1 h. Added oxalyl chloride (5.0 g, mol) to the mixture and let warm slowly to room temperature over 2 h. Quenched the reaction by pouring the mixture into saturated ammonium chloride (aq, 500 mL). Extracted organic layer, and washed aqueous layer repeatedly with diethyl ether (3 x 300 mL), combined the extracts and removed solvent under reduced pressure. The resulting residue was purified by column chromatography (10:90 v/v CH₂Cl₂:hexanes) to obtain **3b** as a yellow liquid (5.01 g, 45%). ¹H

NMR (300 MHz, CDCl₃) δ 2.64 (d, $^3J_{\text{HH}} = 6.6$ Hz, 4H) 1.81-1.89 (m, 2H), 1.16-1.36 (m, 16H) 0.81-0.89 (m, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 200.59 (C=O), 40.24, 34.94, 33.22, 28.81, 26.46, 22.86, 14.03, 10.81. IR (ATIR): 2931, 2919, 2854, 1705 (C=O str.), 1456, 1377, 997, 925, 719, 690, 687, 578.

5,8-Dibromo-2,3-bis(2-ethylhexyl)quinoxaline, 4b. A solution of 3,6-dibromobenzene-1,2-diamine (**2**) (5.6 g, 21 mmol) and **3b** (6.0 g, 21 mmol) in acetic acid (200 mL) was heated to reflux for 24 h. The solution was cooled to room temperature and poured into H₂O (200 mL), neutralized with 10 % KOH (aq) and extracted with diethyl ether (3 x 100 mL). The organic extracts were combined and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography (20:80 v/v CH₂Cl₂:hexanes) to afford **4b** as a viscous yellow liquid (6.7 g, 47 %). ¹H NMR (300 MHz, CDCl₃) δ 7.81 (s, 2H), 2.99 (d, = 6.9 Hz, 4H), 2.12-2.20 (m, 2H), 1.23-1.46 (m, 16H), 0.85-0.96 (m, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 158.13, 138.96, 131.87, 123.34, 38.80, 38.05, 32.76, 28.84, 26.00, 23.04, 14.12, 10.90. IR (ATIR): 2908, 2842, 1585, 1465, 1394, 1301, 1259, 1168, 1097, 1018, 935, 811, 723, 656, 588, 430. HRMS *calc.* for C₂₄H₃₆Br₂N₂ = 510.1245, *obs.* = 510.1233 Δ = 2.4 ppm.

2,3-Bis(4-(octyloxy)phenyl)-5,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoxaline, 7. Dibromide **4a** (3.85 g, 5.5 mmol) was added to anhydrous 1,4-dioxane (70 mL) under argon. Bis(pinacolato)diboron (3.5 g, 14 mmol), Pd(dppf)Cl₂ (0.4 g, 0.5 mmol) and potassium acetate (1.35 g, 13.8 mmol) were added to a solution of dibromide **4a** (3.85 g, 5.5 mmol) in anhydrous 1,4-dioxane (70 mL) under argon. The solution was degassed by freeze-pump-thaw (2 x 15 min cycles) and heated to 100 °C for 24 h. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂ (100 mL) and the solution was extracted with H₂O (100 mL). The organic layer was

concentrated under reduced pressure and the residue was subjected to column chromatography (30:70 v/v EtOAc:CH₂Cl₂) to afford **7** as a white solid (2.5 g, 58%): mp = 96–98 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.93 (s, 2H, quinoxaline C–H), 7.68 (d, ³J_{HH} = 8.7 Hz, 4H, phenyl C2–H), 6.83 (d, ³J_{HH} = 9.0 Hz, 4H, phenyl C3–H), 3.97 (t, ³J_{HH} = 6.6 Hz, 4H, –OCH₂–), 1.79 (p, ³J_{HH} = 7.5 Hz, 4H), 1.47 (s, 24H), 1.27–1.44 (m, 20H), 0.89 (t, ³J_{HH} = 6.9 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 159.71 (phenyl C4), 150.77 (quinoxaline C2 and C3), 143.02 (quinoxaline C1 and C4), 134.98 (quinoxaline C6 and C7), 131.90 (phenyl C2), 131.56 (quinoxaline C5 and C8), 113.82 (phenyl C3), 84.11 (–OC(CH₃)₂–), 67.98 (–OCH₂–), 31.82, 29.38, 29.28, 29.25, 26.05, 25.06, 22.67, 14.12. IR (ATIR): 2929 (Ar C–H str.), 2865, 1608, 1513, 1475, 1367, 1309, 1245 (C–O str.), 1178, 1143, 1025, 1022, 987, 858, 831, 817, 688, 604, 543 cm^{–1}.

2,3-Bis(4-(octyloxy)phenyl)-5,8-bis(3-octylthiophen-2-yl)quinoxaline, 8. 2-Bromo-3-octylthiophene (0.62 g, 2.2 mmol) was added to a mixture of **7** (0.45 g, 0.56 mmol) in THF (9 mL) and 2 M aqueous Na₂CO₃ (4 mL). The solution was degassed by freeze-pump-thaw (2 × 15 min each cycle) and Pd(PPh₃)₄ (0.1 g, 0.1 mmol) was added. The solution was stirred under argon at 70 °C for 24 h, poured into H₂O (50 mL) and extracted with CH₂Cl₂ (2 × 100 mL). The combined extracts were concentrated under reduced pressure and the residue was subjected to column chromatography (20:80 v/v CH₂Cl₂:hexanes) to afford **8** as a viscous yellow liquid (0.48 g, 92%). ¹H NMR (300 MHz, CDCl₃) δ 7.75 (s, 2 H, quinoxaline C–H), 7.58 (d, ³J_{HH} = 8.7 Hz, 4H, phenyl C2–H), 7.45 (d, ³J_{HH} = 4.9 Hz, 2H, thiophene C5–H), 7.10 (d, ³J_{HH} = 4.8 Hz, 2H, thiophene C4–H), 6.81 (d, ³J_{HH} = 8.7 Hz, 4H, phenyl C3–H), 3.96 (t, ³J_{HH} = 6.3 Hz, 4H, –OCH₂–), 2.68 (t, ³J_{HH} = 8.1 Hz, 4H, Th–CH₂–), 1.79 (p, ³J_{HH} = 7.2 Hz, 4H), 1.56–1.66 (m, 4H), 1.16–1.48 (m, 40H), 0.84–0.92 (m, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 159.79, 151.18, 141.10, 138.98, 133.32, 132.95, 131.58, 131.38, 130.47, 128.53, 125.66, 114.03, 67.98, 31.84, 30.85,

29.55, 29.38, 29.24, 26.05, 22.68, 22.65, 14.13, 14.11. IR (ATIR): 2924 (Ar C–H str.), 2852, 1604, 1511, 1467, 1384, 1334, 1294, 1247 (C–O str.), 1174, 1029, 966, 836, 723, 671, 547 cm^{-1} . Elemental Analysis: Theoretical: C, 77.70%; H, 8.91%; N, 3.02%; S, 6.91%. Found: C, 77.80%; H, 8.98%; N, 2.98%; S, 6.78%.

S-2. ^1H NMR Spectra

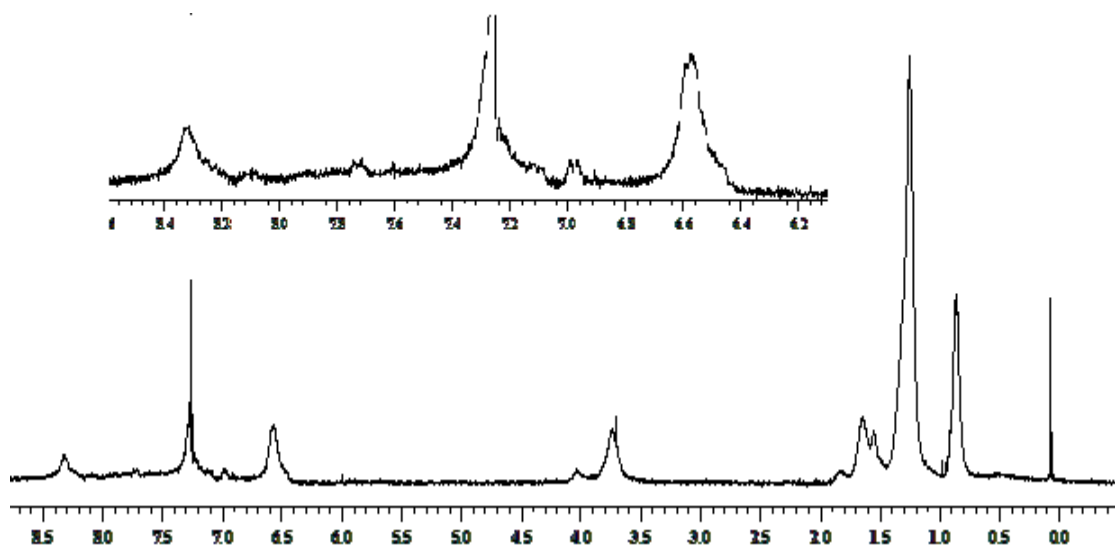


Figure S1. ^1H NMR of Poly(2,3-(4-octyloxyphenyl)quinoxaline-5,8-diyl), $\text{PQ}(\text{C8})\text{Br}_2$.

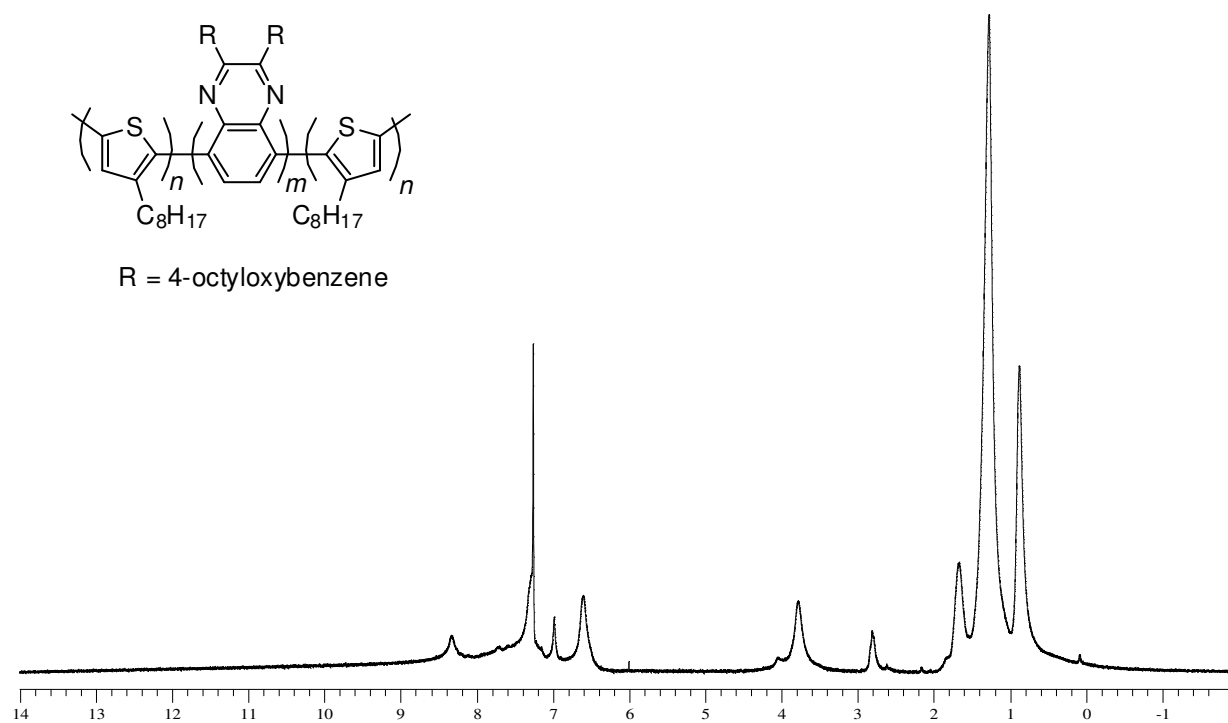


Figure S2. ^1H NMR of P3OT-PQ(C8)-P3OT triblock.

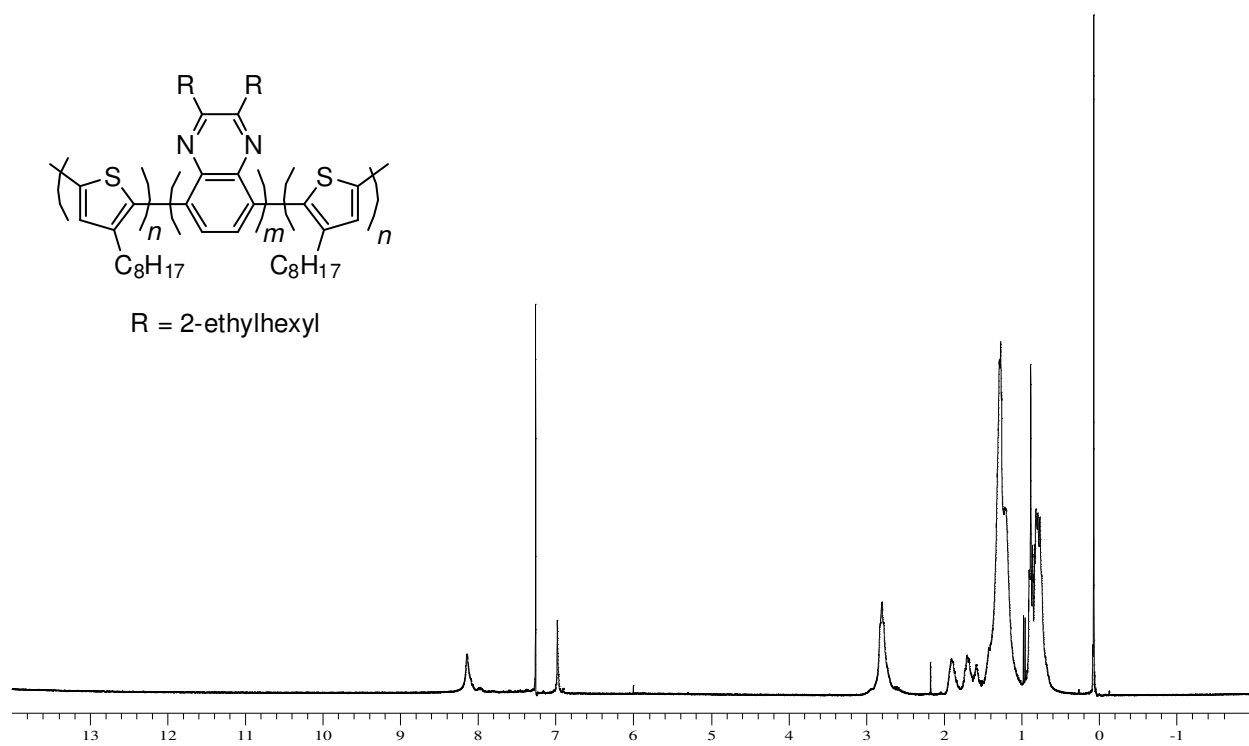


Figure S3. ^1H NMR of P3OT-PQ(EH)-P3OT triblock.

S-3. IR spectra of polyquinoxaline with Br and B(OR)₂ end groups

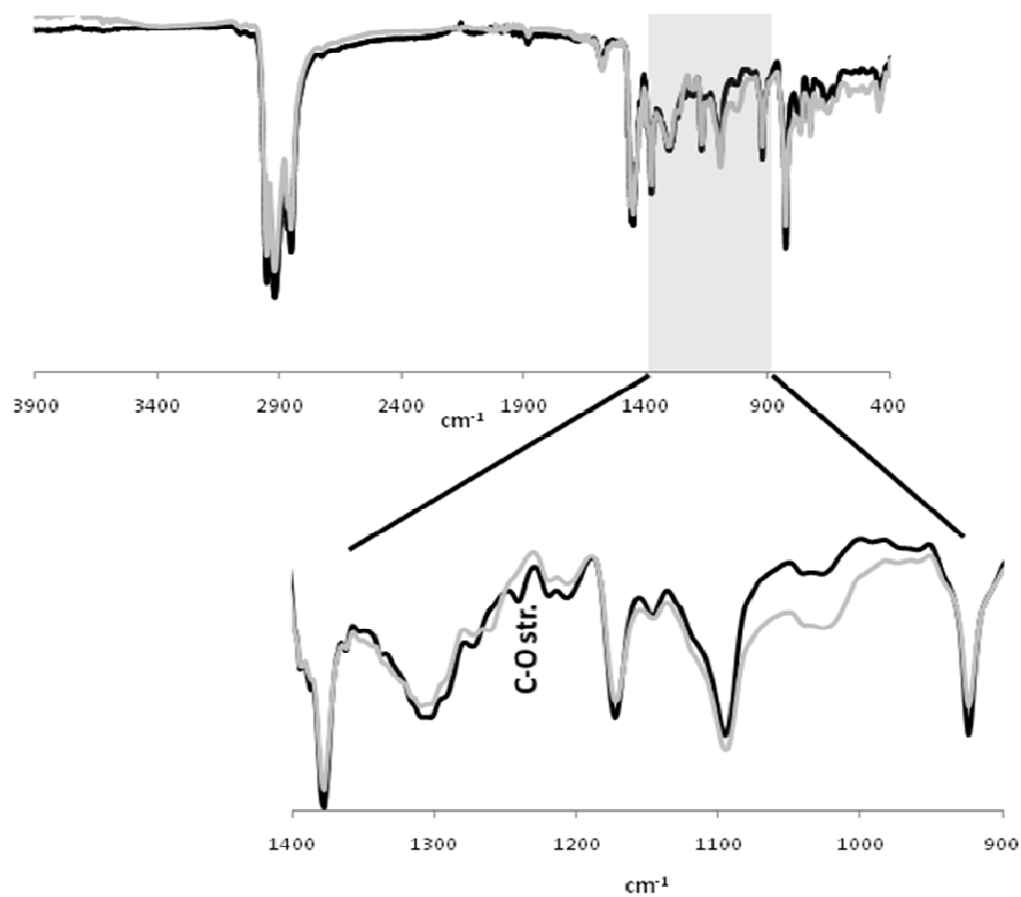


Figure S4. IR spectra of **PQ(EH)Br₂** (gray line) and **PQ(EH)-(BOR)₂** (black line).

S-4. Solid State UV-visible Absorption Spectra

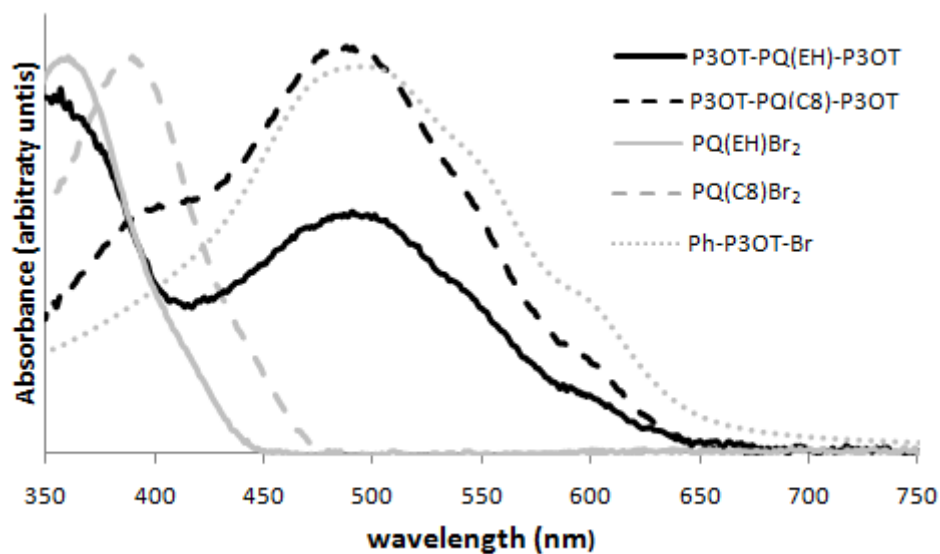


Figure S5. Normalized solid state absorption spectra of **Ph-P3OT-Br** (dotted line), **PQ(C8)Br₂** (gray dashed line) **PQ(EH)Br₂** (gray solid line), **P3OT-PQ(C8)-P3OT** (black dashed line) and **P3OT-PQ(C8)-P3OT** (black solid line) were cast from solutions (10 mg/mL in chloroform) onto quartz slides.

S-5. Wide-Angle X-ray diffraction of homopolymers

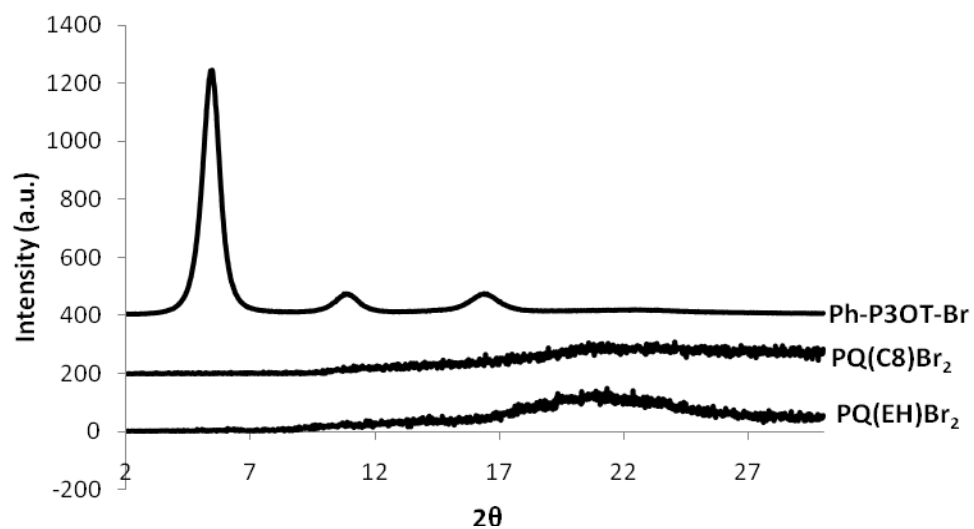


Figure S6. Wide-Angle X-ray diffractogram of films of **Ph-P3OT-Br**, **PQ(C8)Br₂** and **PQ(EH)Br₂** cast onto silicon wafers from xylenes and annealed at 120 °C for 1 hour.