Supporting Information

Synthesis and Characterization of Poly(5,8-Quinoxaline Ethynylene)s

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1. Synthesis and spectral characterization of homolog 3-5b

5,8-Dibromo-2,3-bis(4-(octyloxy)phenyl)quinoxaline, 3b. $NaBH_4$ (9 g, 238 mmol) was added in four equal portions 20 minutes apart to a solution of 4,7-dibromobenzo[c][1,2,5]thiadiazole (6.1 g, 21 mmol) and $CoCl_2 \cdot 6H_2O$ (0.1g, 0.4 mmol) in EtOH (100 mL) under argon and stirred for an additional 30 min. The solvent was removed under reduced pressure and the residue was taken up in H_2O (100 mL), neutralized with 10 % HCl (50 mL) and extracted with CH_2Cl_2 (2 x 200 mL). The organic extracts were combined and the solvent was removed under reduced pressure to afford 3,6-dibromobenzene-1,2-diamine as a colorless solid (3.5 g). The crude solid was used without further purification. A solution of 3,6-dibromobenzene-1,2-diamine (3.5 g, 13 mmol) and 1,2-bis(4-(octyloxy)phenyl)ethane-1,2-dione (5.0 g, 11 mmol) in acetic acid (200 mL) was heated to reflux for 24 h. The solution was cooled to room temperature and poured into H_2O (200 mL). The precipitate was filtered and the solid residue was purified by column chromatography (30:70 v/v CH_2Cl_2:hexanes) to afford **3b** as a yellow solid (4.4 g, 56 %), mp

=81-83 °C . ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 2H, quinioxaline C-H), 7.65 (d, $^{3}J_{HH}$ = 8.7 Hz, 4H, Ph C2-H), 6.87 (d, $^{3}J_{HH}$ = 8.7 Hz, 4H, Ph C3-H), 3.99 (t, $^{3}J_{HH}$ = 6.6 Hz, 4H, -OCH_2-), 1.78-1.82 (m, 4H), 1.28-1.49 (m, 20H), 0.89 (t, $^{3}J_{HH}$ = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.41 (Ph C4), 153.53 (quinoxaline C2 and C3), 138.95 (quinoxaline C1 and C4), 132.44 (quinoxaline C6 and C7), 131.63 (Ph C2), 130.26 (Ph C1), 123.38 (quinoxaline C5 and C8), 114.31 (Ph C3), 68.05 (C-O), 31.79, 29.33, 29.21, 29.16, 26.00, 22.63, 14.09. IR (ATIR): 2912 (Ar C-H str.), 2846, 1600, 1512, 1468, 1377, 1242, 1173 (C-O str.), 985, 821, 717, 656, 540 cm^{-1}. HRMS *calc.* for $C_{36}H_{44}Br_2N_2O_2$ = 694.1770, *obs.* = 694.1767 Δ = 0.4 ppm. Elemental Analysis: Theoretical: C, 62.07%; H, 6.37%; N, 4.02%. Found: C, 61.81%; H, 6.31%; N, 4.21%.

2,3-Bis(4-(octyloxy)phenyl)-5,8-bis((trimethylsilyl)ethynyl)quinoxaline, 4b.

$Pd(PPh_3)Cl_2$ (0.2 g, 0.3 mmol) and CuI (0.06 g, 0.31 mmol) were added to a solution of dibromo-quinoxaline **3b** (2.18 g, 3.1 mmol) in THF (12 mL) and triethylamine (4 mL) and degassed by two freeze-pump-thaw cycles. Trimethylsilylacetylene (0.92 mL, 6.5 mmol) was added to the mixture and the solution was heated at 50 °C for 24 h. The mixture was poured into H_2O (100 mL) and extracted with CH_2Cl_2 (2 x 50 mL). The organic extracts were combined and the solvent was removed under reduced pressure. The residue was purified by column chromotography (30:70 v/v CH_2Cl_2:hexanes) followed by recrystallization from isopropanol to afford the protected quinoxaline monomer **4b** as a yellow solid (1.78 g, 77%): mp = 105-106 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (s, 2H, quinoxaline C-H), 7.70 (d, $^{3}J_{HH}$ = 8.7 Hz, 4H, Ph C2-H), 6.85 (d, $^{3}J_{HH}$ = 8.7 Hz, 4H, Ph C3-H), 3.98 (t, $^{3}J_{HH}$ = 6.6 Hz, 4H, -OCH_2-), 1.75-1.82 (m, 4H), 1.26-1.49 (m, 20H), 0.89 (t, $^{3}J_{HH}$ = 6.6 Hz, 6H), 0.35 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.24 (Ph C4), 152.36 (quinoxaline C2 and C3), 140.68 (quinoxaline C1 and C4), 132.54

(quinoxaline C6 and C7), 131.58 (Ph C2), 131.05, 123.04, 122.20, 114.09 (Ph C3), 103.21, 68.03 (C-O), 31.81, 29.34, 39.22, 26.03, 22.67, 14.10, 0.01. IR (ATIR): 2915 (Ar C-H str.), 2848, 2146, 1602, 1509, 1467, 1374, 1261, 1243 (C-O str.), 1176, 1041, 831, 754, 626, 546.

2,3-Bis(4-(octyloxy)phenyl)-5,8-diethynylquinoxaline, 5b. A solution of tetra-*n*-butylammonium fluoride (1M in THF, 3 mL, 3 mmol) was added to a solution of protected quinoxaline **4b** (1.00g, 1.37 mmol) in THF (11 mL). The solution was stirred at room temperature for 40 min and quenched with H_2O (1 mL). The solvent was removed and H_2O was added (50 mL) and extracted with CH_2Cl_2 (2 x 50 mL). The organic extracts were combined and the solvent was removed under reduced pressure. The residue was purified by column chromatography (50:50 v/v CH_2Cl_2:hexanes) to afford diethynyl-quinoxaline **5b** as a yellow solid (0.68 g, 85%): mp = 94-96 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 2H, quinoxaline C-H), 7.62 (d, $^3J_{HH}$ = 9 Hz, 4H, Ph C2-H), 6.86 (d, $^3J_{HH}$ = 9 Hz, 4H, Ph C3-H), 3.98 (t, $^3J_{HH}$ = 6.6 Hz, 4H, O-CH_2-), 3.61 (s, 2H, C≡C-H), 1.68-1.83 (m, 4H), 1.29-1.46 (m, 20H), 0.88 (t, $^3J_{HH}$ = 6.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.13 (Ph C4), 153.16 (quinoxaline C2 and C3), 140.86 (quinoxaline C1 and C4), 133.10 (quinoxaline C6 and C7), 131.53 (Ph C2), 130.89 (Ph C1), 122.64 (quinoxaline C5 and C8), 114.15 (Ph C3), 84.99 (C≡C-H), 80.10 (C≡C-H), 67.91 (C-O), 31.74, 31.52, 29.29, 29.11, 25.96, 22.58, 14.02. IR (ATIR): 3267 (C≡C-H str.), 2916 (Ar C-H str.), 2848, 2144 (C≡C str.), 1603, 1510, 1467, 1375, 1292, 1257, 1243 (C-O str.), 1174, 1022, 831, 755, 627, 538.

2. Synthesis and spectral characterization of polymers

Poly(5,8-(2,3-bis(4(2-ethylhexyloxy)phenyl)quinoxaline-*alt*-(2,5-didodecyloxy)-1,4-phenylene ethynylene), PQE(EH)-*alt*-PPE(C12). A solution of diethynyl-quinoxaline **5a** (1.2 g, 2.0 mmol) and 1,4-bis(dodecyloxy)-2,5-diiodobenzene (1.3 g, 2.0 mmol) in THF (20 mL) was degassed by two freeze-pump-thaw cycles. Diisopropylamine (5 mL, 35 mmol), CuI (70 mg, 0.37 mmol), and $Pd(PPh_3)_4$ (0.40 g, 0.37 mmol) were added and the solution was heated at 45 °C for 24 h. The solution was poured into methanol (200 mL) and the resulting precipitate was isolated by filteration. The precipitated residue was subjected to sequential extraction with acetone, hexane and chloroform in a Soxhlet extractor. The solvent was removed from the chloroform fraction under reduced pressure afforded the alternating quinoxaline and dialkoxy copolymer **PQE-*alt*-PPE** as a red solid (96 mg, 5%). The remaining polymer was a red solid (1.34 g, 70%), and insoluble in common organic solvents thus was not characterized further. ^{1}H NMR (300 MHz, $CHCl_3$) δ 7.75-7.63 (2H), 7.5-7.4 (4H), 7.41-7.35 (4H) 6.98-6.83 (2H), 3.9-3.88 (8H), 1.38-1.21 (62H), 0.93-0.81 (18H). IR (ATIR): 2910, 2908, 2841 (Ar C-H str.), 1254 (C-O str), 1038 (C-N) 1363 (C-C str.), 1593, 995, 785, 689 cm^{-1}. GPC (THF, UV-vis detector) M_n = 23 kg/mol, PDI = 2.1.

Poly(2,5-didodecyloxy-1,4-phenyene ethynylene), PPE(C12). A solution of 1,4-bis(dodecyloxy)-2,5-diethynylbenzene (0.395 g, 1.01 mmol) and 1,4-bis(dodecyloxy)-2,5-diiodobenzene (0.554 g, 1.01 mmol) in THF (20 mL) was degassed by two freeze-pump-thaw cycles. Diisopropylamine (4.0 mL, 28 mmol), CuI (31 mg, 0.16 mmol), and $Pd(PPh_3)_4$ (0.18 g, 0.16 mmol) were added and the solution was heated to 45 °C for 24 h. The solution was poured

into methanol (200 mL) and the resulting precipitate was isolated by filteration. The precipitated polymer was subjected to sequential extraction with acetone and chloroform in a Soxhlet extractor. The solvent was removed from the chloroform fraction under reduced pressure afforded poly(2,5-didodecyloxy-1,4-phenyene ethynylene), **PPE(C12)**, as an orange solid (0.55 g, 72%). ^{1}H NMR (300 MHz, $CHCl_3$) δ 7.3-7.29 (2H), 7.0-6.9 (2H), 4.13-3.96 (8H), 1.89-1.80 (8H), 1.24 (72H), 0.87 (12H). IR (ATIR): 2954 (Ar C-H str.), 1198 (C-O str), 1375 (C-C str.), 2916, 793, 690 cm^{-1}. GPC (THF, UV-vis detector) M_n = 7 kg/mol, PDI = 2.4. Elemental Analysis: Theoretical: C, 73.74%; H, 10.18%. Found: C, 72.81%, H, 9.93%.

Poly(2,3-bis(4-(2-ethylhexyl)oxyphenyl)quinoxaline-5,8-diyl), PQ(EH). In an argon filled glove-box, $Ni(COD)_2$ (0.71 g, 2.6 mmol) was added to a Schlenk flask containing a solution of dibromide **4a** (1.5 g, 2.2 mmol), 2,2'-bipyridine (0.44 g, 2.8 mmol) and 1,5-cyclooctadiene (1 mL, 8 mmol) in anhydrous *N*,*N*-dimethyformamide (25 mL). The mixture was stirred at 60 °C for 48 h, and then poured into MeOH (100 mL). The solution was filtered and the resulting gray precipitate was dissolved in $CHCl_3$ (50 mL) and the solution was stirred with 10% aqueous HCl (20 mL) for 30 min. The organic layer was separated and stirred with saturated aqueous NaCl (20 mL) for 30 min. The organic layer was separated and the polymer was precipitated by pouring the solution into acetone (200 mL). The solution was filtered and **PQ(EH)** was obtained as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (br s, 2H, quinoxaline C-H), 7.34 (b, 4H, phenyl C-H), 6.59 (b, 4H, phenyl C-H) 3.64 (b, 4H, -OCH_2-), 1.56-1.67 (m, 2H), 1.38-1.24 (m, H), 0.87 (b, 12H). IR (ATIR): 2927, 2856, 1604, 1511, 1467, 1384, 1342, 1294, 1243, 1172, 1027, 977, 831, 736, 665, 592, 540 cm^{-1}. GPC (THF, UV-vis detector) 4.28 kDa, PDI = 1.93.

3. ^{1}H NMR Spectra of 3-5 (a and b) and PQE(EH)

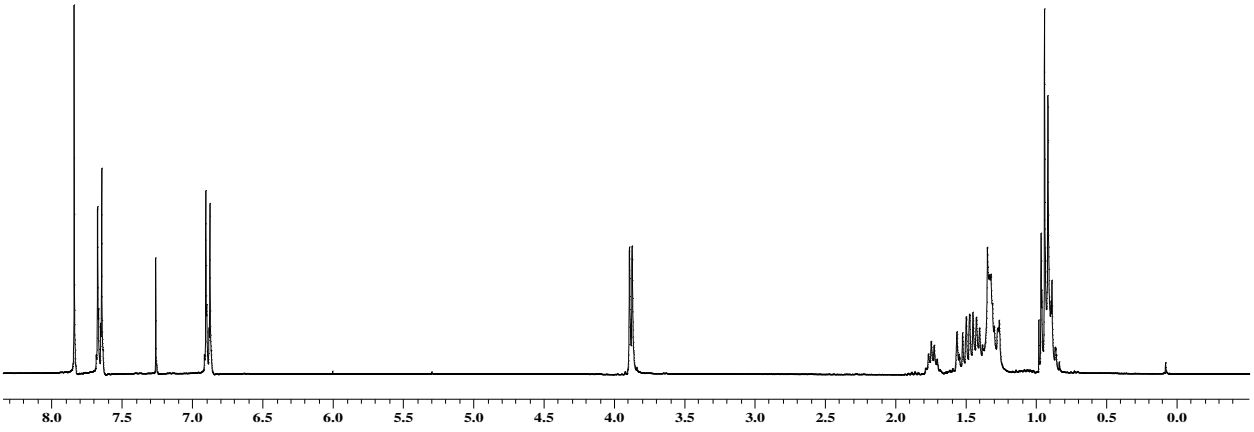

Figure S.1. ^{1}H NMR of 5,8-Dibromo-2,3-bis(4-(2-ethylhexyloxy)phenyl)quinoxaline, **3a**.

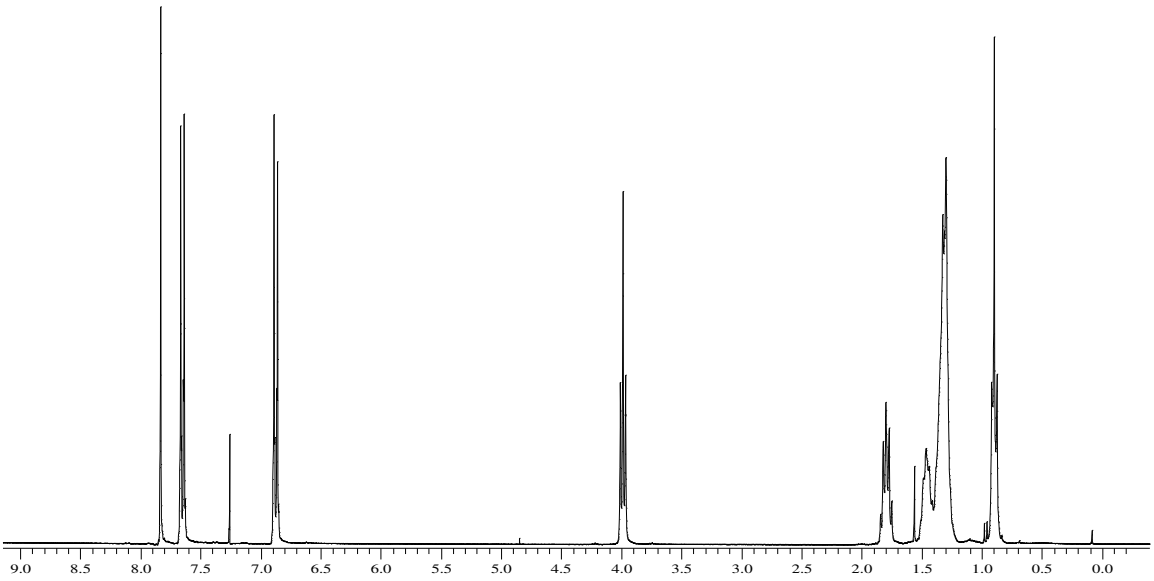

Figure S.2. ^{1}H NMR of 5,8-dibromo-2,3-bis(4-(octyloxy)phenyl)quinoxaline, **3b**.

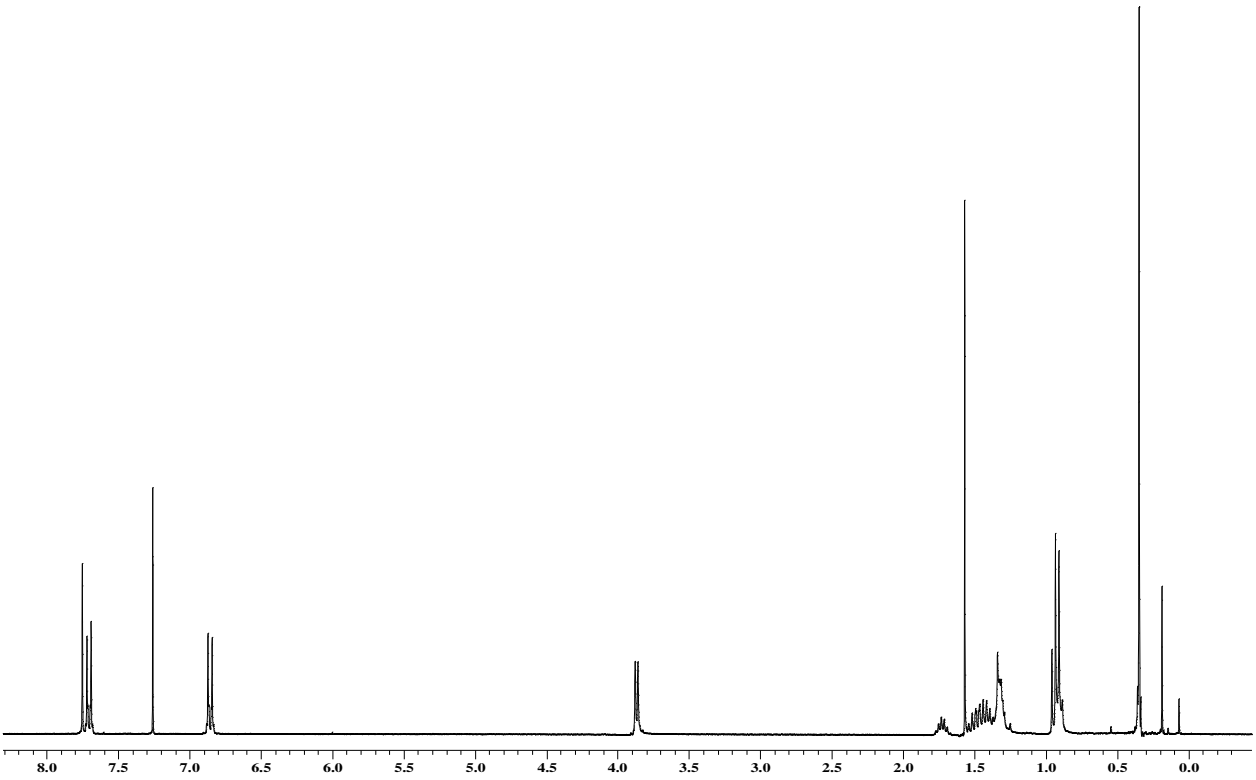

Figure S.3. ^{1}H NMR of 2,3-Bis(4-(2-Ethylhexyloxy)phenyl)-5,8-bis((trimethylsilyl)ethynyl)-quinoxaline, **4a**.

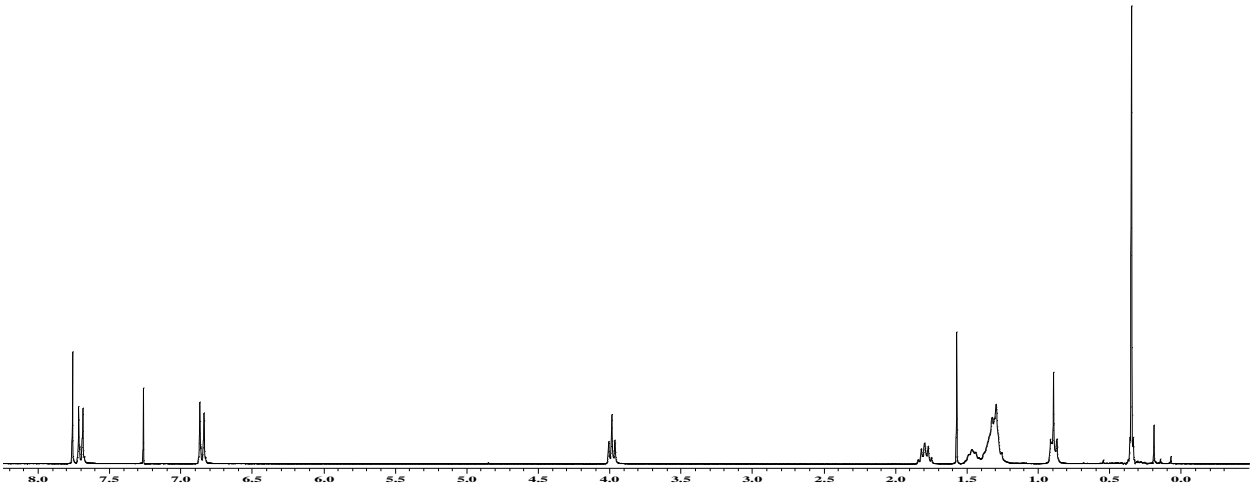

Figure S.4. ^{1}H NMR of 2,3-bis(4-(octyloxy)phenyl)-5,8-bis((trimethylsilyl)ethynyl)quinoxaline, **4b**.

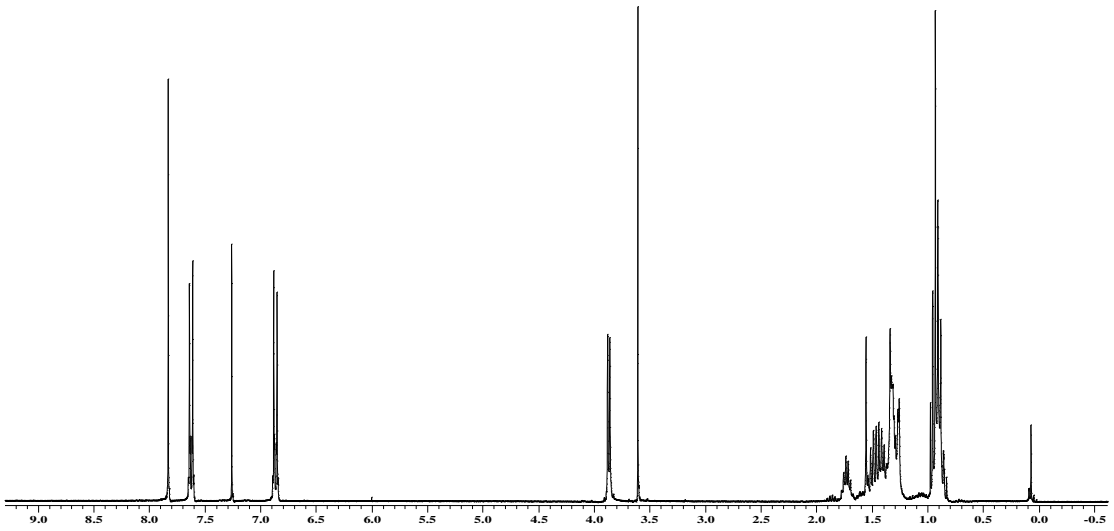

Figure S.5. ^{1}H NMR of 2,3-bis(4-(2-ethylhexyloxy)phenyl)-5,8-diethynylquinoxaline, **5a**.

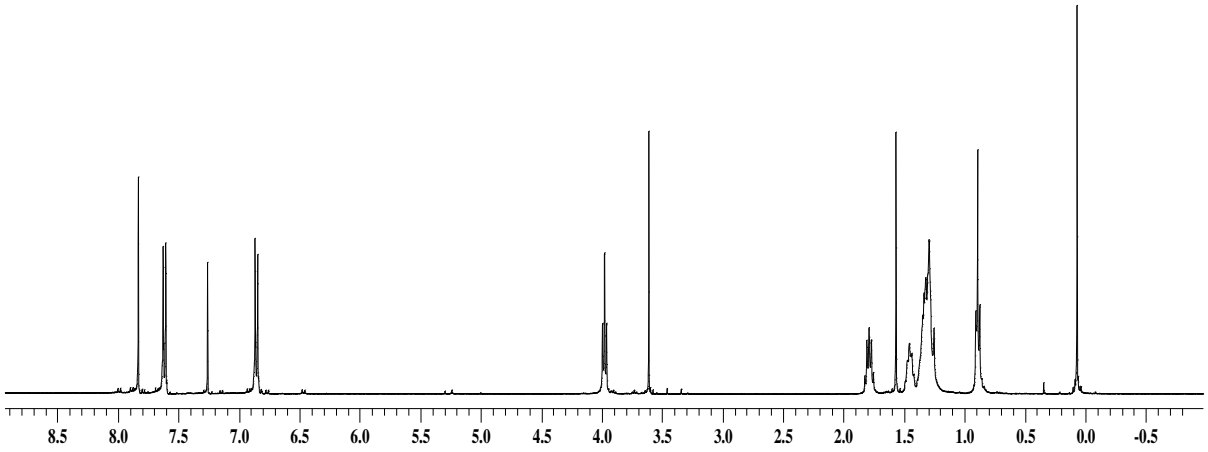

Figure S.6. ^{1}H NMR of 2,3-bis(4-(octyloxy)phenyl)-5,8-diethynylquinoxaline, **5b**.

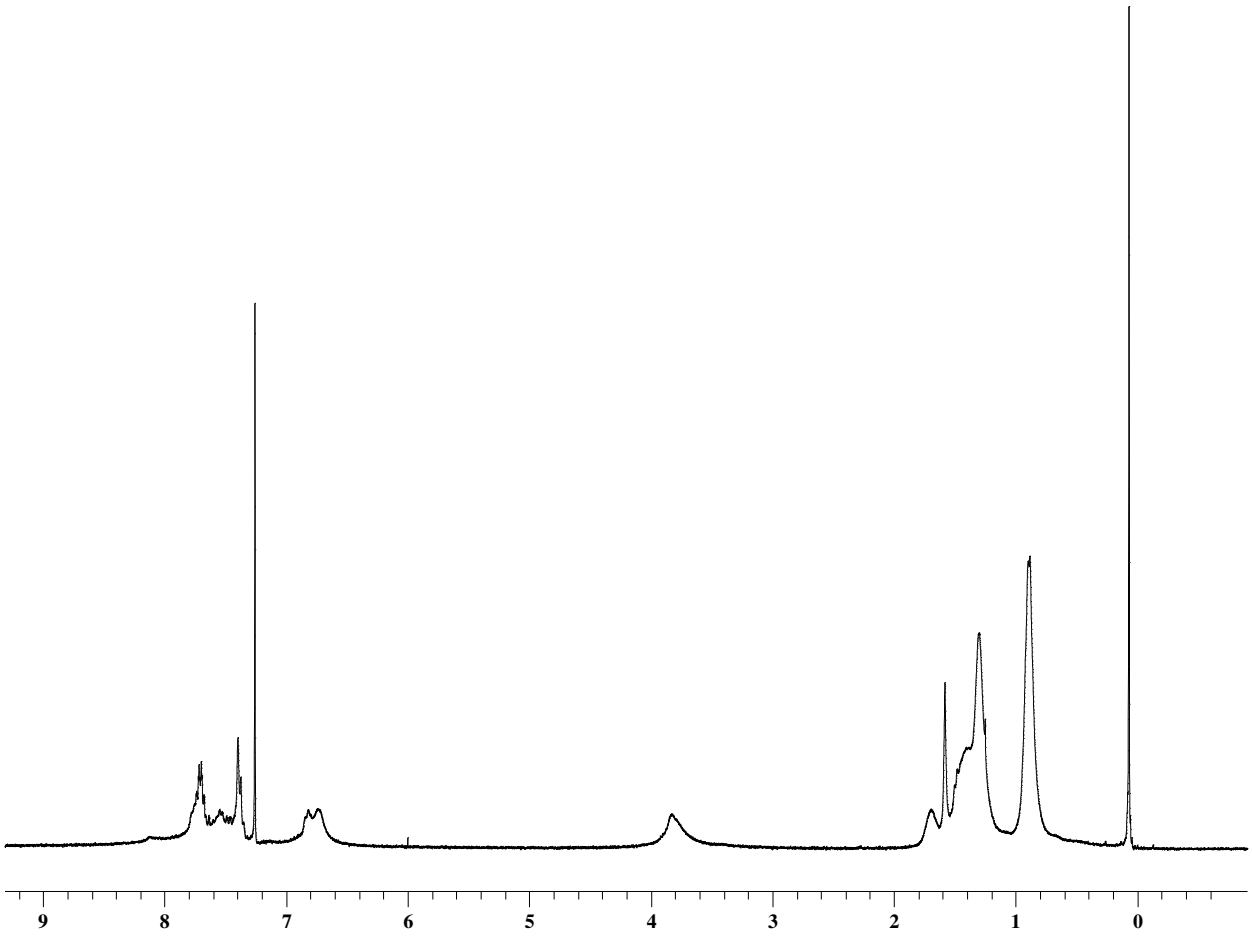

Figure S.7. ^{1}H NMR of poly(5,8-quinoxaline ethynylene), PQE(EH).