Supporting Information

2-Aryl-*2H*-benzotriazoles as building blocks for new low-bandgap poly(arylene-ethynylene)s

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1-(2-Nitrophenyl)-2-phenyldiazene (6a). A solution of aniline (**5a**) (0.857 g, 9.20 mmol) and 1-nitro-2-nitrosobenzene (**4**) (1.40 g, 9.20 mmol) was stirred in acetic acid (200 mL) for 48 h at room temperature. The colour changes from green to red. The solution was poured on ice/water and the resulting solid was collected by filtration and purified by column chromatography on silica gel using dichloromethane as eluent to furnish a dark red crystalline solid (1.60 g, 77%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.90–7.88 (m, 3 H), 7.70–7.63 (m, 2 H), 7.58–7.51 (m, 4 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 152.55, 145.42, 133.23, 132.39, 130.70, 129.36, 124.06, 123.50, 118.48. EI MS *m/z* (M^+) calcd for $C_{12}H_9N_3O_2$: 227.1; found: 227.1. Anal. calcd for $C_{12}H_9N_3O_2$: C, 63.43; H, 3.99; N, 18.49; found: C, 63.18; H, 4.17; N, 18.46.

2-Phenyl-*2H*-benzotriazole (7a). A mixture of dye **6a** (1.2 g, 5.28 mmol), EtOH (20 mL) and 4 N aqueous NaOH (25 mL) was stirred at 80 °C when formamidinesulfinic acid (1.33 g, 12.3 mmol) was

added in portions. After stirring for 30 min at 80 °C, while the colour of the solution turns from deep red to pale yellow, a further portion of formamidinesulfinic acid (0.67 g, 6.2 mmol) was added and stirring was continued for 1 hour. The mixture was poured on ice and the resulting colourless precipitate was collected by filtration and purified by crystallization from ethanol to yield the product as colourless needles (0.80 g, 78%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.37 (d, J = 7.8 Hz, 1 H), 7.94 (dd, J = 6.5 Hz, 1 H), 7.58 (t, J = 7.7 Hz, 1 H), 7.50–7.43 (m, 3 H). ^{13}C NMR (100MHz, CD_2Cl_2): δ 145.08, 140.45, 129.50, 129.01, 127.22, 120.55, 118.36. IR (cm^{-1}) ν 3066.9, 1594.2, 1564.0, 1487.5, 1460.5, 1445.6, 1413.0, 1339.7, 1318.5, 1286.7, 1221.4, 1145.8, 1071.4, 1021.2, 963.1, 918.0, 809.8, 759.5, 742.7, 683.6, 665.5, 628.3, 611.8, 557.2, 544.3, 501.1, 438.0. EI MS *m/z* (M^+) calcd for $C_{12}H_9N_3$: 195.1; found: 195.2. Anal. calcd for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.52; found: C, 73.68; H, 4.67; N, 21.36.

4,7-Dibromo-2-phenyl-*2H*-benzotriazole (8a). To a solution of **7a** (1.12 mg, 5.74 mmol) in HBr/acetic acid (45 % w/v, 30 mL) at a temperature of 150 °C, bromine (7.2 mL, 140 mmol) was added dropwise over a period of 5 h. After stirring for another 2 h, the mixture was poured on a mixture of ice and 10% Na_2SO_3. The resulting colourless solid was collected by filtration and washed with water and methanol. Purification by crystallization from ethanol (80 mL) gave a colourless solid (1.11 g, 55%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.40–8.38 (m, 2 H), 7.64–7.54 (m, 3 H), 7.51 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.42, 139.87, 130.49, 129.98, 129.64, 120.90, 110.35. IR (cm^{-1}) ν 3073.0, 1592.1, 1494.0, 1463.1, 1417.4, 1343.8, 1318.2, 1308.1, 1282.9, 1233.1, 1191.8, 1068.0, 1024.9, 971.9, 952.6, 934.8, 910.9, 820.7, 751.5, 717.7, 686.0, 669.5, 601.3, 573.1, 558.4, 491.9, 412.0. EI MS *m/z* (M^+) calcd for $C_{12}H_7Br_2N_3$: 352.9; found: 352.9. Anal. calcd for $C_{12}H_7Br_2N_3$: C, 40.83; H, 2.00; N, 11.90; found: C, 41.13; H, 2.12; N, 12.03.

2-Phenyl-*2H*-benzotriazole-*b*-alkyne-*b*-2,5-bis(2-ethylhexyloxy)benzene Copolymer (11a). Experimental procedure is the same as described for the synthesis of polymer **11b** in the main text. The polymer was received as a dark orange solid (210 mg, 88%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52 (bs, 2 H), 7.71 – 7.43 (bm, 5 H), 7.22 (s, 2 H), 4.15 – 3.91 (bm, 4 H), 1.97 – 1.85 (bm, 2 H), 1.74 – 1.24 (m, 16 H), 1.04 – 0.93 (m, 6 H), 0.89 – 0.80 (m, 6 H). IR (cm^{-1}) v 2958.0, 2920.1, 2851.1, 1493.7, 1462.5, 1415.7, 1377.5, 1259.2, 1218.3, 1088.6, 1015.4, 862.0, 796.4, 757.9, 720.9, 675.3. GPC (THF, polystyrene): P_n = 210, M_w/M_n = 4.1.