Versatile one-step introduction of multiple hydrogen-bonding sites onto extended π-conjugated systems

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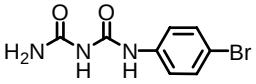
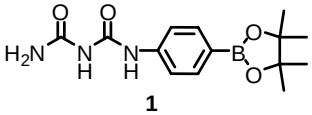
Procedures for the synthesis of **1 – 4**

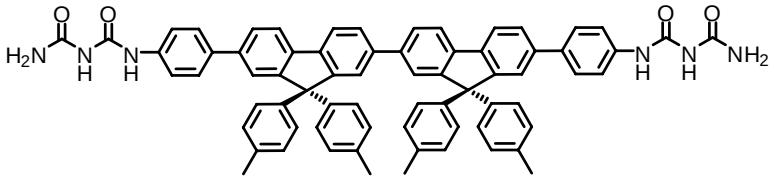


Synthesis of 4-bromo-benzenebiuret: A mixture of 4-bromoaniline (5.16 g, 30 mmol), 1-nitrobiuret (5.8 g, 39 mmol), H_2O (60 mL) was heated at reflux for 3 hours. The precipitate was filtered and washed with water, MeOH and ether. (white solid 5.6 g, 72%). mp. 218 ^oC (DSC); IR (neat) ν 3326, 3246, 3176, 1685, 1596, 1541, 1490, 1394, 1304, 1266, 1218, 1073, 1007, 819, 745, 659 cm^{-1}; ^1H NMR (d_6-DMSO, 300 MHz) δ 10.07 (s, 2H), 8.91 (s, 2H), 7.44 (dd, 4H), 6.88 (bs, 2H); ^{13}C NMR (d_6-DMSO, 75.5 MHz) δ 155.3, 151.9, 137.5, 131.6, 121.0, 114.5; MS (m/z, FAB^+) 257 (40); HRMS (m/z, FAB^+) Calcd for $C_8H_8BrN_3O_2$ 256.9800, found 257.9881.



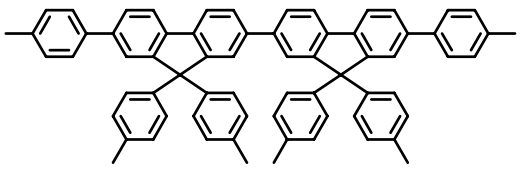
1

Synthesis of 4-pinacolatoboronic ester-benzenebiuret (1): A mixture of 4-bromobenzenebiuret (1.03 g, 4 mmol), 4,4,5,5-tetramethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolane (1.52 g, 6 mmol), KOAc (1.16 g, 11.8 mmol), $Pd(dppf)Cl_2$ (0.15 g, 0.2 mmol) in THF (30 mL) was refluxed for two days. The reaction was quenched by adding water and extracted with THF. The combined organic solution was washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation to provide the crude product. The desired product was isolated by recrystallization from ether/hexane to afford pale white solid (0.7 g, 60%). mp. 255-258 ^oC; IR (neat) ν 3307, 2977, 1697, 1588, 1539, 1398, 1360, 1313, 1272, 1200, 1143, 1092, 1018, 962, 858, 732, 669, 654, 589 cm^{-1}; ^1H NMR (d_6-DMSO, 300 MHz) δ 10.13 (s, 1H), 8.94 (s, 1H), 7.61 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 7.9 Hz, 2H), 6.98-6.80 (bs, 2H), 1.28 (s, 12H); ^{13}C NMR (d_6-DMSO, 75.5 MHz) δ 155.4, 151.8, 141.1, 135.4, 122.5, 117.9, 83.4, 24.6; MS (m/z, FAB^+) 305 (75); HRMS (m/z, FAB^+) Calcd for $C_{14}H_{21}BN_3O_4$ 306.1625, found ($M + H^+$) 306.1624.



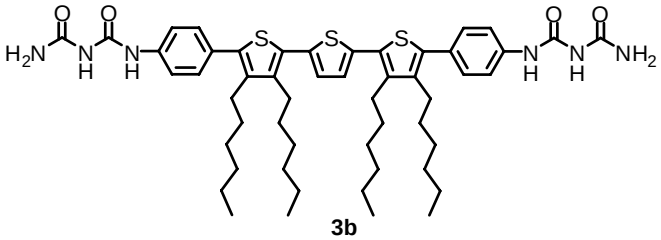
2b

Synthesis of compound 2b: A mixture of $Pd(PPh_3)_4$ (0.04 g, 0.035 mmol), K_2CO_3 (0.65 g, 4.7 mmol) 2-bromo-7-[2-bromo-9,9-di(p-tolyl)fluoren-7-yl]-9,9-di(p-tolyl)fluorene (0.66 g, 0 78 mmol), 4-pinacolatoboronic ester-benzenebiuret (**1**) (0.59 g, 1.9 mmol) in degassed THF (65 mL) and water (15 mL) re was refluxed for two days. The reaction was quenched by adding water and extracted with THF. The combined organic solution was washed and dried over over sodium sulfate. Purification was performed with silica-gel column chromatography, eluting with 1:1 THF/CH_2Cl_2. (pale white solid 0.68 g, 85%). mp. (nd) (DSC); IR (neat) ν 3392, 1716, 1685, 1697, 1541, 1508, 1463, 1397, 1327, 1204, 811 cm^{-1}; ^1H NMR (d_6-DMSO, 300 MHz) δ 10.06 (s, 2H), 8.88 (s, 2H), 7.99 (d, J = 7.14 Hz, 4H), 7.68-7.50 (m, 16H), 7.09 (bs, 20H), 2.22 (s, 12H); ^{13}C NMR (d_6-DMSO, 75.5 MHz) δ 155.4, 152.1, 152.0, 151.9, 142.5, 139.3, 138.6, 138.0, 135.8, 134.5, 129.0, 127.5, 127.1, 123.6, 123.4, 121.1, 119.4, 64.5, 20.4; MS (m/z, FAB^+) 1044 (5); HRMS (m/z, FAB^+) Calcd for $C_{70}H_{56}N_6O_4$ 1044.4363, found 1044.4354.



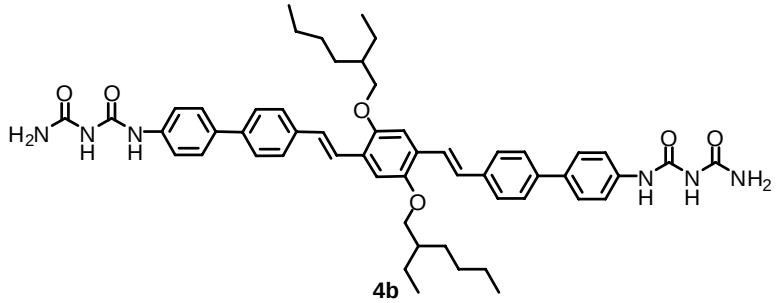
2c

Synthesis of compound 2c: A mixture of 4-methylphenylboronic acid (0.15 g, 1.1 mmol), 2-bromo-7-[2-bromo-9,9-di(p-tolyl)fluoren-7-yl]-9,9-di(p-tolyl)fluorene (0.34 g, 0.4 mmol), K_2CO_3 (0.3 g, 2.2 mmol), $Pd(PPh_3)_4$ (0.02 g, 0.02 mmol) in THF (30 mL) and water (10 mL) was refluxed for two days. The reaction was quenched by adding water and extracted with $CHCl_3$. The organic solution was washed with brine and dried over sodium sulfate. Purification was performed with silica-gel column chromatography, eluting with 1:4 $CHCl_3$/Hex (white solid 0.24 g, 69%). mp. 211 ^oC (DSC); IR (neat) ν 3015, 2913, 1505, 1495, 1454, 1245, 1185, 1017, 811, 729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.81-7.76 (m, 4H), 7.59-7.54 (m, 8H), 7.46 (d, J = 7.89 Hz, 4H), 7.23-7.07 (m, 12H), 7.04 (d, J = 8.28 Hz, 8H), 2.38 (s, 6H), 2.30 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.0, 140.6, 139.0, 138.7, 138.5, 136.9, 136.2, 129.4, 129.0, 128.1, 127.0, 126.6, 126.4, 124.7, 120.4, 120.2, 65.0, 21.1, 20.9; MS (m/z, FAB^+) 870 (100); HRMS (m/z, FAB^+) Calcd for $C_{68}H_{54}$ 870.4226, found 870.4213.



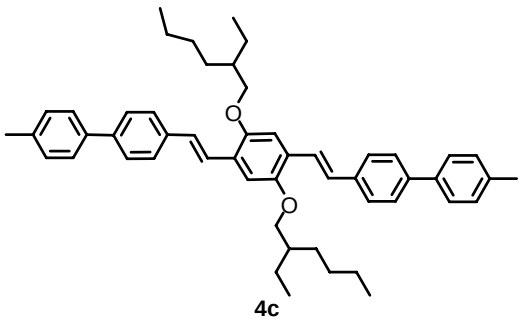
3b

Synthesis of compound 3b: A mixture of $Pd(PPh_3)_4$ (0.04 g, 0.035 mmol), K_2CO_3 (0.6 g, 4.3 mmol), 2-bromo-5-(5-(5-bromo-3,4-dihexylthiophen-2-yl)thiophen-2-yl)-3,4-dihexylthiophene (0.45 g, 0.6 mmol), 4-pinacolatoboronic ester-benzenebiuret (**1**) (0.47 g, 1.54 mmol) in degassed THF (50 mL) and water (10 mL) was refluxed for two days. The reaction was worked up by adding water and extracted with THF, and the organic solution was washed with brine and dried over sodium sulfate. Purification was performed with silica-gel column chromatography, eluting with 2:3 THF/CH_2Cl_2. (yellow solid 0.31 g, 73%). mp. (nd) (DSC); IR (neat) ν 3271, 2954, 2927, 2856, 1691, 1587, 1535, 1500, 1465, 1407, 1313, 1291, 1199, 1116, 1061, 983, 831 cm^{-1}; ^1H NMR (d_6-Acetone, 300 MHz) δ 10.30 (s, 2H), 8.47 (s, 2H), 7.65 (d, J = 8.67 Hz 4H), 7.44 (m, J = 8.67 Hz 4H), 7.18(s, 2H), 6.46 (bs, 4H), 2.83-2.80 (m, 4H), 2.68-2.63 (m, 4H), 1.51-1.41 (m, 10H), 1.36-1.26 (m, 22H), 0.92-0.83 (m, 12H); ^{13}C NMR (d_6-Acetone, 75.5 MHz) δ 156.4, 152.4, 140.4, 139.7, 138.9, 137.7, 136.5, 130.2, 129.9, 129.7, 126.5, 119.8, 32.0, 31.8,31.3, 27.8, 23.0, 22.9, 14.1, 14.0; MS (m/z, FAB^+) 938 (95); HRMS (m/z, FAB^+) Calcd for $C_{52}H_{71}N_6O_4S_3$ 939.4699, found ($M + H^+$) 939.4699.



4b

Synthesis of compound 4b: A mixture of $Pd(PPh_3)_4$ (0.017 g, 0.015 mmol), K_2CO_3 (0.25 g, 1.8 mmol), 1,4-bis(2-ethylhexyloxy)-2,5-bis(4-bromostyryl)benzene (0.21 g, 0.3 mmol), 4-pinacolatoboronic ester-benzenebiuret (**1**) (0.25 g, 0.82 mmol) in degassed THF (65 mL) and water (15 mL) was refluxed for two days. The reaction was worked up by adding water and extracted with THF, and the organic solution was washed with brine and dried over sodium sulfate. Purification was performed with silica-gel column chromatography, eluting with 3:2 THF/$CHCl_3$. (yellow solid 0.21 g, 78%). mp. (nd) (DSC); IR (neat) ν 2988, 2857, 1701, 1596, 1564, 1503, 1421, 1383, 1316, 1238, 1200, 1044, 963, 843, 810, 751 cm^{-1}; ^1H NMR (d_6-DMSO, 300 MHz) δ 10.08 (s, 2H), 8.92 (s, 2H), 7.71-7.67 (m, 8H), 7.62-7.53 (m, 8H), 7.45 (d, J = 6.39 Hz 4H), 7.36 (s, 2H), 6.85 (bs, 4H), 4.01 (d, J = 4.92 Hz 4H), 1.80 (s, 2H), 1.53-1.23 (m, 16H), 1.00-0.89 (m, 12H); ^{13}C NMR (d_6-DMSO, 50 MHz) δ 150.6, 147.7, 134.7, 126.4, 126.2, 126.1, 126.0, 125.0, 121.9, 119.2, 118.0, 114.0, 111.0, 71.6, 30.0, 28.2, 23.4, 21.8, 13.0,10.5; MS (m/z, FAB^+) 892 (6); HRMS (m/z, FAB^+) Calcd for $C_{54}H_{64}N_6O_6$ 892.4887, found 892.4878.



4c

Synthesis of compound 4c: A mixture of 4-methylphenylboronic acid (0.15 g, 1.1 mmol), 1,4-bis(2-ethylhexyloxy)-2,5-bis(4-bromostyryl)benzene (0.348 g, 0.5 mmol), K_2CO_3 (0.4 g, 2.9 mmol), $Pd(PPh_3)_4$ (0.03 g, 0.026 mmol) in THF (30 mL) and water 10 (mL) was refluxed for two days. The reaction was quenched by adding water and extracted with CH_2Cl_2. The organic solution was washed with brine and dried over sodium sulfate. Purification was performed with silica-gel column chromatography, eluting with 1:3.5 CH_2Cl_2/Hex to give the desired product. (bright green solid 0.31 g, 85%). mp. 175 ^oC (DSC); IR (neat) ν 3376, 2951, 2907, 2866, 1713, 1644, 1501, 1463, 1422, 1334, 1178, 1026, 966, 805 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 8H), 7.58-7.53 (m, 6H), 7.28-7.17 (m, 8H), 3.99 (d, J = 5.25 Hz, 4H), 2.42 (s, 6H), 1.88-1.84 (m, 2H), 1.64-1.39 (m, 16H), 1.05-0.92 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.3, 140.0, 137.9, 137.1, 136.8, 129.5, 128.2, 127.1, 126.8, 126.7, 123.4, 110.3,71.8, 39.8, 31.0, 29.3, 24.3, 23.1, 21.1, 14.1, 11.3; MS (m/z, FAB^+) 718 (100); HRMS (m/z, FAB^+) Calcd for $C_{52}H_{62}O_2$ 718.4750, found 718.4752.

Table. S-1 Absorption and emission maxima of **2b**, **2c, 4b,** and **4c** in THF solution.

	Abs (nm)	Emission (nm)
2b	359	400, 423, 451
2c	352	391, 413, 440
4b	340, 411	464, 491, 537
4c	340, 410	459, 485, 530

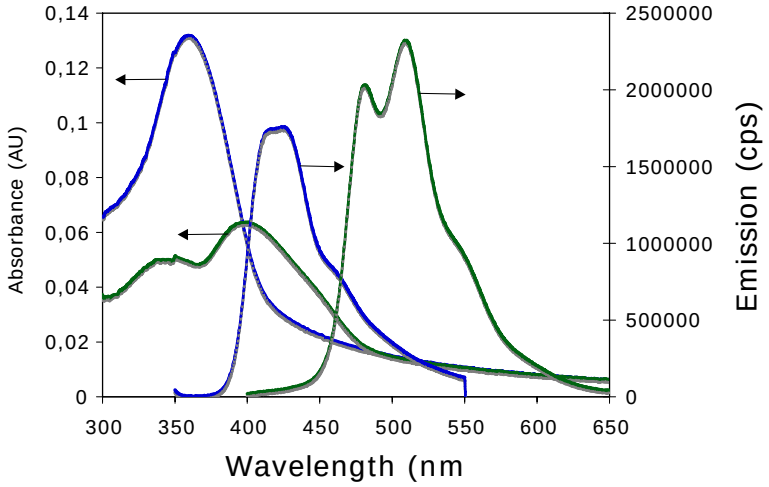
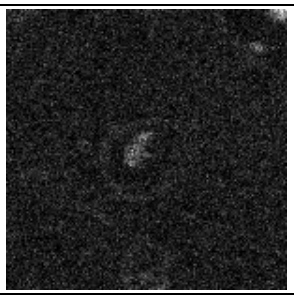
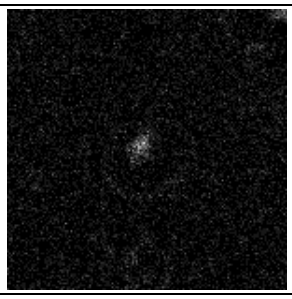
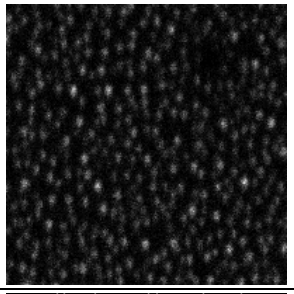
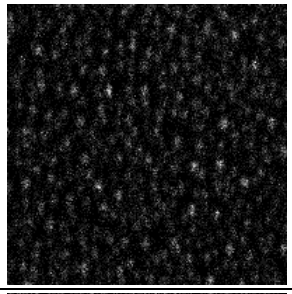
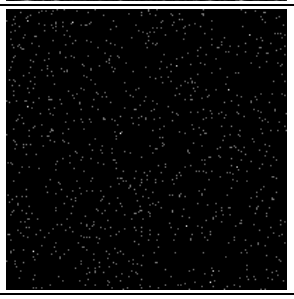
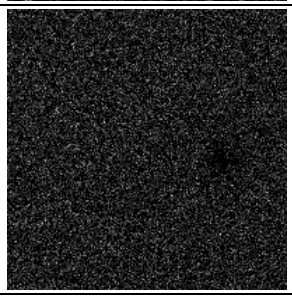


Fig. S-1 Absorption and emission maxima of films of **2b** (blue lines) and **4b** (green lines) deposited from THF solution onto glass substrates.

Table S-2 Confocal fluorescence images (10 x 10 μm) of films of **2b**, **2c**, **4b**, and **4c**.

	400 nm < λ ex < 450 nm	502.5 nm < λ ex < 537.5 nm
2b		
2c		
4b		
4c