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Preparation of conjugated 6,6'-bibenzo[*b*]selenophenes

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^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 Mercury spectrometer at 400 MHz and 100.3 MHz, respectively, at 303K in $CDCl_3$/TMS or DMSO-d_6 solution. The ^{1}H chemical shifts are given relative to TMS, ^{13}C – relative to chloroform or DMSO. The melting points were determined on a 'Digital melting point analyser' (Fisher), the results are given without correction. Diffraction data were collected on a Nonius KappaCCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystal structures were solved by direct methods and refined by full-matrix least squares.

4,4'-Dialkynylbiphenyls 1a-c: A vial charged with palladium(II) chloride (30 mg, 0.16 mmol), triphenylphosphine (80 mg, 0.32 mmol) and copper(I) iodide (60 mg, 0.32 mmol) in 4 ml of dry DMF was flushed with Ar for 15 min at 40 ^{o}C. Then solution of **1** (0.5 g, 1.6 mmol) and terminal alkyne (6.41 mmol) in dry DMF (5 ml), and diisopropylamine (2 ml) were added to the mixture. After 20 h of heating at 75 ^{o}C and usual workup the crude product was purified by flash chromatography on silica gel using the mixture petroleum ether – ethyl acetate as eluent (**1a**,**c**) or purified by crystallization from dichloromethane (**1b**).

4,4'-(Dihept-1-yn-1-yl)-1,1'-biphenyl (1a): yellowish solid, mp 72-74 ^{o}C, yield: 93%. GC-MS: *m*/*z* 342.2 [M^{+}]. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.93 (t, 6H, *J* = 7.2 Hz, C<u>H</u>$_3$), 1.32-1.47 (m, 8H, C<u>H</u>$_2$), 1.54-1.66 (m, 4H, C<u>H</u>$_2$), 2.42 (t, 4H, *J* = 7.0 Hz, C_2C<u>H</u>$_2$), 7.44-7.46 (m, 4H, 2,2',6,6'-C<u>H</u>), 7.49-7.51 (m, 4H, 3,3',5,5'-C<u>H</u>). ^{13}C NMR ($CDCl_3$, 100.3 MHz), δ, ppm: 13.6, 19.1, 21.9, 28.1, 30.8, 80.0, 91.0, 122.9, 126.3, 131.6, 139.1. Found (%): C, 90.94; H, 8.80. Calc. for $C_{26}H_{30}$ (%): C, 91.17; H, 8.83.

4,4'-(1,1'-Biphenyl-4,4'-diyl)bis(2-methylbut-3-yn-2-ol) (1b): white solid, mp > 200 ^{o}C, yield: 96%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 1.63 (s, 12H, C<u>H</u>$_3$), 2.07 (s, 2H, O<u>H</u>), 7.46–7.48 (m, 4H, 2,6;2',6-'C<u>H</u>), 7.51–7.53 (m, 4H, 3,5;3,'5-C<u>H</u>). ^{13}C NMR ($CDCl_3$, 100.3 MHz), δ, ppm: 1.93; 31.4; 65.6; 81.9; 94.7; 122.0; 126.7; 132.1; 139.9. Found (%): C, 83.01; H, 10.14. Calc. for $C_{22}H_{22}O_2$ (%): C, 82.99; H, 10.05.

4,4'-Bis[2-(1-hydroxycyclohexyl)ethynyl]biphenyl (1c): white solid, mp 185-188 ^{o}C, yield: 58%. ^{1}H NMR (DMSO-d_6, 400 MHz), δ, ppm: 1.16–1.27 (m, 2H, 2,5-C<u>H</u>-cyclohexanol); 1.48-1.66 (m, 14H, C<u>H</u>$_2$), 1.83-1.87 (m, 4H, C<u>H</u>$_2$), 5.44 (s, 2H, OH), 7.46 - 7.49 (m, 4H, 2,2',6,6'-C<u>H</u>), 7.68–7.70 (m, 4H, 3,3',5,5'-C<u>H</u>). ^{13}C NMR (DMSO-d_6, 100.3 MHz), δ, ppm: 22.7, 24.8, 66.9, 82.3, 95.9, 122.0, 126.6, 131.7, 138.5. Found (%): C, 84.21; H, 7.65. Calc. for $C_{28}H_{30}O_2$ (%): C, 84.38; H, 7.59.

General procedure for the preparation of 3,3'-dibromobibenzo[*b*]selenophenes 2a-c: To the solution of selenium dioxide (3 eq) in HBr (2.5 equiv.), 4,4'-dialkynylbiphenyl **1a-c** and cyclohexene (3 equiv.) in dioxane were added and the mixture was stirred at room temperature for 48 h. After the consumption of substrate **1a-c** (TLC), water (50 ml) was added and mixture was extracted with ethyl acetate (100 ml). The organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated and the residue was purified by flash chromatography on silica gel using the mixture petroleum ether – ethyl acetate (**2a**) or methylene chloride – ethyl acetate (**2b**,**c**) as eluent.

3,3'-Dibromo-2,2'-dipentyl-6,6'-bibenzo[*b*]selenophene (2a): yellow solid, mp 115-117 ^{o}C, yield: 45%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.93 (t, 6H, *J* = 6.8 Hz, C<u>H</u>$_3$), 1.35-1.48 (m, 8H, C<u>H</u>$_2$), 1.72-1.79 (m, 4H, C<u>H</u>$_2$), 3.01 (t, 4H, *J* = 7.6 Hz, C<u>H</u>$_2$), 7.68 (dd, 2H, *J* = 1.5 Hz, *J* = 8.4 Hz, 5,5'-C<u>H</u>), 7.85 (d, 2H, *J* = 8.4 Hz, 4,4'-C<u>H</u>),8,05 (d, 2H, *J* = 1.5 Hz, 7,7'-C<u>H</u>). ^{13}C NMR ($CDCl_3$, 100.3 MHz), δ, ppm: 13.6, 22.1, 30.5, 30.9, 31.9, 106.8, 123.5, 124.4, 124.8, 137.3, 138.1, 139.2, 144.5. Found (%): C, 47.09; H, 4.20. Calc. for $C_{26}H_{28}Br_2Se_2$ (%): C, 47.44; H, 4.29.

3,3'-Dibromo-2,2'-bis(2-hydroxyprop-2-yl)-6,6'-bibenzo[*b*]selenophene (2b): yellowish solid, mp 164-167 ^{o}C, yield: 48%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 1.86 (s, 12 H, C<u>H</u>$_3$), 2.62 (s, 2H, O<u>H</u>), 7.71 (dd, 2H, *J* = 1.5 Hz, *J* = 8.4 Hz, 5,5'-C<u>H</u>), 7.89 (d, 2H, *J* = 8.4 Hz, 4,4'-C<u>H</u>), 8.10 (d, 2H, *J* = 1.5 Hz, 7,7'-C<u>H</u>). ^{13}C NMR ($CDCl_3$, 100.3 MHz), δ, ppm.: 29.2, 74.4, 101.4, 123.6, 124.7, 125.2, 137.7, 141.2, 154.0. Found (%): C, 41.50; H, 3.25. Calc. for $C_{22}H_{20}Br_2O_2Se_2$ (%): C, 41.67; H, 3.18.

3,3'-Dibromo-2,2'-bis(1-hydroxycyclohexyl)-6,6'-bibenzo[*b*]selenophene (2c): white solid, mp 168-170 ^{o}C, yield 40%. ^{1}H NMR (DMSO-d_6, 400 MHz), δ, ppm: 1.27 – 1.33 (m, 2H, 2,5-C<u>H</u>-cyclohexanol), 1.58-1.71 (m, 14H, C<u>H</u>$_2$), 2.37-2.45 (m, 4H, C<u>H</u>$_2$), 6.26 (s, 2H, O<u>H</u>), 7.79 (d, 2H, *J* = 8.4 Hz, 4,4'-C<u>H</u>), 7.83 (dd, 2H, *J* = 1.5 Hz, *J* = 8.4 Hz, 5,5'-C<u>H</u>),

8.44 (d, 2H, *J* = 1.5 Hz, 7,7'-C<u>H</u>). ^{13}C NMR (DMSO-d_6, 100.3 MHz), δ, ppm: 21.1, 24.6, 34.2, 73.6, 98.8, 123.6, 124.0, 124.3, 136.1, 137.5, 141.1, 159.3. Found (%): C, 46.84; H, 4.08. Calc. for $C_{28}H_{28}Br_2O_2Se_2$ (%): C, 47.09; H, 3.95.

2,2'-bis(2-Hydroxyprop-2yl)-6,6'-bibenzo[*b*]selenophene (**3**): A vial charged with **2b** (0.2 g, 0.32 mmol), *tert*-octylamine (0.95 mmol), copper (2 mg, 0.03 mmol), copper (I) iodide (6 mg, 0.03 mmol) and potassium phosphate (0.26 g, 1.26 mmol) in 5 ml of 2-dimethylaminoethanole was flushed with Ar for 10 min. After 72 h of heating at 100 ^{o}C the mixture was cooled to room temperature and poured into a beaker with ethyl acetate. Then aqueous ammonium chloride was added and mixture was stirring for 10 minutes. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated and the residue was purified by flash chromatography on silica gel using the mixture dichloromethane – ethyl acetate as eluent. mp > 200 ^{o}C, yield 80%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 1.73 (s, 12H, C<u>H</u>$_3$), 7.32 (s, 2H, 3,3'-C<u>H</u>), 7.61 (dd, 2H, *J* = 1.5 Hz, *J* = 8.4 Hz, 5,5'-C<u>H</u>), 7.74 (d, 2H, *J* = 8.4 Hz, 4,4'-C<u>H</u>), 8.11 (d, 2H, *J* = 1.5 Hz, 7,7'-C<u>H</u>). ^{13}C NMR ($CDCl_3$, 100.3 MHz), δ, ppm: 25.3, 32.1, 73.0, 121.1, 123.9, 124.2, 125.2, 137.1, 141.3, 141.5, 160.5. Found (%): C, 55.06; H, 4.74. Calc. for $C_{22}H_{22}O_2Se_2$ (%): C, 55.47; H, 4.66.

3,3'-Dibromobi-6,6'-benzo[*b*]selenophene (**4**): To a flask charged with NaH (0.34 g, 14.19 mmol) in DMF (10 ml) compound **2b** (0.9 g, 1.42 mmol) was added and the mixture was stirred at 120 ^{o}C for 3 h. Then the mixture was cooled to 0 ^{o}C and water (100 ml) was added. After extraction with ethyl acetate (2 x 150 ml) the organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated, and the residue was purified by crystallization from isopropyl alcohol. Yield 22%, mp > 200 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 7.77 (dd, 2H, *J* = 1.5 Hz, *J* = 8.4 Hz, 5,5'-C<u>H</u>), 7.96 (d, 2H, *J* = 8.4 Hz, 4,4'-C<u>H</u>), 7.99 (s, 2H, 2,2'-C<u>H</u>), 8.19 (d, 2H, *J* = 1.5 Hz, 7,7'-C<u>H</u>). ^{13}C NMR ($CDCl_3$, 100.3 MHz), δ, ppm: 109.2, 124.3, 125.0, 125.2, 125.6, 137.9, 138.6, 140.2. Found (%): C, 37.05; H, 1.59. Calc. for $C_{16}H_8Br_2Se_2$ (%): C, 37.10; H, 1.56.

3,3'-Dicyano-bis-2,2'-(2-hydroxyprp-2-yl)-6,6'-bibenzo[*b*]selenophene (**5**): A vial charged with compound **2b** (0.1 g, 0.16 mmol), zinc cyanide (0.05 g, 0.38 mmol) and $Pd(PPh_3)_4$ (40 mg, 0.03 mmol) in dry DMF (3 ml) was flushed with Ar for 5 min. Then the mixture was heated at 140 ^{o}C in microwave reactor for 3 min. After cooling to room temperature the mixture was poured into brine (20 ml) and extracted with ethyl acetate (2 x 50 ml). The organic phase was washed with brine (2 x 50 ml), dried over anhydrous Na_2SO_4,

filtered, concentrated, and the residue was purified by flash chromatography on silica gel using the mixture petrol ether - dichloromethane – ethyl acetate as the eluent. Yield 72%, mp > 200 ^{o}C, LC-MS: *m/e* 528 [M^{+}]. ^{1}H NMR (DMSO-d_6, 400 MHz), δ, ppm: 1.71 (s, 12H, C<u>H</u>$_3$), 6.50 (s, 2H, O<u>H</u>), 7.86 (d, 2H, *J* = 8.4 Hz, 4,4'-C<u>H</u>), 7.92 (dd, 2H, *J* = 1.5 Hz, *J* = 8.4 Hz, 5,5'-C<u>H</u>), 8.56 (d, 2H, *J* = 1.5 Hz, 7,7'-C<u>H</u>). ^{13}C NMR (DMSO-d_6, 100.3 MHz), δ, ppm: 29.9, 72.2, 100.6, 115.0, 123.2, 124.3, 124.9, 136.5, 138.5, 140.2, 180.5. Found (%): C, 54.59; H, 3.88; N, 5.25. Calc. for $C_{24}H_{20}N_2O_2Se_2$ (%): C, 54.77; H, 3.83; N, 5.32.

5-Silyl-2-trimethylstannylthiophenes 6a-b: A flask charged with (allyl)dimethyl(2-thienyl)silane or (3-chloropropyl)dimethyl-2-thienylsilane (13.8 mmol) in THF was cooled to −50 ^{o}C and *n*-BuLi (6.17 ml, 2.4 N) was added dropwise. After 1 h, chlorotrimethylstannane (2.77 g, 13.8 mmol) in THF was added, and mixture was stirred at room temperature over night. Then aqueous sodium carbonate and ethyl acetate were added and the mixture was stirred for 15 min. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated, and the residue was purified by distillation *in vacuo*.

5-[(3-Chloropropyl)dimethylsilyl]-2-trimethylstannylthiophene (**6a**): bp 125 ^{o}C (1 mmHg), yield 65%. GC-MS: *m/e* 382 [M + 1]. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm.: 0.34 (s, 6H, C<u>H</u>$_3$Si), 0.38 (s, 9H, C<u>H</u>$_3$Sn), 0.86-0.90 (m, 2H, C<u>H</u>$_2$Si), 1.79-1.86 (m, 2H, C<u>H</u>$_2$), 3.50 (t, 2H, *J* = 6.8 Hz, C<u>H</u>$_2$Cl,), 7.30 (d, 1H, *J* = 3.1 Hz, 3-C<u>H</u>), 7.39 (d, 1H, *J* = 3.1 Hz, 4-C<u>H</u>). ^{13}C NMR ($CDCl_3$, 100.3 MHz), δ, ppm: -8.1, -1.8, 14.4, 27.5, 47.8, 135.2, 136.0, 143.5, 143.9.

5-(Allyldimethylsilyl)-2-trimethylstannylthiophene (**6b**): bp 85 ^{o}C (1 mmHg), yield 60%. GC-MS: *m/e* 346 [M + 1]. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.34 (s, 6H, C<u>H</u>$_3$Si), 0.39 (s, 9H, C<u>H</u>$_3$Sn), 1.81 (d, 2H, *J* = 8.0 Hz, C<u>H</u>$_2$), 4.88-4.94 (m, 2H, C<u>H</u>$_2$=CH), 5.78-5.88 (m, 1H, C<u>H</u>=CH$_2$), 7.31 (d, 1H, *J* = 3.1 Hz, 3-C<u>H</u>), 7.42 (d, 1H, *J* = 3.1 Hz, 4-C<u>H</u>). ^{13}C NMR ($CDCl_3$, 100.3 MHz), δ, ppm: -8.1, -2.1, 24.5, 113.7, 134.2, 135.3, 136.0, 143.3, 143.9.

Compounds 7a-c: A vial charged with **2a**,**b** or **4** (0.30 mmol), **6a,b** (1.20 mmol), $Pd(PPh_3)_4$ (75 mg, 0.06 mmol) and $AsPh_3$ (20 mg, 0.06 mmol) in 5 ml xylene was flushed with Ar for 10 min. Then the mixture was heated at 120 ^{o}C for 24-48 h. After cooling to room temperature the mixture was poured into aqueous Na_2CO_3 (50 ml) and ethyl acetate (100 ml) and stirred for 15 min. The organic phase was washed with brine (2 x 50 ml), dried over anhydrous Na_2SO_4, filtered, concentrated, and the residue was purified by flash chromatography on silica gel using the mixture petroleum ether – ethyl acetate as eluent.

3,3'-Bis{5-[(3-chloropropyl)dimethylsilyl]thiophen-2-yl}-2,2'-dipentyl-6,6'-bibenzo[*b*]selenophene (**7a**): yellow oil, yield: 70%. ESI-MS: *m/e* 934.0 [M^+]; 978.0 [M + $HCOO^-$]. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.39 (s, 12H, C<u>H</u>$_3$Si), 0.85-0.96 (m, 10H, C<u>H</u>$_3$C<u>H</u>$_2$), 1.24-1.40 (m, 8H, C<u>H</u>$_2$), 1.68-1.92 (m, 8H, C<u>H</u>$_2$), 2.94 (t, 4H, *J* = 7.2 Hz, C<u>H</u>$_2$-Ar), 3.49-3.55 (m, 4H, C<u>H</u>$_2$), 7.13 (d, 2H, *J* = 3.3 Hz, 3-C<u>H</u>-thiophene), 7.31 (d, 2H, *J* = 3.3 Hz, 4-CH-thiophene), 7.57-7.62 (m, 4H, 4,4'-C<u>H</u>, 5,5'-C<u>H</u>), 8.10 (s, 2H, 7,7'-C<u>H</u>). ^{13}C NMR ($CDCl_3$, 100.3 MHz), δ, ppm: -2.2, 13.6, 14.0, 22.0, 27.2, 30.9, 32.0, 47.4, 123.3, 123.8, 124.6, 124.8, 128.3, 128.7, 134.2, 134.9, 136.9, 138.7, 139.2, 141.7, 142.1, 150.2.

3,3'-Bis(5-allyldimethylsilylthiophen-2-yl)-2,2'-dipentyl-6,6'-bibenzo[*b*]-selenophene (**7b**): yellow oil, yield: 68%. ESI-MS: *m/e* 862.0 [M+1], 901.0 [M + $HCOO^-$]. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.38-0.42 (m, 12H, C<u>H</u>$_3$Si), 0.88 (t, 6H, *J* = 7.2 Hz, CH_2C<u>H</u>$_3$), 1.19-1.39 (m, 8H, C<u>H</u>$_2$$CH_3$), 1.67-1.75 (m, 4H, C<u>H</u>$_2$), 1.83-1.89 (m, 4H, C<u>H</u>$_2$), 2.94 (t, 4H, *J* = 7.2 Hz, C<u>H</u>$_2$), 4.90-4.96 (m, 4H, <u>CH$_2$</u>=CH), 5.80-6.26 (m, 2H, CH_2=<u>CH</u>), 7.12-7.13 (d, 2H, *J* = 3.3 Hz, 3-C<u>H</u>-thiophene), 7.30-7.32 (m, 2H, *J* = 3.3 Hz, 4-C<u>H</u>-thiophene), 7.57-7.61 (m, 4H, 4,4'-C<u>H</u>, 5,5'-C<u>H</u>), 8,10 (s, 2H, 7,7'-C<u>H</u>). ^{13}C NMR ($CDCl_3$, 100.3 MHz), δ, ppm: -2.2, -1.2, 13.9, 22.3, 24.5, 31.2, 32.3, 113.8, 123.6, 124.1, 124.9, 128.7, 128.9, 134.0, 134.5, 137.2, 139.0, 139.5, 142.0, 142.4, 144.5, 150.5.

3,3'-Bis(5-allyldimethylsilylthiophen-2-yl)-6,6'-bibenzo[*b*]selenophene (**7c**): yellow oil, yield: 40%. ESI-MS: *m/e* 722.0 [M+1]. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm.: 0.41-0.45 (m,12H, C<u>H</u>$_3$Si), 1.86-1.92 (m, 4H, C<u>H</u>$_2$), 4.94-5.00 (m, 4H, <u>CH$_2$</u>=CH), 5.83-5.94 (m, 2H, CH_2=<u>CH</u>), 7.33 (d, 2H, *J* = 3.3 Hz, 3-C<u>H</u>- thiophene), 7.40 (d, 2H, *J* = 3.3 Hz, 4-C<u>H</u>-thiophene), 7.75 (dd, 2H, *J*=1.5 Hz, *J* = 8.4 Hz, 5,5'-C<u>H</u>), 8.06 (s, 2H, 7,7'-C<u>H</u>), 8.18 (d, 2H, *J* = 8.4 Hz, 4,4'-C<u>H</u>), 8.24 (d, 2H, *J* = 1.5 Hz, 2,2'-C<u>H</u>). ^{13}C NMR ($CDCl_3$, 100.3 MHz), δ, ppm: -2.2, -1.3, 22.6, 24.4, 114.0, 124.4, 124.5, 126.7, 127.3, 133.6, 133.9, 134.9, 137.5, 138.1, 138.8, 142.6, 144.0.