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New Indolo[3,2-*b*]carbazole Derivatives for Field-Effect Transistor Applications

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Electronic Supplementary Information

Material synthesis

3,9-dibromo-5,11-di(t-butyloxycarbonyl)-indolo[3,2-b]carbazole (**2**) :

In a flame-dried flask, 5,11-dihydroindolo[3,2-*b*]carbazole (0.950 g, 2.29 mmol) was solubilized in anhydrous THF (40 mL). After successively adding di-*tert*-butyl dicarbonate (1.25 g, 5.73 mmol) and dimethylaminopyridine (70 mg, 0.573 mmol) the reaction was stirred at room temperature for 10 hours. The solvent was evaporated under reduced pressure. The crude product was solubilized in dichloromethane and filtered through a pad of silica to afford 1.25 compound **2** as a white powder. mp >350°C (86%). δ_H(400MHz, CD_2Cl_2) 1.82 (s, 18H), 7.52 (dd, *J* 1.5 and 8.2 Hz, 2H), 7.94 (d, *J* 8.5 Hz, 2H), 8.52 (s, 2H), 8.86 (s, 2H). δ_C(100MHz, CD_2Cl_2) Cannot be performed on this

compound due to very low solubility in common deuterated solvent. Molecular Mass: Calcd for $C_{28}H_{26}N_2O_4Br_2$: 612.0259. Found: 612.0268.

3,9-di(2-(5-octylthiophene)-5,11-di(t-butyloxycarbonyl)-indolo[3,2-b]carbazole (**3**) :

In a flask fitted with a condenser, compound **2** (0.950 g, 1.50 mmol) and 2-octyl-5-(tributyltin)thiophene (1.89 g, 5.26 mmol) in anhydrous and degassed THF (30 mL). $PdCl_2(PPh_3)_2$ (10 mg, 0.075 mmol) was added before refluxing the solution for 18h. The mixture was then dropped into methanol and filtered. The crude compound was recristallized in hexanes and dichloromethane to afford 0.745 g a yellow powder with an mp of 250°C (59%). δ_H(400MHz, CD_2Cl_2) 0.89 (t, *J* 7.1 Hz, 6H), 1.35 (m, 20H), 1.73 (m, 4H), 1.85 (s, 18H), 2.86 (t, *J* 7.8, 4H), 6.81 (m, 2H), 7.27 (d, *J* 3.6 Hz, 2H), 7.64 (dd, *J* 1.7 and 8.2 Hz, 2H), 8.05 (d, *J* 8.2 Hz, 2H), 8.54 (s, 2H), 8.91 (s, 2H). δ_C(100MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. Molecular Mass: Calcd for $C_{42}H_{48}N_2S_4$: 644.3259. Found: 644.3270. In the HRMS, it seems the BOC protecting groups are substituted by hydrogens.

3,9-di(p-octylphenyl)-5,11-di(t-butyloxycarbonyl)-indolo[3,2-b]carbazole (**4**) :

In a flask fitted with a condenser, compound **2** (1.10 g, 1.74 mmol), 4-octylbenzeneboronic acid (1.02 g, 4.35 mmol), K_3PO_4 (1.60 g, 6.96 mmol), palladium(II) acetate (8 mg, 0.035 mmol) 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (29 mg, 0.070 mmol) were solubilized in degassed THF (35 mL) and the solution was refluxed for 16h. The mixture was extracted with dichloromethane and washed with BRINE and water. The crude compound was filtered through silica using dichloromethane as eluant

and recrystallization in hexanes and dichloromethane afforded 1.13 g of the title compound as a yellow powder mp 210°C (73%). δ_H(400MHz, CD_2Cl_2) 0.87 (t, *J* 6.5 Hz, 6H), 1.32 (m, 20H), 1.65 (m, 4H), 1.83 (s, 18H), 2.66 (t, *J* 7.7, 4H), 7.30 (d, *J* 7.7 Hz, 4H), 7.64 (d, *J* 7.7 Hz, 4H), 8.11 (d, *J* 7.7 Hz, 2H), 8.58 (s, 2H), 8.94 (s, 2H). δ_C(100MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. Molecular Mass: Calcd for $C_{46}H_{52}N_2$: 632.4130. Found: 632.4119. In the HRMS, it seems the BOC protecting groups are substituted by hydrogens.

trans-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))-1-(p-octylbenzene) (**5**) :

1-iodo-4-octylbenzene (5.72 g, 18.1 mmol), palladium(II) acetate (87 mg, 0.45 mmol) and triphenylphosphine (0.240 g, 0.91 mmol) were solubilized in dry toluene (53 mL). Tributylamine (8.6 mL, 36.2 mmol) and vinylboronic acid pinacol ester (5.00, 32.5 mmol) were then added and the reaction was heated at 110°C for 12h. After cooling down to room temperature, the mixture was extracted in toluene and washed with HCl 10%, water and BRINE. The crude product was purified by column chromatography using 25% ethyl acetate in hexanes. The title compound was afforded as yellowish oil in 47% yield. δ_H(400MHz, CD_2Cl_2) 0.88 (t, *J* 7.1 Hz, 3H), 1.35 (m, 22H), 1.59 (m, 2H), 2.59 (t, J = 7.3, 2H), 6.12 (d, *J* 18.9 Hz, 1H), 7.09 (d, *J* 7.9 Hz, 2H), 7.39 (m, 3H). δ_C(100MHz, CD_2Cl_2) 14.25, 22.80, 24.95, 29.38, 29.45, 29.60, 31.47, 32.01, 35.93, 83.40, 127.16, 128.77, 135.11, 144.22, 149.67 Molecular Mass: Calcd for $C_{22}H_{35}BO_2$: 342.2730. Found: 342.2722.

3,9-bis(p-octylphenylenevinylene)-5,11-di(t-butyloxycarbonyl)-indolo[3,2-b]carbazole (**6**) :

To a solution of compound **5** (2.53 g, 7.39 mmol), **2** (1.56 g, 2.46 mmol) and a drop of Aliquat 336 in degassed THF (50 mL) and K_2CO_3 2M was added $PdCl_2(PPh_3)_2$ (70 mg, 0.098 mmol). After refluxing for 12h, the mixture was dropped in methanol and filtered. The solid was washed with HCl 5%, water, methanol and three times with acetone to afford 1.644 g of a yellow powder mp >260°C (76%). δ_H(400MHz, CD_2Cl_2) 0.87 (t, *J* 6.7 Hz, 6H), 1.29 (m, 20H), 1.61 (m, 4H), 1.85 (s, 18H), 2.61 (t, *J* 7.3, 4H), 7.20 (d, *J* 8.2 Hz, 4H), 7.24 (s, 4H), 7.48 (d, *J* 7.6 Hz, 4H), 7.57 (d, *J* 7.6 Hz, 2H), 8.03 (d, *J* 8.2 Hz, 2H), 8.51 (s, 2H), 8.86 (s, 2H). δ_C(100MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. Molecular Mass: Calcd for $C_{50}H_{56}N_2$: 684.4443. Found: 644.4454. In the HRMS, it seems the BOC protecting groups are substituted by hydrogens.

3,9-di(2-(5-octylthiophene)-5,11-dihydroxyindolo[3,2-b]carbazole (**7**) :

After compound **3** (0.600 g, 0.710 mmol) was solubilized in dichloromethane (14 mL), trifluoroacetic acid (14 mL) was added and the solution was stirred at room temperature for 2h. The precipitate was filtered and washed with methanol to afford 0.353 g of the title compound as a yellowish powder mp >350°C, decomposition. (77%). δ_H(400MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. δ_C(100MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. Molecular Mass: Calcd for $C_{42}H_{48}N_2S_2$: 644.3259. Found: 644.3264. Anal. Calcd. for $C_{42}H_{48}N_2S_2$: C, 78.20; H, 7.50; N, 4.30; S, 9.90. Found: C, 76.77; H, 7.45; N, 4.33; S, 8.77%.

3,9-di(p-octylbenzene)-5,11-dihydroxyindolo[3,2-b]carbazole (**8**) :
This product was obtained (via compound **4** (1.05 g, 1.19 mmol)) following the same procedure used for the synthesis of compound **7** to provide 0.767 g of the title product as a yellow solid mp >300 °C, decomposition. (95%). δ_H(400MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. δ_C(100MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. Molecular Mass: Calcd for $C_{46}H_{52}N_2$: 644.3259. Found: 644.3264. Anal. Calcd. for $C_{46}H_{52}N_2$: C, 87.30; H, 8.30; N, 4.40. Found: C, 86.22; H, 8.32; N, 4.46%.

3,9-bis(p-octylphenylenevinylene)-5,11-dihydroxyindolo[3,2-b]carbazole (**9**) :
This product was obtained (via compound **6** (1.60 g, 1.81 mmol)) following the same procedure used for the synthesis of compound **7** to provide 1.02 g of the title product as a yellow solid mp 275 °C, decomposition. (82%). δ_H(400MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. δ_C(100MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. Molecular Mass: Calcd for $C_{50}H_{56}N_2$: 684.4443. Found: 684.4454. Anal. Calcd. for $C_{50}H_{56}N_2$: C, 87.70; H, 8.20; N, 4.10. Found: C, 85.72; H, 8.24; N, 4.05%.

3,9-di(2-(5-octylthiophene))-5,11-dimethylindolo[3,2-b]carbazole (**10**):
To a solution of compound **7** (0.200 g, 0.310 mmol), benzyltriethylammonium chloride (0.014 g, 0.062 mmol) and iodomethane (0.180 g, 1.24 mmol) in DMSO (4 mL) was

added 0.6 mL of a 50% aqueous NaOH solution. The mixture was stirred for 1h at room temperature before warming up to 50°C for 4h. The reaction was stopped by dropping it into methanol. After filtration, the crude compound was washed successively water, DMF and methanol (3 times each). 0.124 g of the title compound was obtained yielding 54%. mp >300°C, decomposition. δ_H(400MHz, THF-d_8) 0.90 (t, *J* 7.0 Hz, 6H), 1.37 (m, 20H), 2.86 (t, *J* 7.4 Hz, 4H), 4.00 (s, 6H), 6.80 (d, *J* 3.4 Hz, 2H), 7.30 (d, *J* 3.6 Hz, 2H), 7.44 (d, *J* 8.5 Hz, 2H), 7.67 (s, 2H), 8.1 (s, 2H), 8.14 (d, *J* 8.1 Hz, 2H). δ_C(100MHz, THF-d_8) Cannot be performed on this compound due to very low solubility in common deuterated solvent. Molecular Mass: Calcd for $C_{44}H_{52}N_2S_2$: 672.3572. Found: 672.3564. Anal. Calcd. for $C_{44}H_{52}N_2S_2$: C, 78.50; H, 7.80; N, 4.20; S, 9.50. Found: C, 77.06; H, 7.77; N, 4.20; S, 8.66%.

3,9-di(p-octylbenzene)-5,11-dimethylindolo[3,2-b]carbazole (**11**):

This product was obtained (via compound **4** (0.600 g, 0.878 mmol)) following the same procedure used for the synthesis of compound **10** to provide 0.495 g of the title product as a yellow solid. mp >300 °C, decomposition. (79%). δ_H(400MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. δ_C(100MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. Molecular Mass: Calcd for $C_{48}H_{56}N_2$: 660.4443. Found: 660.4454. Anal. Calcd. for $C_{48}H_{56}N_2$: C, 87.20; H, 8.50; N, 4.20. Found: C, 86.45; H, 8.36; N, 4.48%.

3,9-bis(p-octylphenylenevinylene)-5,11-dimethylindolo[3,2-b]carbazole (**12**):

This product was obtained (via compound **6** (0.700 g, 1.02 mmol)) following the same procedure used for the synthesis of compound **10** to provide 0.595 g of the title product as a yellow solid. mp 300 °C, degradation. (81%). δ_H(400MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. δ_C(100MHz, CD_2Cl_2) Cannot be performed on this compound due to very low solubility in common deuterated solvent. Molecular Mass: Calcd for $C_{52}H_{60}N_2$: 712.4756. Found: 712.4745. Anal. Calcd. for $C_{52}H_{60}N_2$: C, 87.60; H, 8.50; N, 3.90. Found: C, 86.14; H, 8.20; N, 4.05%.

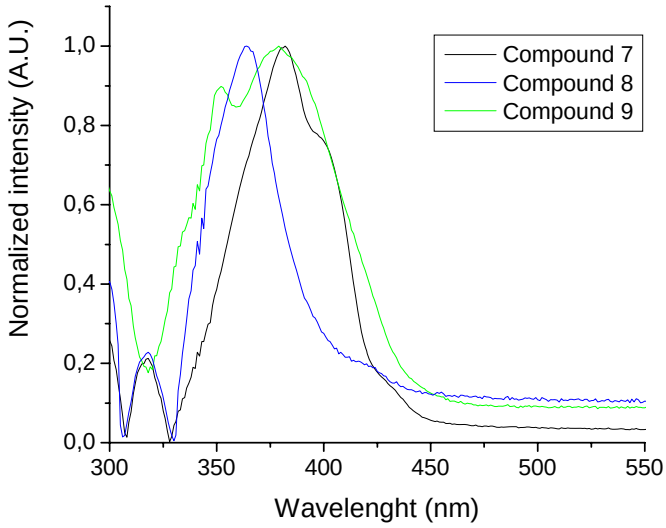

Figure 1S. UV-vis absorption spectra of compounds **7**, **8** and **9** in solution in N,N-dimethylformamide.

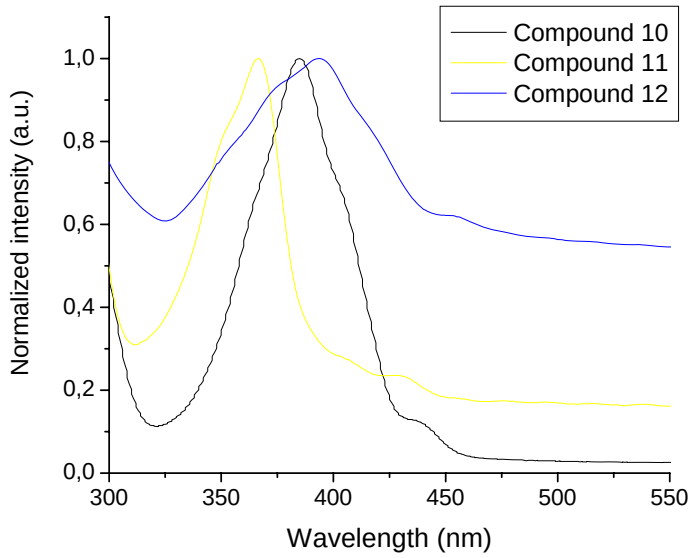

Figure 2S. UV-vis absorption spectra of compounds **10**, **11** and **12** in solution in dichloromethane.

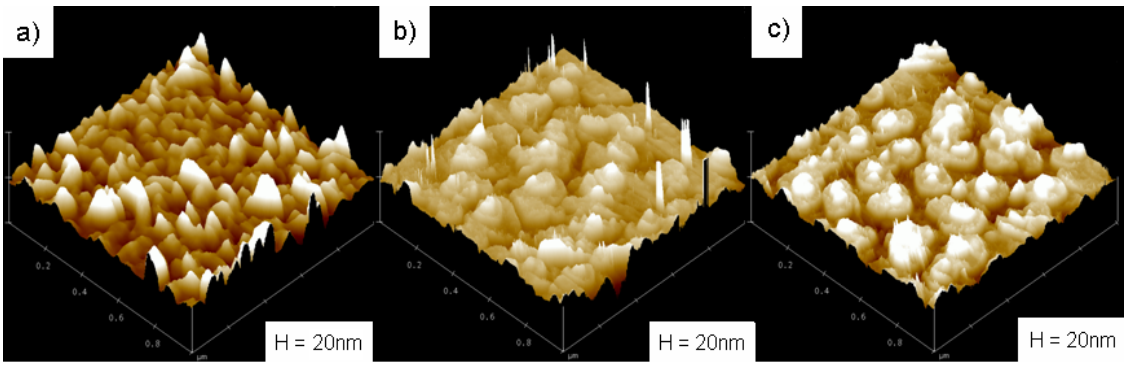

Figure 3S. AFM images of vacuum-depoisted thin films (40 nm) of compound **11**. a) at room temperature b) at 75°C and c) at 125°C. The size of all images is 1 μm^2.

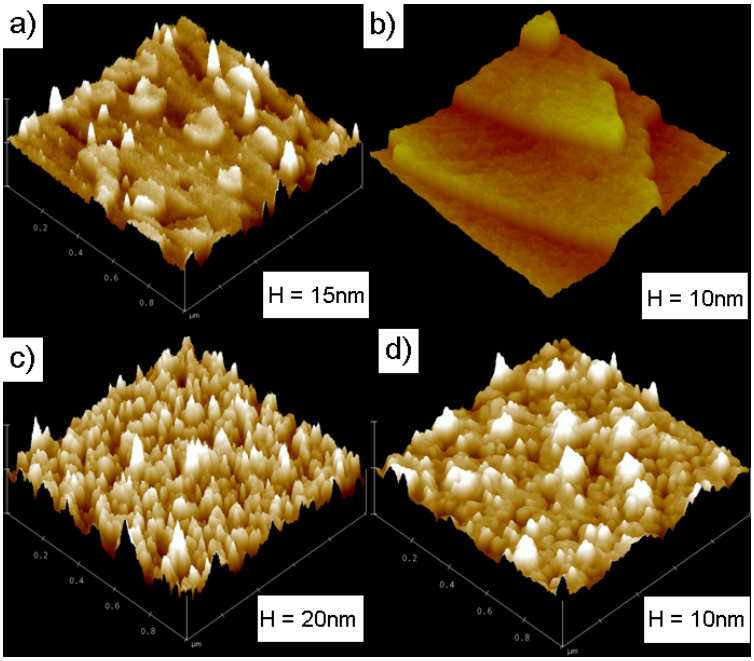

Figure 4S. AFM images of vacuum-deposited thin films (40 nm) of compound a) **7** with T_D = 175°C b) **10** with T_D = 125°C c) **9** with a T_D = 125°C and d) **12** with a T_D = 75°C. The size of all images is 1 μm^2.