

Supporting Information

Role of the Alkylation Patterning in the Performance of OTFTs: The Case of Thiophene-Functionalized Triindoles

Roger Bujaldón ^{1,2,†}, Alba Cuadrado ^{1,2,†}, Dmytro Volyniuk ³, Juozas V. Grazulevicius ³, Joaquim Puigdollers ⁴ and Dolores Velasco ^{1,2,*}

¹ Grup de Materials Orgànics, Departament de Química Inorgànica i Orgànica, Secció de Química Orgànica, Universitat de Barcelona, Martí i Franquès, 1, E-08028 Barcelona, Spain

² Institut de Nanociència i Nanotecnologia (IN²UB), Universitat de Barcelona, E-08028 Barcelona, Spain

³ Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu pl. 19, LT-50254 Kaunas, Lithuania

⁴ Departament d'Enginyeria Electrònica, Universitat Politècnica de Catalunya, Jordi Girona 1–3, E-08034 Barcelona, Spain

* Correspondence: dvelasco@ub.edu

† These authors contributed equally to this work.

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Synthetic procedures and characterization

- Synthesis of 5-bromo-1-methylindolin-2,3-dione (**2a**)

5-bromoisatin (7.7 g, 33.9 mmol) and NaH (13.5 g, 60% dispersion in mineral oil, 97.6 mmol) were dissolved in anhydrous DMF (50 mL) and stirred at room temperature for 30 min under nitrogen. Then, methyl iodide (3 mL, 50.8 mmol) was added and the solution was further stirred overnight. After, the product was precipitated by adding water to the mixture and filtered off. The solid was thoroughly washed with water and dried. Compound **2a** was obtained as a red solid in a yield of 98% (7.9 g, 33.2 mmol). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.73–7.71 (m, 2H), 6.80 (d, *J* = 8 Hz, 1H), 3.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 182.1, 157.5, 150.2, 140.6, 128.1, 118.6, 116.7, 111.6, 26.4.

- Synthesis of 5-bromo-1-hexylindolin-2,3-dione (**2b**)

5-bromoisatin (7.5 g, 33.4 mmol), K₂CO₃ (13.8 g, 99.5 mmol) and 1-bromohexane (7 mL, 49.7 mmol) were dissolved in anhydrous DMF (50 mL) and stirred at room temperature for 24 h under nitrogen. Then, the product was precipitated by adding water to the mixture and filtered off. The solid was thoroughly washed with water and dried. Compound **2b** was obtained as a red solid in a yield of 92% (9.5 g, 30.7 mmol). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.70–7.68 (m, 2H), 6.80 (d, *J* = 9 Hz, 1H), 3.70 (t, *J* = 7 Hz, 2H), 1.71–1.63 (m, 2H), 1.36–1.28 (m, 6H), 0.88 (t, *J* = 7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 182.6, 157.5, 149.9, 140.6, 128.3, 118.9, 116.5, 112.0, 40.6, 31.5, 27.3, 26.7, 22.6, 14.1.

- Synthesis of 5-bromo-1-decylindolin-2,3-dione (**2c**)

5-bromoisatin (5.0 g, 22.2 mmol), K₂CO₃ (9.2 g, 66.6 mmol) and 1-bromodecane (5.5 mL, 26.5 mmol) were dissolved in anhydrous DMF (40 mL) and stirred at room temperature for 24 h under nitrogen. Then, the product was precipitated by adding water to the mixture and filtered off. The solid was thoroughly washed with water and dried. Compound **2c** was obtained as a red solid in a yield of 99% (8.0 g, 22.0 mmol). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.70–7.67 (m, 2H), 6.80 (d, *J* = 8 Hz, 1H), 3.70 (t, *J* = 7 Hz, 2H), 1.71–1.64 (m, 2H), 1.34–1.25 (m, 14H), 0.87 (t, *J* = 7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 182.6, 157.5, 149.9, 140.6, 128.3, 118.9, 116.5, 112.0, 40.6, 32.0, 29.6, 29.6, 29.6, 29.4, 27.3, 27.0, 22.8, 14.2.

- Synthesis of 5-bromo-1-methylindolin-2-one (**3a**)

2a (3.1 g, 12.9 mmol) was dissolved in DMSO (7 mL) and an aqueous solution of NH₂NH₂ (23 mL) and the mixture was stirred under reflux for 24 h. After cooling to room temperature, the mixture was poured into a solution of HCl (4 M) and the product was extracted with ethyl acetate. The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The product was purified by flash column chromatography using a mixture of hexane and ethyl acetate (10:1 v/v). Compound **3a** was obtained as a yellow solid in a yield of 65% (1.9 g, 8.3 mmol). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.41 (d, *J* = 8 Hz, 1H), 7.36 (s, 1H), 6.69 (d, *J* = 8 Hz, 1H), 3.52 (s, 2H), 3.19 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 174.2, 144.2, 130.8, 127.5, 126.3, 114.9, 109.5, 35.5, 26.2.

- Synthesis of 5-bromo-1-hexylindolin-2-one (**3b**)

2b (3.49 g, 11.3 mmol) was dissolved in an aqueous solution of NH₂NH₂ (30 mL) and was stirred overnight under reflux. After cooling to room temperature, the solution was diluted with aqueous HCl (4 M). The product was extracted with dichloromethane. The combined organic extract was dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography using a mixture of hexane and dichloromethane (1:1 v/v) as eluent. Compound **3b** was obtained as a white solid in a yield of 90% (2.98 g, 10.1 mmol). ¹H NMR (400 MHz,

CDCl₃) δ (ppm): 7.40–7.39 (m, 2H), 6.70 (d, J = 8 Hz, 1H), 3.67 (t, J = 7 Hz, 2H), 3.51 (s, 2H), 1.60–1.67 (m, 2H), 1.25–1.37 (m, 6H), 0.88 (t, J = 7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 174.3, 143.9, 130.8, 127.8, 126.8, 114.8, 109.8, 40.3, 35.7, 31.6, 27.4, 26.7, 22.7, 14.1.

- Synthesis of 5-bromo-1-decylindolin-2-one (**3c**)

2c (3.5 g, 9.6 mmol) was dissolved in an aqueous solution of NH₂NH₂ (15 mL) and the mixture was stirred under reflux for 24 h. After cooling to room temperature, the mixture was poured into a solution of HCl (4 M) and the product was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography using a mixture of hexane and dichloromethane (1:1 v/v). Compound **3c** was obtained as a yellow solid in a yield of 73% (2.4 g, 7.0 mmol). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.40–7.33 (m, 2H), 6.69 (d, J = 8 Hz, 1H), 3.66 (t, J = 7 Hz, 2H), 3.51 (s, 2H), 1.67–1.60 (m, 2H), 1.23–1.25 (m, 14 H), 0.87 (t, J = 7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 174.3, 143.9, 130.8, 127.8, 126.8, 114.8, 109.8, 40.3, 35.7, 32.0, 29.7, 29.6, 29.4 (2C), 27.5, 27.1, 22.8, 14.3.

- Synthesis of 3,8,13-tribromo-5,10,15-trimethyl-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-c]carbazole (**4a**)

3a (1.7 g, 7.5 mmol) was dissolved in POCl₃ (17 mL) and the mixture was stirred under reflux for 8 h. After cooling to room temperature, the mixture was carefully and slowly poured into stirring water and the formation of a precipitate could be observed. The resulting solution was neutralized with NaOH and then, the precipitate was filtered off, thoroughly washed with water and dried. Compound **4a** was obtained as a pale grey solid in a yield of 58% (0.91 g, 1.5 mmol). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.48 (d, J = 2 Hz, 3H), 7.57 (dd, J = 9 Hz, J = 2 Hz, 3H), 7.45 (d, J = 9 Hz, 3H), 4.37 (s, 9H).

- Synthesis of 3,8,13-tribromo-5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-c]carbazole (**4b**)

3b (3.0 g, 10.1 mmol) was dissolved in POCl₃ (9 mL) and the mixture was stirred under reflux for 7 h. After cooling to room temperature, the mixture was carefully and slowly poured into stirring water and the resulting solution was neutralized with NaOH. The product was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude was dissolved in the minimum volume of ethyl acetate and precipitated by the addition of hexane. The resulting solid was filtered off and dried. Compound **4b** was obtained as a white solid in a yield of 39% (1.1 g, 1.3 mmol). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.27 (d, J = 2 Hz, 3H), 7.53 (dd, J = 9 Hz, J = 2 Hz, 3H), 7.45 (d, J = 9 Hz, 3H), 4.68 (t, J = 8 Hz, 6H), 2.03–1.95 (m, 6H), 1.42–1.23 (m, 18 H), 0.84 (t, J = 7 Hz, 9H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 139.5, 139.3, 125.7, 124.7, 123.9, 113.2, 111.8, 102.2, 47.3, 31.7, 30.3, 26.5, 22.7, 14.1.

- Synthesis of 3,8,13-tribromo-5,10,15-tridecyl-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-c]carbazole (**4c**)

3c (1.5 g, 4.3 mmol) was dissolved in POCl₃ (4 mL) and the mixture was stirred under reflux for 7 h. After cooling to room temperature, the mixture was carefully and slowly poured into stirring water and the resulting solution was neutralized with NaOH. The product was extracted with ethyl acetate. The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography using a mixture of hexane and ethyl acetate (20:1 v/v). Compound **4c** was obtained as a white solid in a yield of 21% (0.32 g, 0.30 mmol). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.29 (d, J = 2 Hz, 3H), 7.53 (dd, J = 9 Hz, J = 2 Hz, 3H), 7.46 (d, J = 9 Hz, 3H), 4.71 (t, J = 8 Hz, 6H), 2.05–1.97 (m, 6H), 1.39–1.20 (m,

42H), 0.86 (t, $J = 7$ Hz, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 139.5, 139.2, 125.7, 124.7, 123.9, 113.2, 111.8, 102.1, 47.2, 32.0, 30.3, 29.7, 29.6, 29.5, 29.4, 26.7, 22.8, 14.3.

- Synthesis of 5,10,15-trimethyl-3,8,13-tri(thiophen-2-yl)-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]carbazole (**1a**)

4a (116 mg, 0.17 mmol), 2-thienylboronic acid (143 mg, 1.1 mmol), K_2CO_3 (462 mg, 3.3 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (9.8 mg, 0.0085 mmol) were dissolved in a mixture of THF and H_2O (12 mL, 6:1 v/v) under nitrogen in a sealed reaction tube. The mixture was stirred at 150 °C under microwave irradiation for 2 h. After cooling to room temperature, the solution was diluted with water and the product was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4 , filtered and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography using a mixture of hexane and dichloromethane (3:2 v/v). Compound **1a** was obtained as a pale yellow solid in a yield of 50% (54 mg, 0.085 mmol). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.65 (d, $J = 2$ Hz, 3H), 7.75 (dd, $J = 8$ Hz, $J = 2$ Hz, 3H), 7.55 (d, $J = 8$ Hz, 3H), 7.40 (dd, $J = 4$ Hz, $J = 1$ Hz, 3H), 7.32 (dd, $J = 5$ Hz, $J = 1$ Hz, 3H), 7.17 (dd, $J = 5$ Hz, $J = 4$ Hz, 3H), 4.46 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 146.3, 141.4, 141.4, 139.4, 128.3, 123.9, 122.5, 121.9, 121.5, 119.8, 110.3, 102.6, 36.4. HRMS (ESI-MS) (m/z): calculated for $\text{C}_{39}\text{H}_{27}\text{N}_3\text{S}_3$ (M^+)⁺ 633.1367, found: 633.1371.

- Synthesis of 5,10,15-trihexyl-3,8,13-tri(thiophen-2-yl)-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]carbazole (**1b**)

4b (200 mg, 0.24 mmol), 2-thienylboronic acid (184 mg, 1.4 mmol), K_2CO_3 (596 mg, 4.3 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (14 mg, 0.012 mmol) were dissolved in a mixture of THF and H_2O (14 mL, 6:1 v/v) under nitrogen. The mixture was stirred under reflux for 24 h. After cooling to room temperature, the solution was diluted with water and the product was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4 , filtered and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography using a mixture of hexane and dichloromethane (5:1 v/v). Compound **1b** was obtained as a pale yellow solid in a yield of 53% (107 mg, 0.13 mmol). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.50 (d, $J = 2$ Hz, 3H), 7.72 (dd, $J = 9$ Hz, $J = 2$ Hz, 3H), 7.62 (d, $J = 9$ Hz, 3H), 7.37 (dd, $J = 4$ Hz, $J = 1$ Hz, 3H), 7.30 (dd, $J = 5$ Hz, $J = 1$ Hz, 3H), 7.15 (dd, $J = 5$ Hz, $J = 4$ Hz, 3H), 4.93 (t, $J = 8$ Hz, 6H), 2.05–1.98 (m, 6H), 1.31–1.10 (m, 18H), 0.74 (t, $J = 7$ Hz, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 146.4, 140.8, 139.4, 128.1, 126.7, 123.9, 123.8, 122.3, 121.8, 119.6, 110.9, 103.4, 47.3, 31.6, 30.0, 26.7, 22.6, 14.1. HRMS (ESI-MS) (m/z): calculated for $\text{C}_{54}\text{H}_{57}\text{N}_3\text{S}_3$ (M^+)⁺ 843.3709, found: 843.3709.

- Synthesis of 5,10,15-tridecyl-3,8,13-tri(thiophen-2-yl)-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]carbazole (**1c**)

4c (200 mg, 0.20 mmol), 2-thienylboronic acid (153 mg, 1.2 mmol), K_2CO_3 (495 mg, 4.3 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (14 mg, 0.012 mmol) were dissolved in a mixture of THF and H_2O (14 mL, 6:1 v/v) under nitrogen. The mixture was stirred under reflux for 24 h. After cooling to room temperature, the solution was diluted with water and the product was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4 , filtered and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography using a mixture of hexane and dichloromethane (5:1 v/v). Compound **1c** was obtained as a pale yellow solid in a yield of 55% (111 mg, 0.11 mmol). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.51 (d, $J = 2$ Hz, 3H), 7.73 (dd, $J = 9$ Hz, $J = 2$ Hz, 3H), 7.63 (d, $J = 9$ Hz, 3H), 7.37 (dd, $J = 4$ Hz, $J = 1$ Hz, 3H), 7.30 (dd, $J = 5$ Hz, $J = 1$ Hz, 3H), 7.15 (dd, $J = 5$ Hz, $J = 4$ Hz, 3H), 4.95 (t, $J = 8$ Hz, 6H), 2.09–1.95 (m, 6H), 1.32–1.03 (m, 42H), 0.84 (t, $J = 7$ Hz, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 146.4, 140.9, 139.6, 128.1, 126.8, 124.0, 123.9, 122.4, 121.9, 119.6, 111.0, 103.5, 47.4, 32.0, 30.1, 29.6 (2C), 29.5,

29.4, 27.0, 22.8, 14.3. HRMS (ESI-MS) (m/z): calculated for $C_{66}H_{81}N_3S_3$ ($M\cdot$) $^+$ 1011.5593, found: 1011.5593.

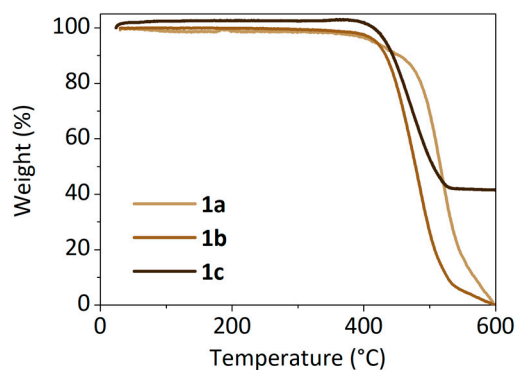


Figure S1. TGA scans of compounds **1a–c**. The decomposition temperatures (T_d) were estimated from the onset.

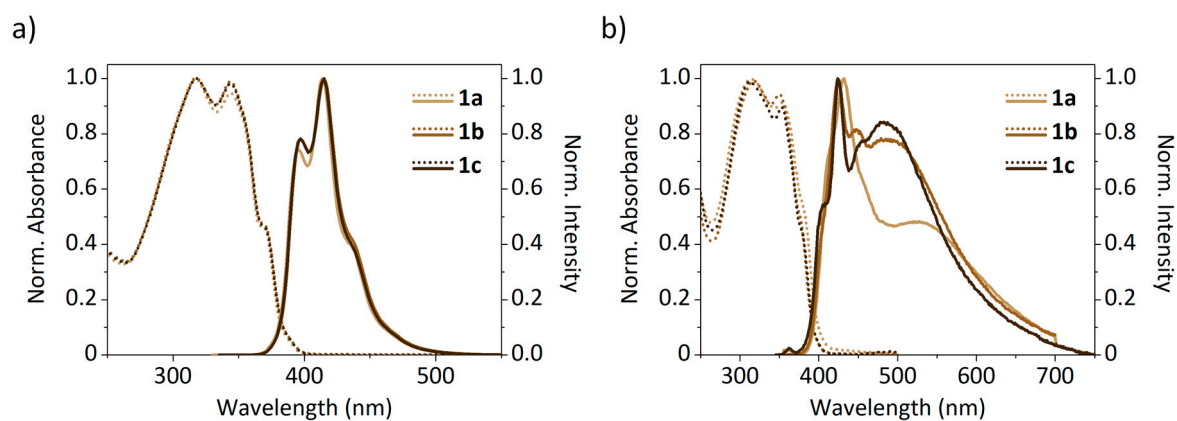


Figure S2. Absorption and emission spectra of compounds **1a–c** in: a) dichloromethane (10 μ M) and b) vacuum-evaporated thin films.

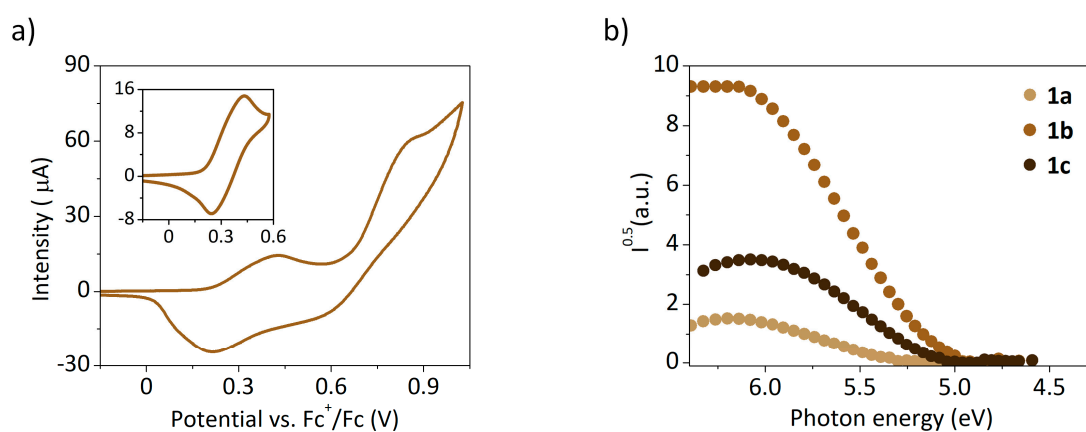


Figure S3. Electrochemical data of compounds **1a–c**: a) cyclic voltammogram of **1b** as representative (the inset shows the first oxidation step) and b) photoemission spectra of compounds **1a–c**.

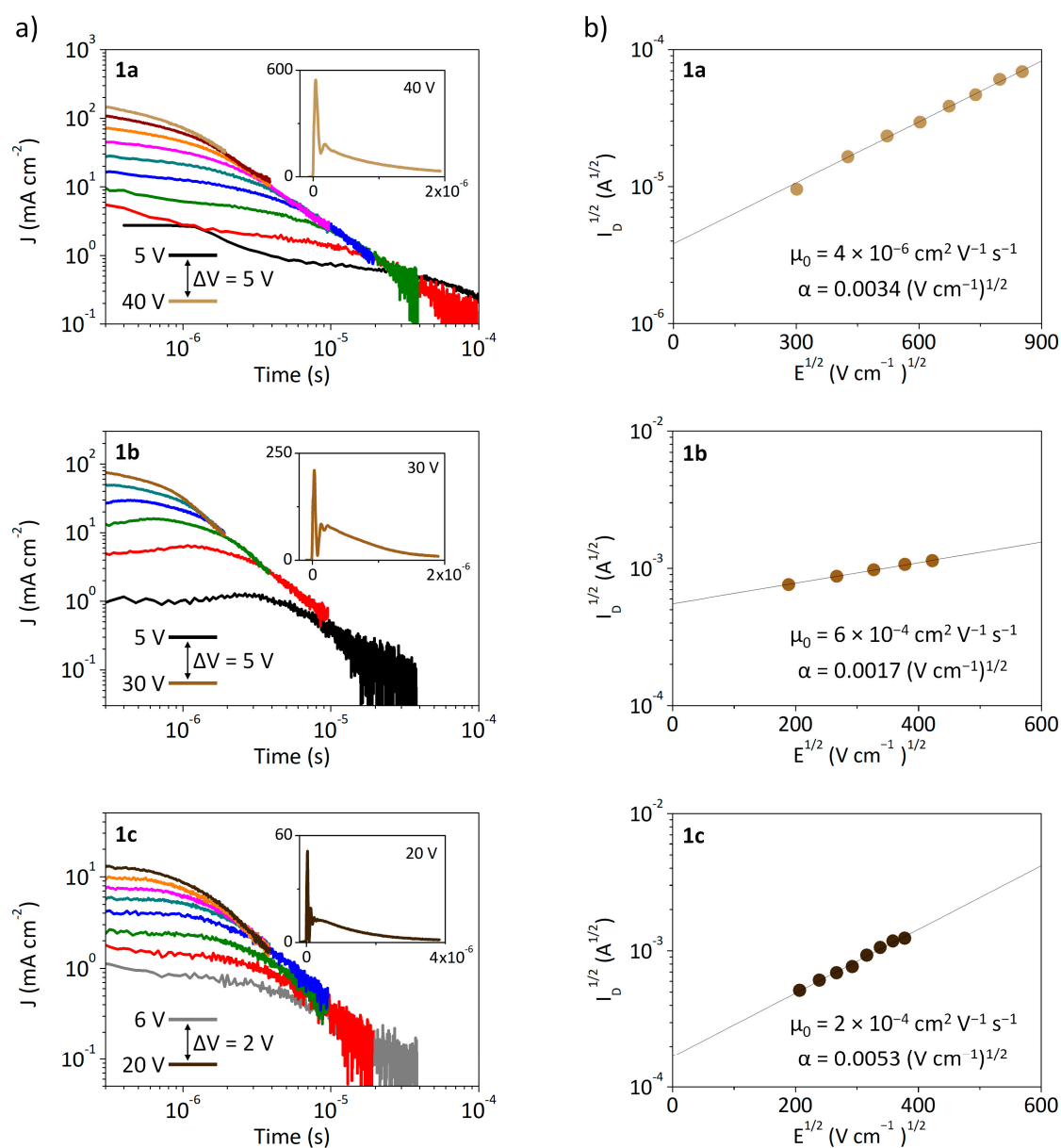


Figure S4. Estimation of the hole mobility of compounds **1a–c** via the TOF technique: a) TOF transients (the inset shows one of the transient curves in the linear plot) and b) electric field dependence of the hole mobility.

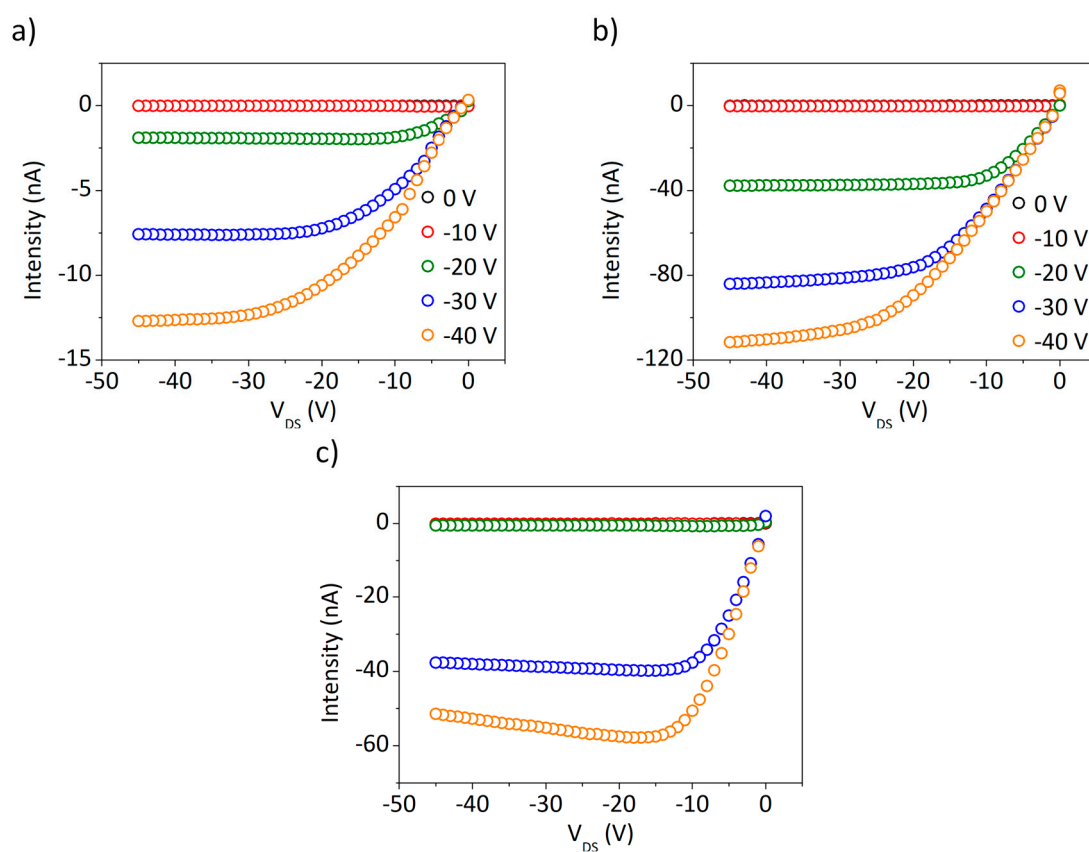


Figure S5. Output characteristics (V_G from 0 to -40 V) of OTS-treated devices based on compounds: a) 1a; b) 1b and c) 1c.

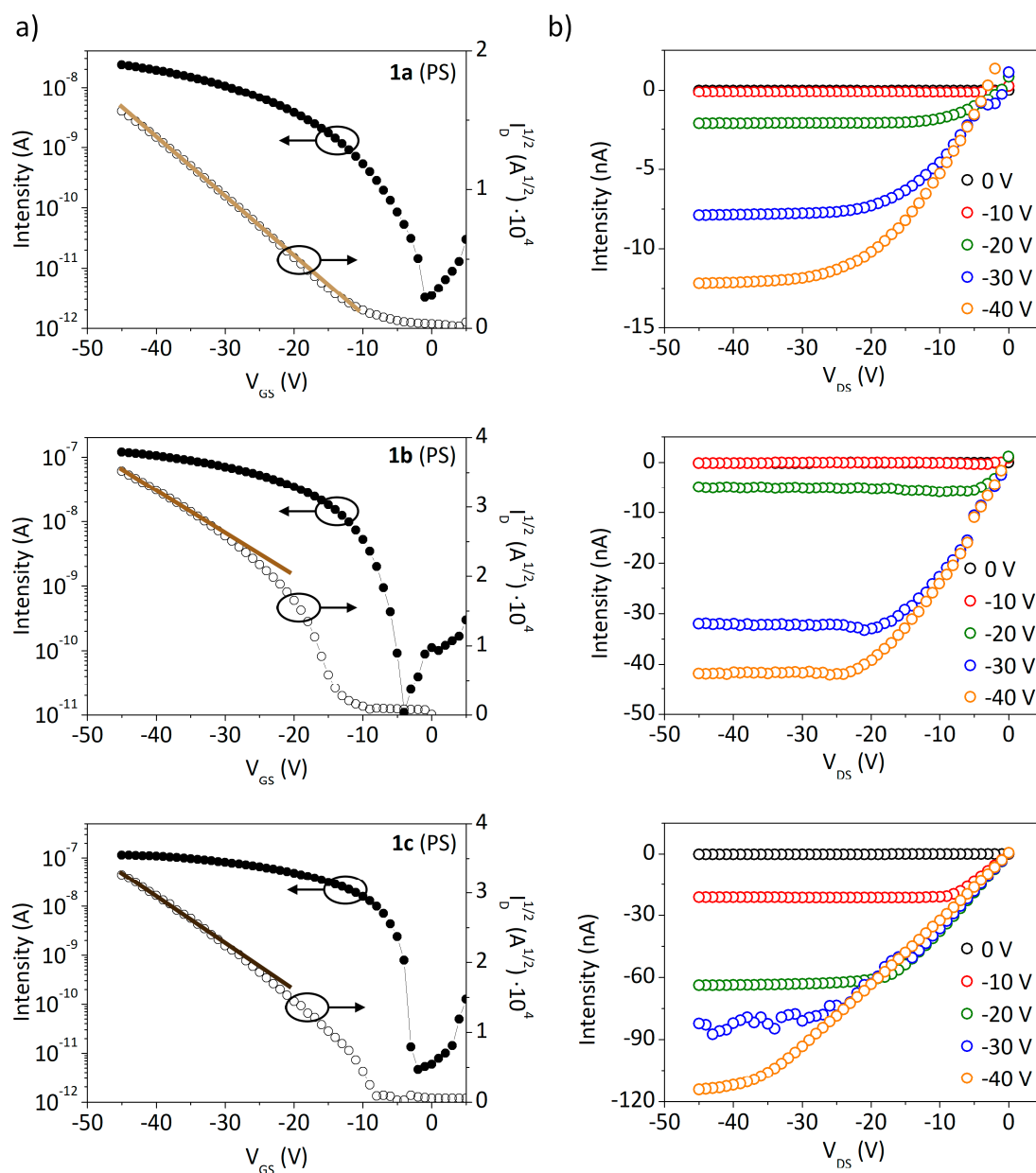


Figure S6. OTFT characteristics of PS-treated devices incorporating derivatives **1a**–**c**: a) transfer and saturation ($V_{DS} = -40$ V) and b) output characteristics.

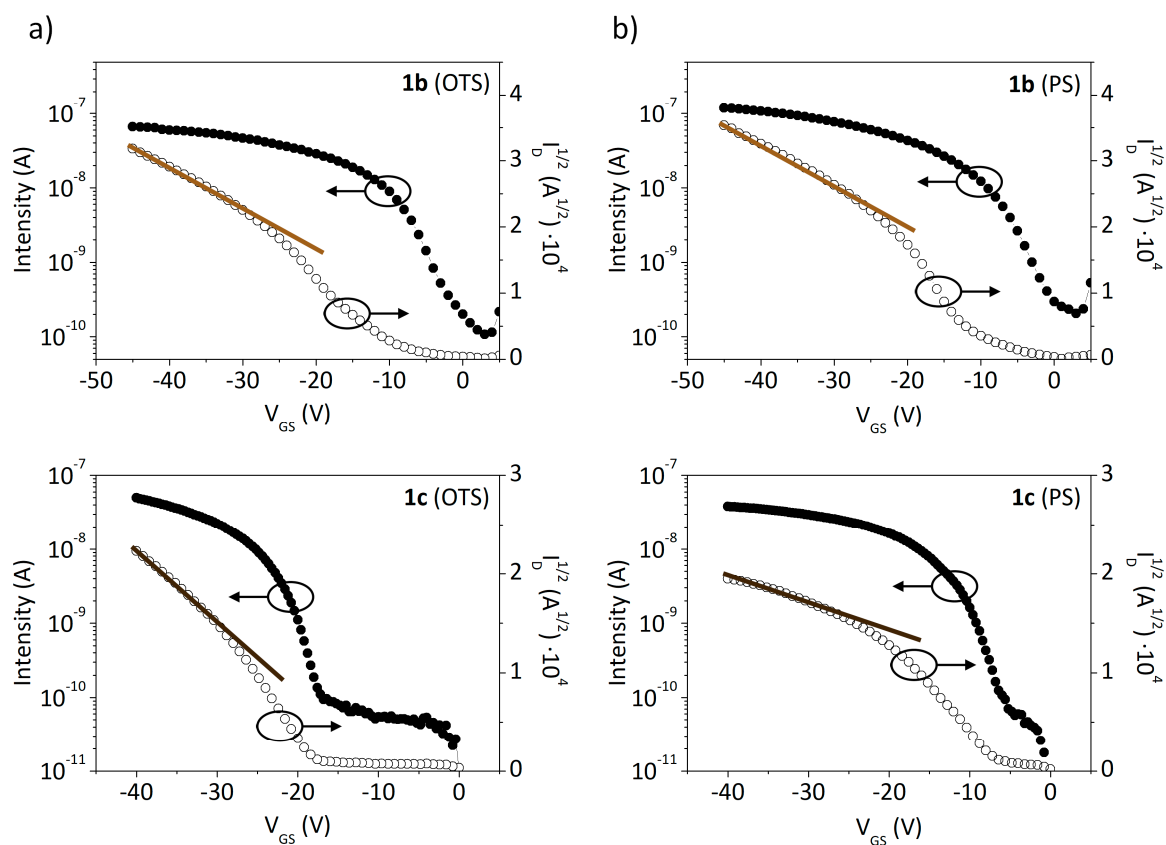


Figure S7. Transfer and saturation ($V_{DS} = -40$ V) characteristics of devices fabricated with compound **1b** after 132 days (above) and **1c** after 122 days (below) over: a) OTS- and b) PS-treated substrates.