

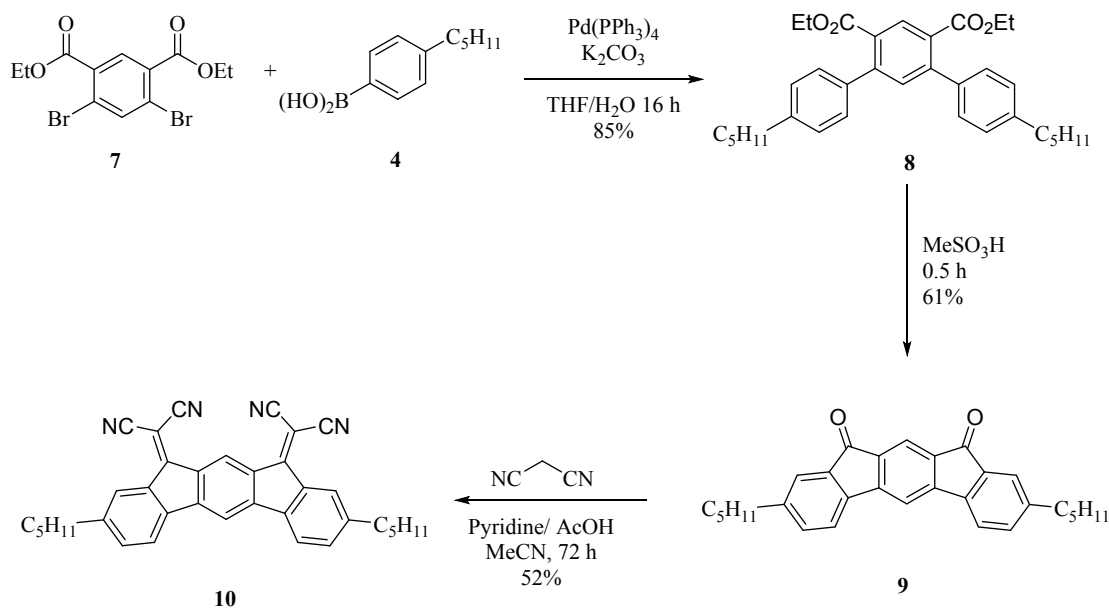
## Supplementary Information

Influence of the gate bias stress on the stability of n-type Organic Field-Effect Transistors based on Dicyanovinylenes-Dihydroindenofluorene semiconductors

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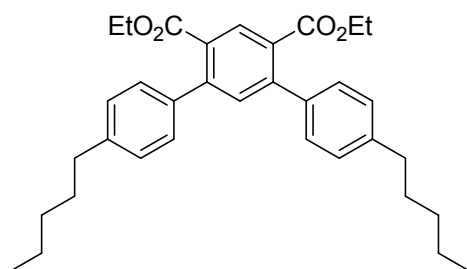
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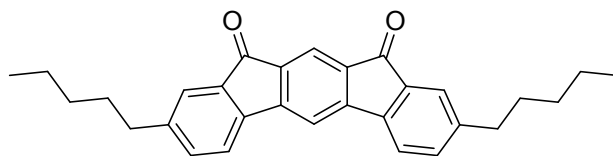
Scheme S1: Synthesis of compound **10**

**Diethyl 4,4'-dipentyl-[1,1':3',1''-terphenyl]-4',6'-dicarboxylate (**8**) :**



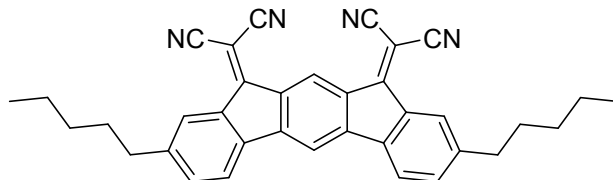
Diethyl 4,6-dibromoisophthalate **7** (0.390 g, 1.0 mmol), 4-pentylphenylboronic acid **4** (0.500 g, 2.2 mmol), tetrakis palladium<sup>0</sup> (0.115 g, 0.10 mmol) and potassium carbonate (0.700 g, 5 mmol) were dissolved in a mixture THF/water (2.5:1, 35 ml) under an argon atmosphere. The resulting mixture was degassed and stirred 16h at 75°C. The resulting mixture was quenched with a saturated solution of ammonium chloride (20ml) and extracted with ethyl acetate (2x25 ml). The combined extracts were dried over MgSO<sub>4</sub>, filtered, evaporated *in vacuo* and purified by column chromatography on silica gel eluting with a gradient of light petroleum – ethyl acetate (100:0 to 95:5) to give **8** as a colorless solid (0.435 g, 85%); mp 71-73 °C (from ethyl acetate)  $\nu_{\text{max}}/\text{cm}^{-1}$  2941, 2908, 2891, 2875, 2860, 1711 (CO), 1456, 1246, 1103, 1024, 844, 606; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>)  $\delta_{\text{H}}$  8.29 (1H, s, Ar-H), 7.41 (1H, s, Ar-H), 7.28-7.25 (4H, d, *J* 8.1, Ar-H), 7.22-7.19 (4H, d, *J* 8.1, Ar-H), 4.18-4.11 (4H, q, *J* 7.5, OCH<sub>2</sub>Me), 2.67-2.62 (4H, t, *J* 7.5, Ar-CH<sub>2</sub>CH<sub>2</sub>), 1.67-1.62 (4H, m, *J* 7.5, Ar-CH<sub>2</sub>CH<sub>2</sub>), 1.37-1.33 (8H, m, CH<sub>2</sub>), 1.07-1.03 (6H, t, *J* 7.5, OCH<sub>2</sub>Me), 0.93-0.88 (6H, m, CH<sub>2</sub>Me); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$  168.1 (CO), 145.2 (C), 142.7 (C), 137.8 (C), 133.3 (CH), 131.8 (CH), 129.9 (C), 128.4 (CH), 128.3 (CH), 61.3 (CH<sub>2</sub>), 35.8 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>).

Compound (**9**) :



Diethyl 4,4''-dipentyl-[1,1':3',1''-terphenyl]-4',6'-dicarboxylate **8** (0.41 g, 0.8 mmol) was dissolved in methane sulfonic acid (8 ml) and stirred 30 minutes at 120 °C. The solution was then poured into 10 % aqueous sodium hydroxide to pH=14. The precipitate formed was collected by filtration, washed with 150 ml water, dissolved in 200 ml of dichloromethane, re-filtered over 4cm of silica gel, the solvent was removed *in vacuo*. Dione **9** was obtained as a red solid (0.215 g, 61%); mp 195-197 °C (from dichloromethane)  $\nu_{\max}/\text{cm}^{-1}$  2927, 2908, 2887, 1703 (CO), 1595, 1232, 1120, 781, 544;  $^1\text{H}$  NMR (300 MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.86 (1H, d,  $J$  0.6, Ar-H), 7.59 (1H, d,  $J$  0.6, Ar-H), 7.52 (2H, s, Ar-H), 7.51-7.50 (2H, m, Ar-H), 7.36-7.33 (2H, dd,  $J$  7.8, 1.5, Ar-H), 2.67-2.62 (4H, t,  $J$  7.5, Ar-CH<sub>2</sub>CH<sub>2</sub>), 1.67-1.59 (4H, m,  $J$  7.5, Ar-CH<sub>2</sub>CH<sub>2</sub>), 1.34-1.25 (8H, m, CH<sub>2</sub>), 0.92-0.88 (6H, m, CH<sub>2</sub>Me);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  192.3 (CO), 152.0 (C), 146.2 (C), 140.6 (C), 135.4 (C), 134.8 (CH), 134.5 (C), 124.6 (CH), 121.0 (CH), 120.2 (CH), 111.9 (CH), 36.0 (CH<sub>2</sub>), 31.5 (CH<sub>2</sub>), 31.0 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>).

Compound (**10**) :



Dione **9** (0.264 g, 0.6 mmol) and malononitrile (0.793 g, 12 mmol) were dissolved in dry acetonitrile (25 ml) under argon atmosphere. Pyridine (1.2 ml, 15 mmol) and acetic acid (0.424 ml, 7.5 mmol) were added via syringe. The resulting mixture was stirred 72 hours at reflux. Upon cooling, water (50 mL) was added and the red precipitate formed was filtered off, washed several times with water and acetone. The filtrate was suspended in 20 ml of chloride methylene with magnetically stirred, during 20 min. The suspension was filtered and the resulting precipitate (**10**) was dried in an oven at 80 °C overnight (0.161, 52%); mp 332-335 °C (from dichloromethane)  $\nu_{\max}/\text{cm}^{-1}$  2945, 2899, 2881, 2226 (CN), 1608, 1558, 1458, 1377, 1265, 902, 847, 752, 586  $^1\text{H}$  NMR  $\delta_{\text{H}}$  (300 MHz;  $\text{CDCl}_3$ ) 9.12 (1H, s, Ar-H), 8.23 (1H, s, Ar-H), 7.72 (2H, s, Ar-H), 7.61-7.59 (2H, d,  $J$  7.8 Ar-H), 7.36-7.33 (2H, dd,  $J$  7.8, Ar-H), 2.71-2.66 (4H, t,  $J$  7.5, Ar-CH<sub>2</sub>CH<sub>2</sub>), 1.64-1.58 (4H, m, Ar-CH<sub>2</sub>CH<sub>2</sub>), 1.35-1.30 (8H, m, CH<sub>2</sub>), 0.88-0.84 (6H, m, CH<sub>2</sub>Me).

## Electrochemistry

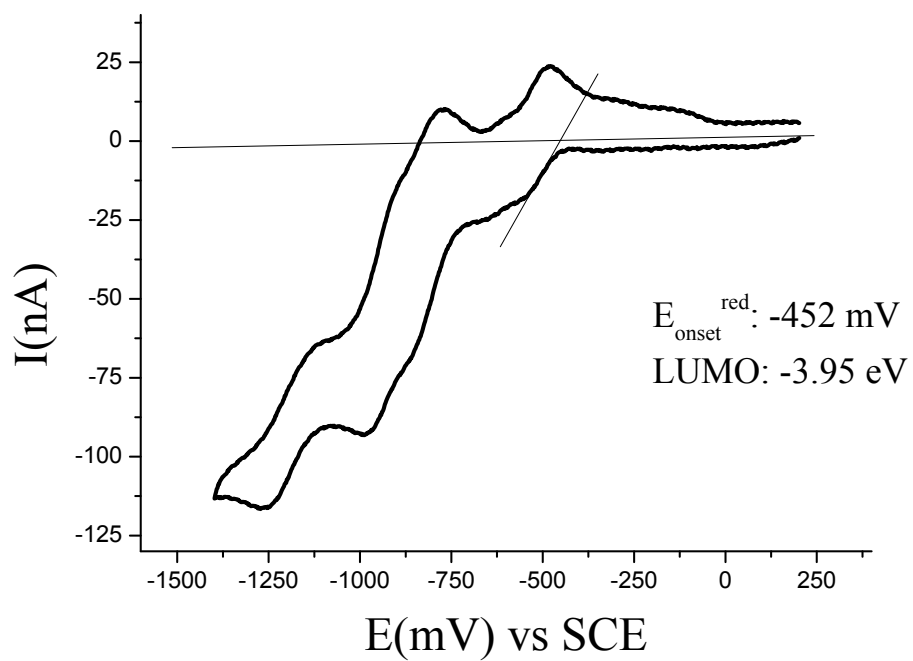


Fig. S1: Cyclic voltammetry at 0.1 V/s in THF/[NBu<sub>4</sub>][PF<sub>6</sub>] 0.2 M in presence of **(10)**, platinum disk working electrode.

## Organic Field Effect transistor

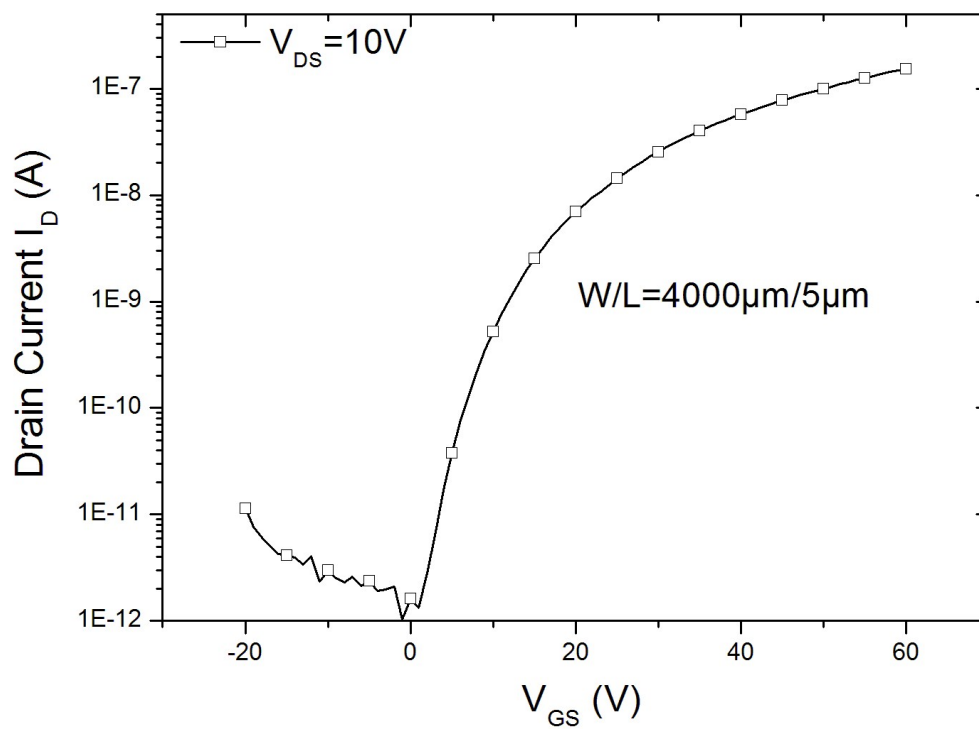


Fig S2. Transfer characteristics in linear regime ( $V_{DS}=10V$ ) of **(10)**-based OFET -  $\mu FE = 1.09 \times 10^{-4} \text{cm}^2/\text{V.s}$