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Supporting Information

Poly-(3-hexylthiophene) bottlebrush copolymers with tailored side-chain lengths and high charge carrier mobilities

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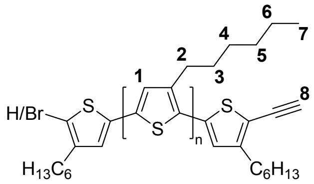
1.Synthesis

1.1. Synthesis of P3HT-Alkyne:

*General procedure for the synthesis of alkyne functionalized P3HT (**P3HT-Alkyne 1-4**):*



The alkyne functionalized P3HT polymers were synthesized according to a reported procedure.[1] A 0.5 M LiCl solution was prepared first by weighing LiCl into a Schlenk flask and subsequently drying for 4 h *in vacuo* at 140 °C. Anhydrous THF was added and the solution was stirred overnight to assure a complete dissolution of the LiCl. The Grignard reagents *t*-BuMgCl and EthynylMgCl were titrated prior to their use according to a published procedure.[2] A dry Schlenk flask was charged with one equivalent 2,5-dibromo-3-hexylthiophene under N_2 atmosphere. 2 mL of the 0.5 M LiCl solution in THF were added for every mmol 2,5-dibromo-3-hexylthiophene. 0.96 equivalents t-BuMgCl were added and the solution was stirred for 24 h to ensure the complete formation of the active Grignard species. The solution was diluted with 7.2 mL THF for every mmol 2,5-dibromo-3-hexylthiophene and the polymerization was started by adding Ni(dppp)Cl_2 (suspension in THF). It is possible to adjust the molecular weight of the polymer by changing the ratio of monomer:Ni(dppp)Cl_2 due to the controlled nature of the polymerization. The polymerization was terminated by adding 0.2 equivalents EthynylMgCl after 30 min. The solution was stirred for further 15 min and the polymer was subsequently precipitated in methanol. The polymer was dried and redissolved in $CHCl_3$. The solution was filtered over a short aluminum oxide column to remove residual LiCl and Ni(dppp)Cl_2, evaporated with the rotary evaporator to get a concentrated solution, and precipitated again in methanol.

Synthesis of ***P3HT-Akyne 1*** *and* ***2****:* The polymerization was carried out at a monomer:Ni(dppp)Cl_2 ratio of 1: 0.06. The major part of obtained P3HT-Alkyne coupled after precipitation as observed by SEC. The raw product was fractioned to recover the uncoupled product. Two fractions **P3HT-Alkyne 1** and **2** were obtained. **P3HT-Alkyne 1** with a lower molecular weight was soluble in Acetone and **P3HT-Alkyne 2** was soluble in a 1:1 mixture of Acetone:Hexane. Both fractions were freeze dried from benzene and obtained as red sticky solids. The residual polymer contained mainly coupled species and was discarded.

P3HT-Alkyne 1 m = 589 mg, $M_{n,SEC}$ = 2,000 g mol^{-1}, $M_{n,MALDI}$ = 1,600 g mol^{-1}, Đ = 1.57

^{1}H NMR (300 MHz, $CHCl_3$): δ (ppm) 6.97 (s, 1H, H-1), 3.53 (s, 1H, H-8), 2.85-2.4 (t, 2H, H-2), 1.80-1.60 (m, 2H, H-3), 1.50-1.25 (m, 6H, H-4 H-5 H-6), 0.98-0.83 (m, 3H, H-7).

IR(ATR): ν(cm^{-1}) 3310 (C≡C-H2), 2095 (C≡C)

P3HT-Alkyne 2 m = 450 mg, $M_{n,SEC}$ = 3,800 g/mol, $M_{n,MALDI}$ = 2,000 g/mol, Đ = 1.36

^{1}H NMR (300 MHz, $CHCl_3$): δ (ppm) 6.98 (s, 1H, H-1), 3.52 (s, 1H, H-8), 2.85-2.4 (m, 2H, H-2), 1.80-1.60 (m, 2H, H-3), 1.50-1.25 (m, 6H, H-4 H-5 H-6), 0.98-0.83 (m, 3H, H-7).

IR(ATR): ν(cm^{-1}) 3311 (C≡C-H), 2096 (C≡C)

Synthesis of ***P3HT-Alkyne 3****:* The polymerization was carried out at a monomer:Ni(dppp)Cl_2 ratio of 1: 0.02. The polymer was obtained as a dark solid after one additional precipitation in hexane. m = 695 mg, $M_{n,SEC}$ = 9,300 g mol^{-1}, $M_{n,MALDI}$ = 6,650 g mol^{-1}, Đ = 1.13

^{1}H NMR (300 MHz, $CHCl_3$): δ (ppm) 6.98 (s, 1H, H-1), 3.52 (s, 1H, H-8), 2.85-2.4 (m, 2H, H-2), 1.80-1.60 (m, 2H, H-3), 1.50-1.25 (m, 6H, H-4 H-5 H-6), 0.98-0.83 (m, 3H, H-7).

IR(ATR): ν(cm^{-1}) 3313 (C≡C-H), 2096 (C≡C)

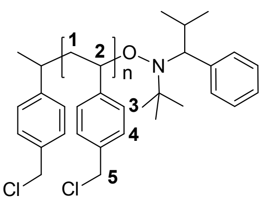
Synthesis of ***P3HT-Alkyne 4****:* The polymerization was carried out at a monomer:Ni(dppp)Cl_2 ratio of 1: 0.0125.

2.75 g, $M_{n,SEC}$ = 17,400, $M_{n,MALDI}$ = 11,400 g/mol; Đ = 1.15

^{1}H NMR (300 MHz, $CHCl_3$): δ (ppm) 6.98 (s, 1H, H-1), 3.53 (s, 1H, H-8), 2.85-2.4 (m, 2H, H-2), 1.80-1.60 (m, 2H, H-3), 1.50-1.25 (m, 6H, H-4 H-5 H-6), 0.98-0.83 (m, 3H, H-7).

IR(ATR): ν(cm^{-1}) 3312 (C≡C-H), 2096 (C≡C).

1.2. Synthesis of Poly(4-chloromethylstyrene) (**PS-Cl**)

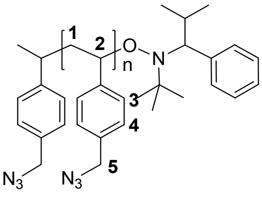


A dry 10 mL Schlenk flask was charged with 123.4 mg (0.33 mmol) *N*-*t*-Butyl-*O*-[1-[4-(chloromethyl)phenyl]ethyl]-*N*-(2-methyl-1-phenylpropyl)hydroxylamine (**2**), 726.1 µg (3.3 µmol) 2,2,5-Trimethyl-4-phenyl-3-azahexane-3-nitroxide (**3**) and 1,445.6 mg 4-chloromethyl-styrene (**1**). 1.3 mL anisole were added and the solution was degassed by four freeze-pump-thaw cycles. The polymerization was initiated by immersion into an oil bath at 125 °C. The conversion was monitored via NMR and the reaction was terminated after 180 min (Conversion = 85 %) by the immersion of the reaction vessel into liquid nitrogen. The polymer was obtained by precipitation into methanol.

m = 1.1 g, $M_{n,SEC}$ = 3,100 g mol^{-1}; Đ = 1.25

^{1}H NMR (300 MHz, $CHCl_3$): δ (ppm) 7.2-6.2 (b, 4H, H-3,H-4), 4.6-4.2 (b, 2H, H-5), 2.6-0.4 (m, 3H, H-1, H-2).

1.3. Synthesis of Poly(4-azidomethylstyrene) (**PS-N$_3$**)



In a dry 25 ml Schlenk flask 400 mg (2.62 mmol chlorine groups) of polymer **4** was dissolved in 10 mL dimethylformamide and 1.7 g (26.2 mmol) sodium azide was added. The reaction was stirred at room temperature for 24 h. After that 15 mL pentane was added and the mixture was washed twice with distilled water. Dichloromethane was added to the turbid organic layer and the mixture was filtered. The polymer was obtained after precipitation from methanol.

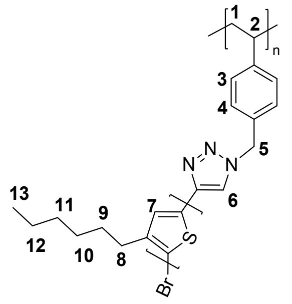
183.7 mg, $M_{n,SEC}$ =3,600 Đ = 1.21

^{1}H NMR (300 MHz, $CHCl_3$): δ (ppm) 7.2-6.2 (b, 4H, H-3,H-4), 4.4-4.0 (b, 2H, H-5), 2.6-0.4 (m, 3H, H-1, H-2).

IR(ATR): ν(cm^{-1}) 2086 (N_3).

1.4. Synthesis of Poly(4-methylstyrene)-*g*-P3HT (**Brush 1-4**)

General procedure for ***Brush 1-4:***



A dry roundbottom flask was charged with poly(4-azidomethylstyrene) (**5**) and with 1.1–1.5 equivalents of an alkyne functionalized P3HT (**P3HT-Alkyne 1-4**). The polymers were dissolved in o-dichlorobenzene. The solution was degassed by purging with nitrogen for 20 min and was heated to 90 °C. After that a degassed stock solution of CuBr/PMDETA was added and the reaction was stirred for 24 h. The reaction mixture was filtered over a short aluminum oxide column and the raw polymers were obtained after precipitation in methanol.

Synthesis of ***Brush 1****:* 375 mg ($3.1 \cdot 10^{-1}$ mmol) **P3HT-Alkyne 1** and 42.0 mg ($2.6 \cdot 10^{-1}$ mmol azide groups) poly(4-azidomethyl-styrene) (**5**) were dissolved in 15 mL o-dichlorobenzene. 0.25 mL of the catalyst stock solution were added. The raw product could be purified from the excess of linear P3HT by preparative SEC.

m = 68 mg, $M_{n,SEC}$ = 21,000 g/mol, Đ = 1.21

^{1}H NMR (300 MHz, $CHCl_3$): δ (ppm) 8.4-7.4 (b, 1H; H-6), 7.2-6.0 (4H, H-1, H-2), 6.96 (s, 1H, H-7), 6.0-5.0 (b, 2H,H-5), 2.85-2.4 (t, 2H, H-8), 1.80-1.60 (m, 2H, H-9), 1.50-1.25 (m, 6H, H-10 H-11 H-12), 0.98-0.83 (m, 3H, H-13).

IR(ATR): ν(cm^{-1}) 2095 (C≡C).

Synthesis of ***Brush 2****:* 270 mg ($1.1 \cdot 10^{-1}$ mmol) **P3HT-Alkyne 2** and 14.7 mg ($9.3 \cdot 10^{-2}$ mmol azide groups) poly(4-azidomethyl-styrene) (**5**) were dissolved in 10 mL o-dichlorobenzene. 0.25 mL of the catalyst stock solution were added. The raw product could be purified from the excess of linear P3HT by preparative SEC.

m = 108 mg, $M_{n,SEC}$ = 36,500 g/mol, Đ = 1.22

^{1}H NMR (300 MHz, $CHCl_3$): δ (ppm) 8.4-7.4 (b, 1H; H-6), 7.2-6.0 (4H, H-1, H-2), 6.96 (s, 1H, H-7), 6.0-5.0 (b, 2H,H-5), 2.85-2.4 (t, 2H, H-8), 1.80-1.60 (m, 2H, H-9), 1.50-1.25 (m, 6H, H-10 H-11 H-12), 0.98-0.83 (m, 3H, H-13).

IR(ATR): ν(cm^{-1}) 2096 (C≡C).

Synthesis of ***Brush 3****:* 110 mg ($1.5 \cdot 10^{-2}$ mmol) **P3HT-Alkyne 3** and 2679 µg ($1.6 \cdot 10^{-2}$ mmol azide groups) poly(4-azidomethyl-styrene) (**5**) were dissolved in 10.2 mL o-dichlorobenzene. 1 mL of the catalyst stock solution was added. The raw product could be purified from the excess of linear P3HT by preparative SEC.

m = 90 mg, $M_{n,SEC}$ = 97,000 g/mol, Đ = 1.09

^{1}H NMR (300 MHz, $CHCl_3$): δ (ppm) 8.0-7.6 (b, 1H; H-6), 7.2-6.0 (4H, H-1, H-2), 6.98 (s, 1H, H-7), 6.0-5.0 (b, 2H,H-5), 2.85-2.4 (t, 2H, H-8), 1.80-1.60 (m, 2H, H-9), 1.50-1.25 (m, 6H, H-10 H-11 H-12), 0.98-0.83 (m, 3H, H-13).

Synthesis of ***Brush 4****:* 500 mg ($4.3 \cdot 10^{-2}$ mmol) **P3HT-Alkyne 4** and 5282 µg ($2.4 \cdot 10^{-2}$ mmol azide groups) poly(4-azidomethyl-styrene) (**5**) were dissolved in 20.4 mL o-dichlorobenzene. 2 mL of the catalyst stock solution were added. The raw product could be purified from the excess of linear P3HT by washing the polymer with THF at room temperature.

m = 139.2 mg, $M_{n,SEC}$ = 144,000 g/mol, Đ = 1.37

^{1}H NMR (300 MHz, $CHCl_3$): δ (ppm) 6.98 (s, 1H, H-7), 2.85-2.4 (t, 2H, H-8), 1.80-1.60 (m, 2H, H-9), 1.50-1.25 (m, 6H, H-10 H-11 H-12), 0.98-0.83 (m, 3H, H-13).

2. Additional Measurements

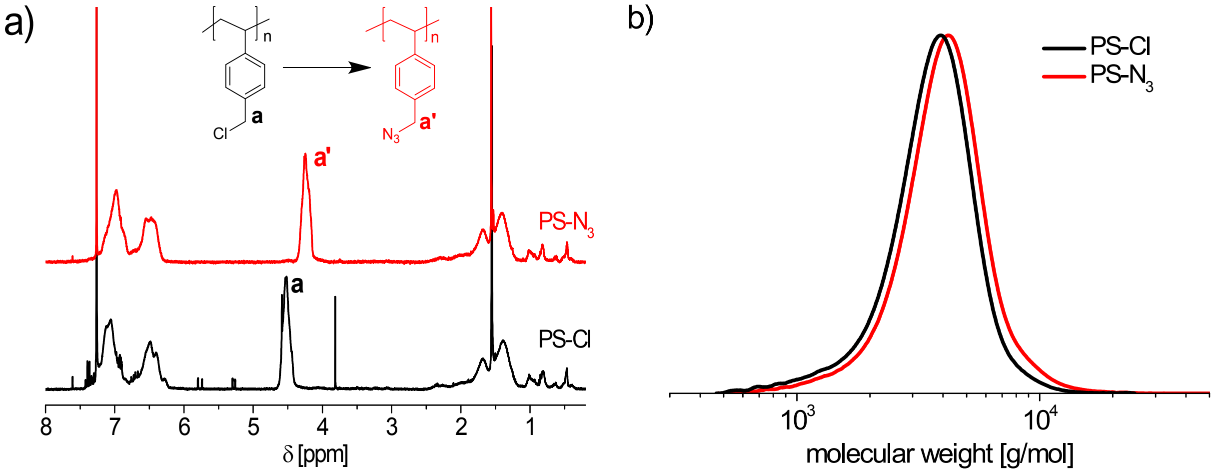


Fig. S1. a) ^{1}H-NMR spectra of **PS-Cl** and **PS-N$_3$**, the shift of the peak at around 4.4 ppm (**a**) in **PS-N$_3$** to 4.2 ppm (**a'**) in **PS-Cl** is a strong indicator for a quantitative substitution of chlorine with azide; b) SEC traces of **PS-Cl** and **PS-N$_3$**

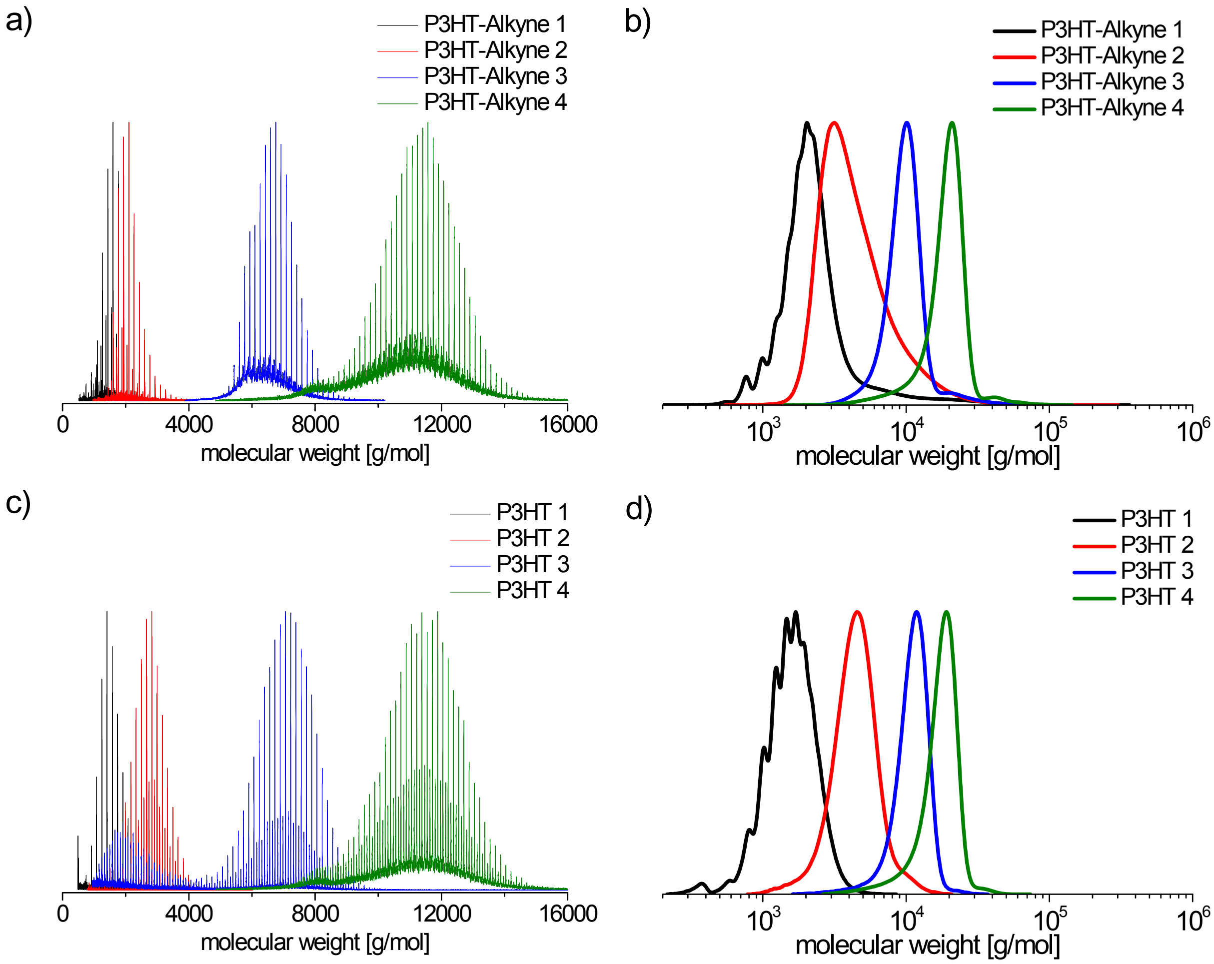


Fig. S2. Maldi-Tof MS of **P3HT-Alkyne 1-4** (a) and **P3HT 1-4** (c) and SEC traces of **P3HT-Alkyne 1-4** (b) and **P3HT 1-4** (d)

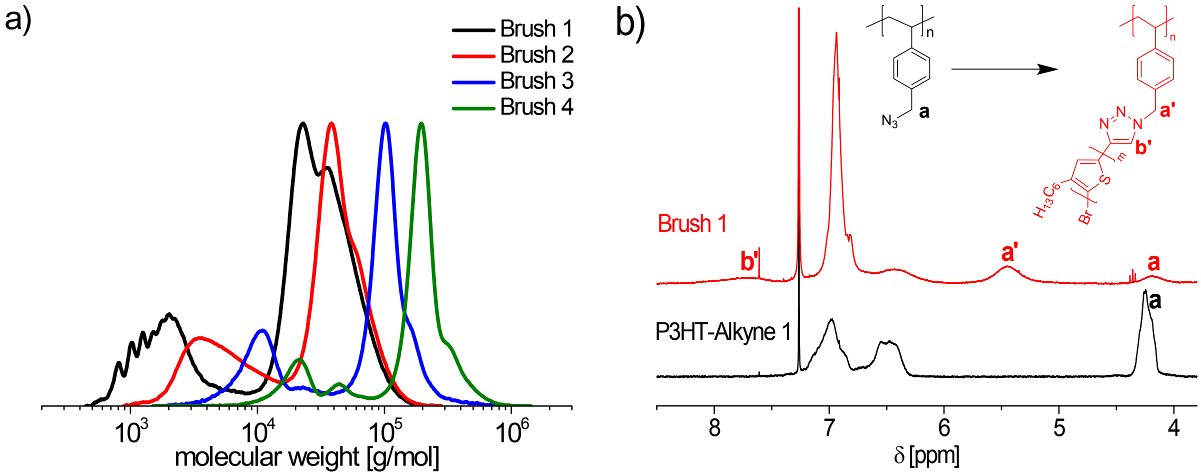


Fig. S3. a) SEC traces of the raw brush polymers **Brush 1-4**. All unpurified brush polymers still contain P3HT-Alkyne. b) Detail of the ^{1}H-NMR spectra of **P3HT-Alkyne 1** and **Brush 1** between 3.5 and 8.5 ppm. Two new peaks emerge in the brush polymer. The peak at 5.4 ppm (**a'**) belongs to the methyl group next to the triazole and the peak at above 7.5 ppm (**b'**) is assigned to the triazole itself. The peak at 4.4 ppm (**a**) is an indicator for a non-quantitative reaction as it can be found in the same position in **PS-N$_3$**.

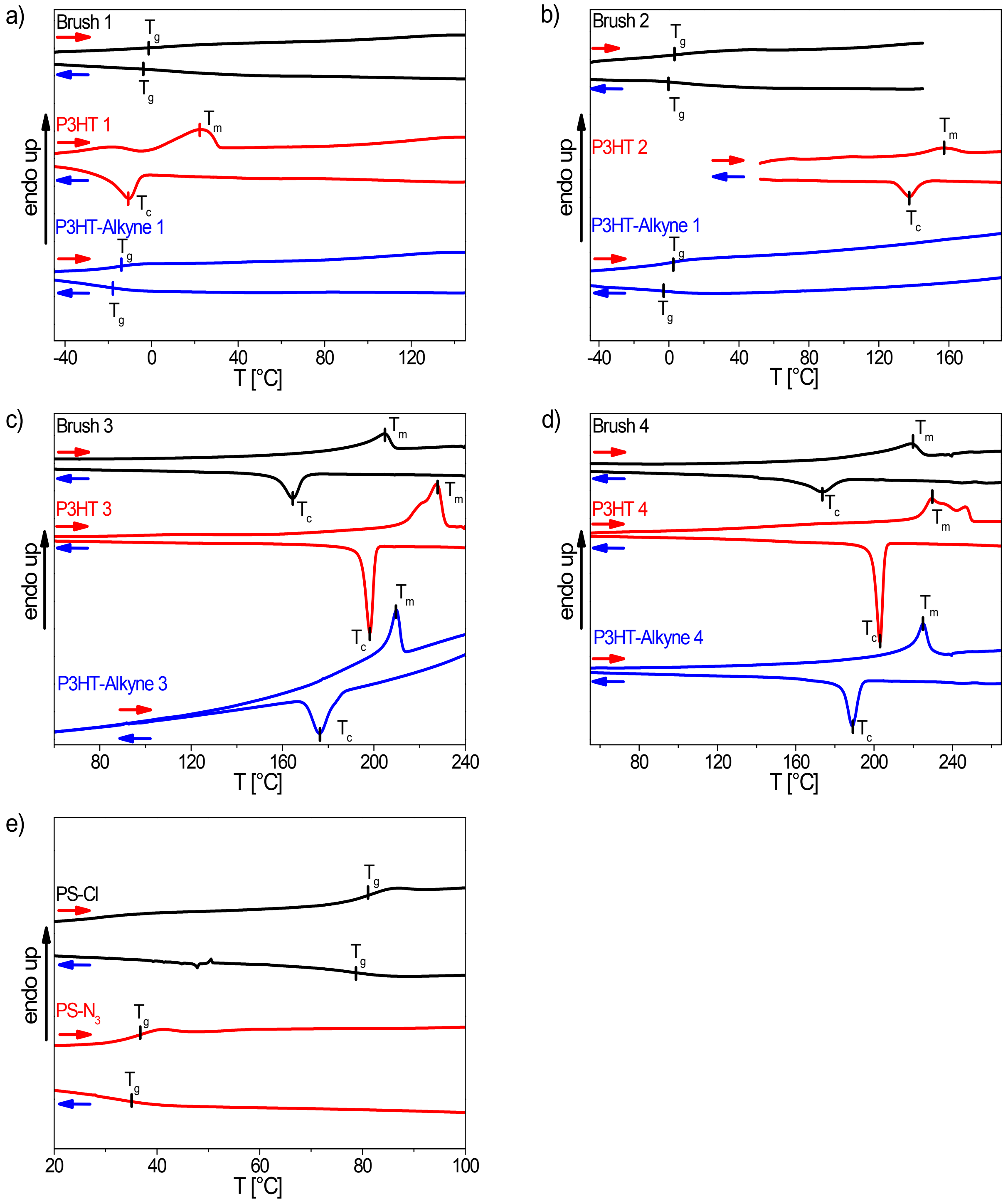


Fig. S4. DSC measurements of **Brush 1-4**, **P3HT-Alkyne 1-4** and **P3HT 1-4** (a-d) and **PS-Cl** and **PS-N**$_3$ (e) at a heating/cooling rate of 10 K/min

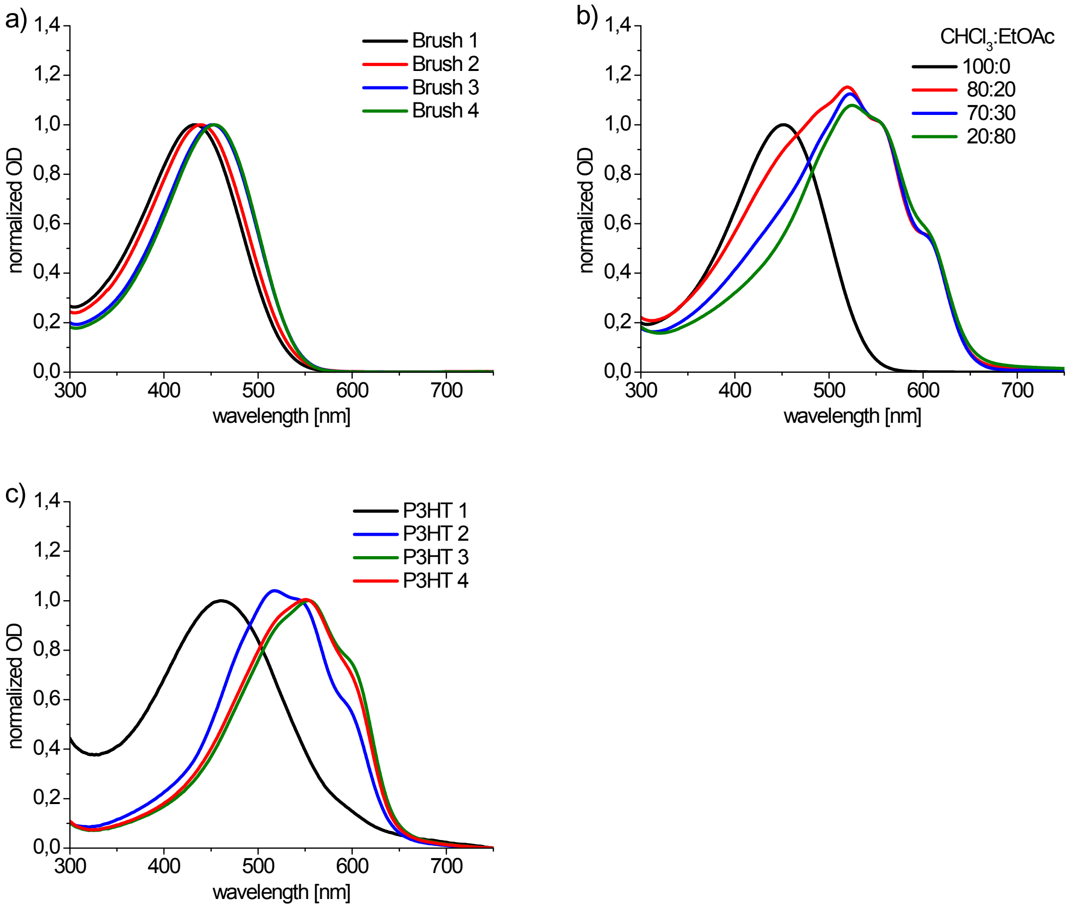


Fig. S5. a) normalized UV-Vis spectra of **Brushes 1-4** in chloroform solutions; b) UV-Vis spectra of **Brush 3** in a mixture of good solvent (CHCl$_3$) and a bad solvent (EtOAc); c) as-cast films of **P3HT 1-4** on ODTS treated glass substrates

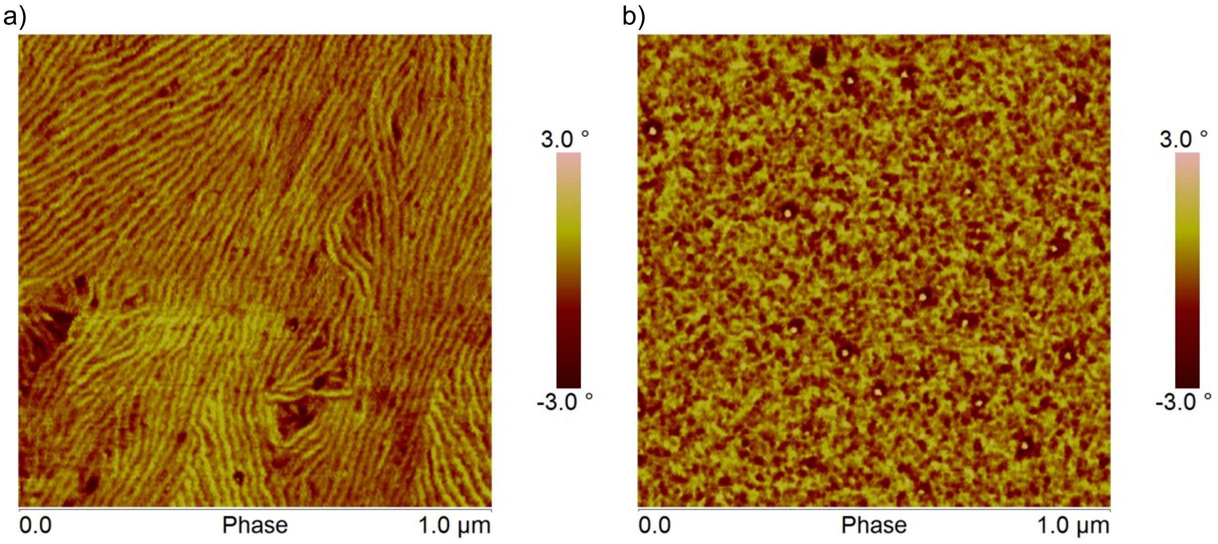


Fig. S6. AMF phase image of **P3HT 3** (a) and **Brush 3** (b) after melt crystallization

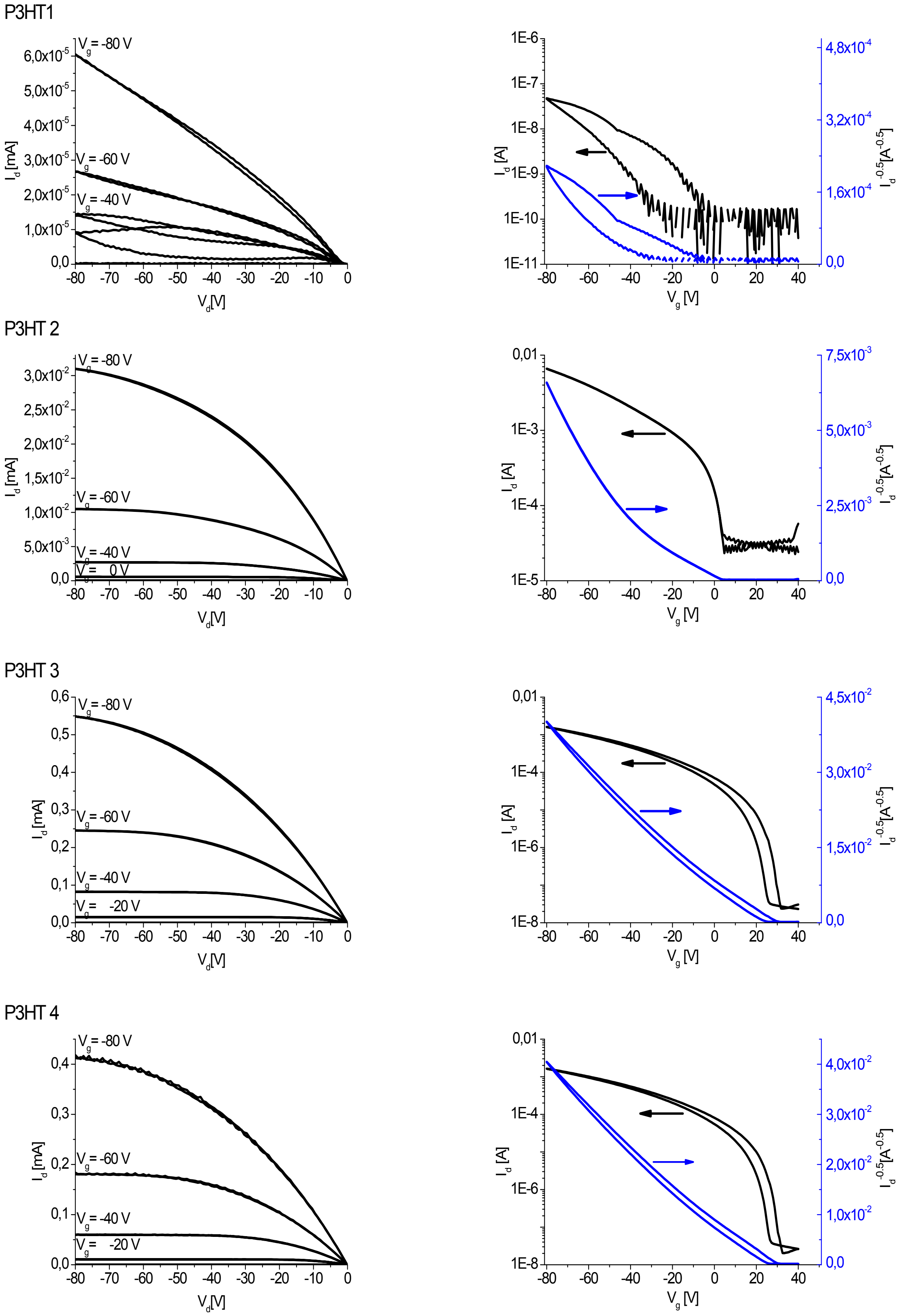
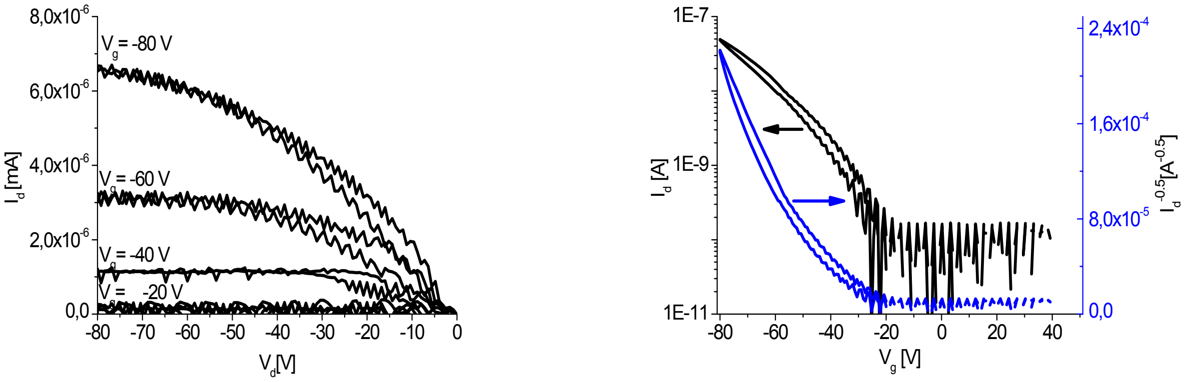
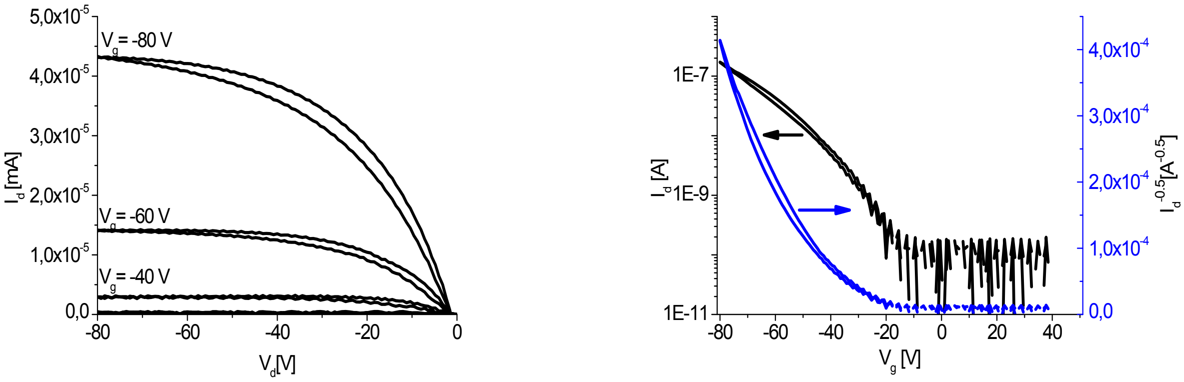


Fig. S7. p-output curves (left) and p-transfer curves (right) of the as-cast **P3HT 1-4**

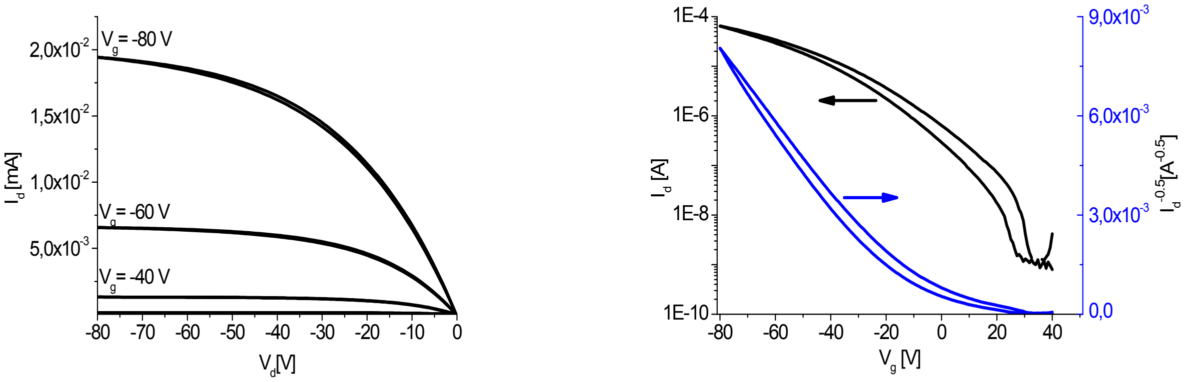
Brush 1



Brush 2



Brush 3



Brush 4

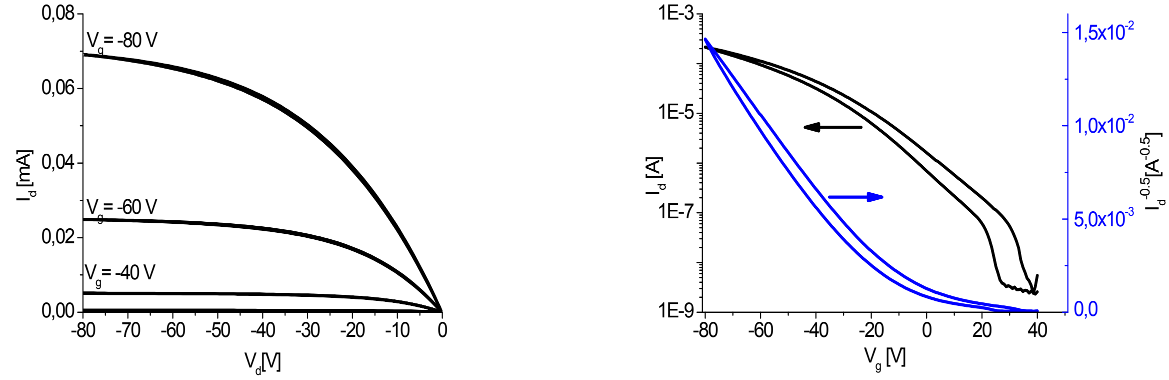


Fig. S8. p-output curves (left) and p-transfer curves (right) of the as-cast **Brush 1-4**

Brush 3 melt crystallized

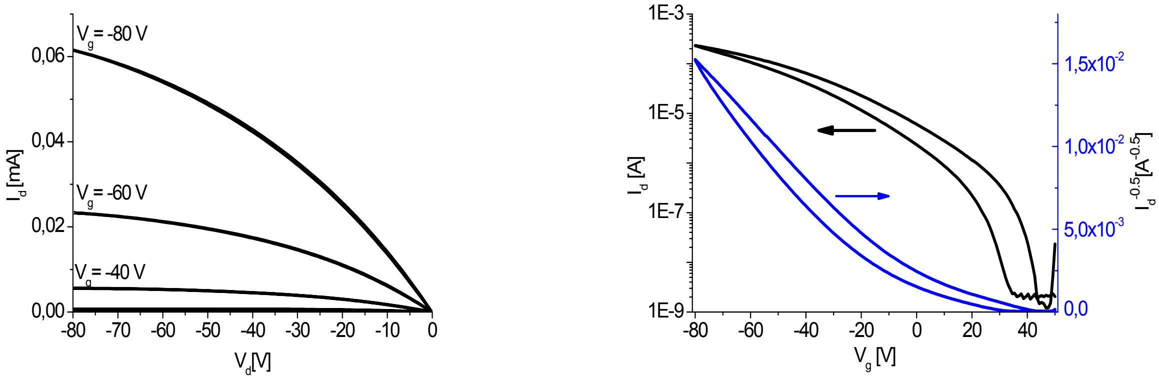


Fig. S9. p-output curve (left) and p-transfer curve (right) of the melt crystallized **Brush 3**

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1 R.H. Lohwasser and M. Thelakkat, *Macromolecules*, 2012, **45**, 3070.

2 A. Krasovskiy and P. Knochel, *Synthesis*, 2006, **5**, 0890.