

Synthesis of polyphthalaldehyde-based block copolymers: utilization of a thermo-sacrificial segment for an easy access to fine-tuned poly(3-hexylthiophene) nanostructured films

Supporting Information:

Representative synthesis of alkyne-terminated P3HT (HC≡C-P3HT) by GRIM. In a previously flamed and dried round-bottom flask, 2,5-dibromo-3-hexylthiophene (0.6 mL, 2.8 mmol) was dissolved in 13 mL of THF. To this solution was added isopropylmagnesium chloride (1.4 mL, 2.8 mmol) to form the Grignard reagent. After 30 min at 0°C, the solution was transferred by cannula and under nitrogen to a suspension of Ni(dppp)Cl₂ (16.8 mg, 0.03 mmol) dispersed in THF (7 mL). After 1 h at 0°C, the iced bath was removed to slowly let the medium warming up to ambient temperature. Once at r.t., 15 mL of anhydrous THF were added to the mixture. After complete solubilization, 0.5 mL of ethynylmagnesium chloride (0.25 mmol, 8 eq / Ni(dppp)Cl₂) was introduced to the reaction flask. After 30 min, the polymer was precipitated in cold methanol. To avoid possible end-group alteration,⁵⁷ no Soxhlet extraction was performed. The as-obtained solid was then isolated by filtration from the methanol fraction and directly washed with an excess of methanol, acetone and hexane to remove residual metal salts, unreacted monomers and oligomers. Yield = 46 %. ¹H NMR (500 MHz, CDCl₃, δ ppm): 6.98 (s, 1H), 3.53 (s, 1H), 2.80 (t, 2H), 1.72 (m, 2H), 1.40-1.30 (m, 6H) 0.9 (s, 3H); SEC: M_n = 20300 g mol⁻¹, Đ_M = 1.20; MALDI-ToF: m/z: 16733 (calcd: 16733, DP of 100, alkyne / Br end-groups).

Representative synthesis of azido-terminated PPA (N₃-PPA). In a glovebox, a previously flamed-dried round bottom flask (of 25 mL) was charged with the PA monomer (500 mg, 3.71×10⁻³ mol) solubilized in 10 g of dried dichloromethane (DCM). The flask was then

sealed with a septum and immersed in a -85°C cooling bath out of the box. Then, in a glovebox, the P_1 -*t*-Bu catalyst (3.6 mg , $1.54 \times 10^{-5}\text{ mol}$) and the 11-azido-1-undecanol initiator (6.60 mg , $3.09 \times 10^{-5}\text{ mol}$) were solubilized by $300\text{ }\mu\text{L}$ of DCM. In a cold room thermostated at 5°C , the activated initiator solution was transferred to the monomer one always kept at -85°C . After 15 minutes, a DCM solution of 2-bromoethyl isocyanate quenching agent (7.0 mg , $4.67 \times 10^{-5}\text{ mol}$ in $300\text{ }\mu\text{L}$ of DCM) was injected to the polymerization medium. The solution was kept under agitation at -85°C for an extra 30 min prior to its precipitation into cold methanol. The azido-terminated polyphthalaldehyde was then filtered out and dried at r.t. until constant weight. Yield = 87 %; SEC: $M_n = 16\,800\text{ g mol}^{-1}$, $\bar{D}_M = 1.42$; MALDI-ToF: m/z : 17153 (calcd: 17153, DP of 125, N_3 / Br end-groups)

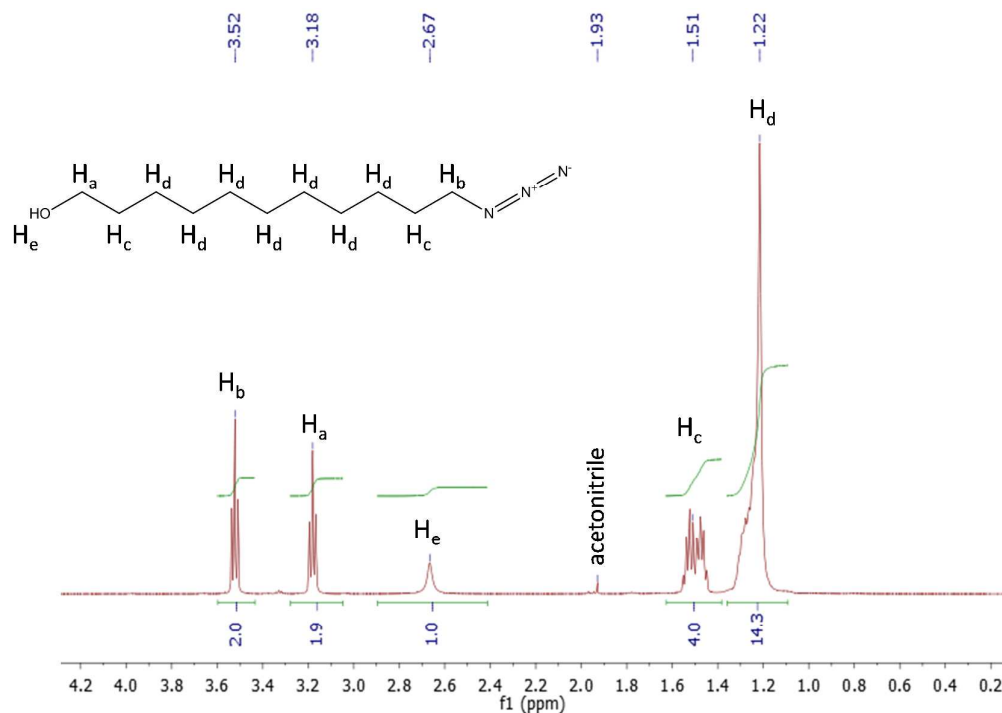


Figure S1 ^1H NMR spectrum of 11-azido-1-undecanol

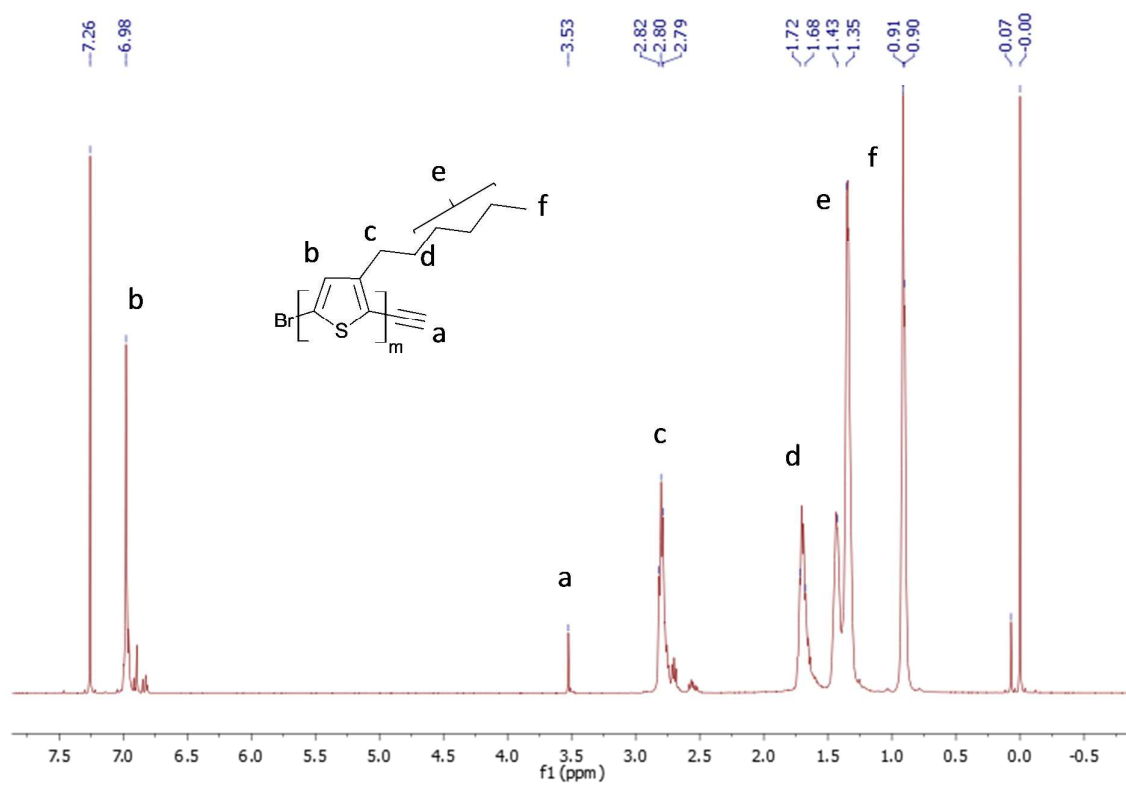


Figure S2 ^1H NMR P3HT₂₇

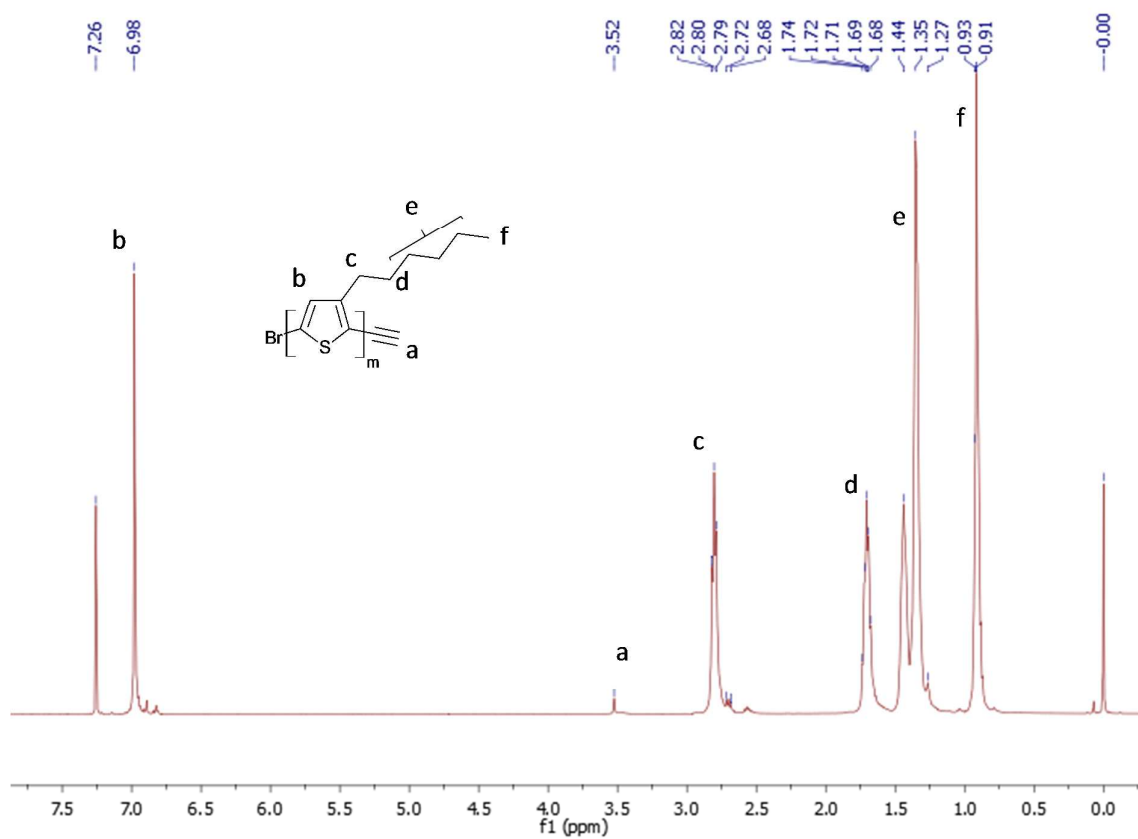


Figure S3 ^1H NMR P3HT₅₄

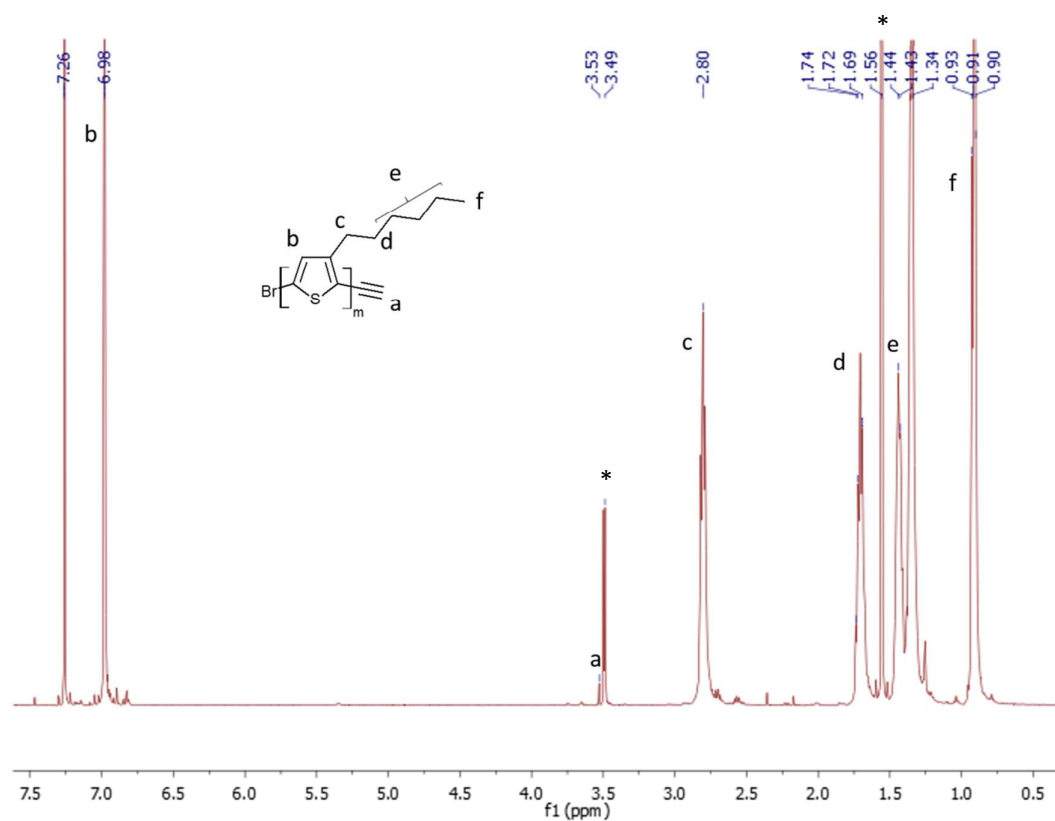


Figure S4 ¹H NMR P3HT₇₈ (* refer to methanol signals)

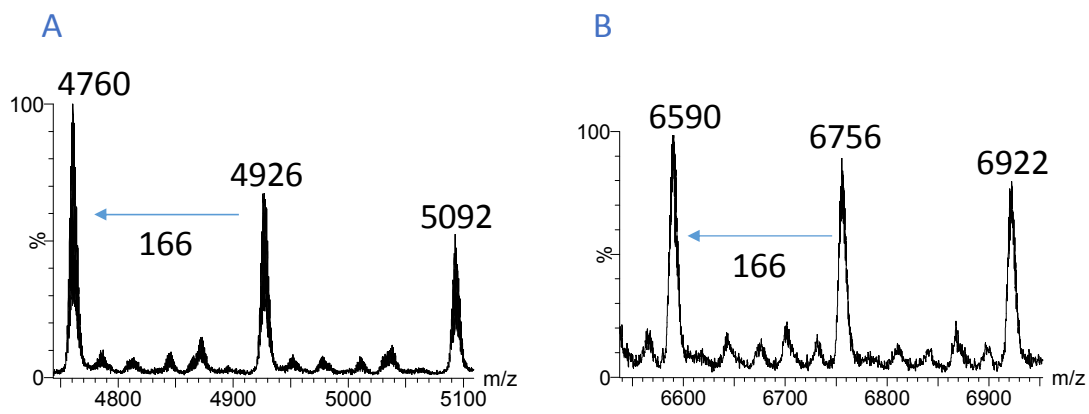


Figure S5 MALDI-(+)-ToF-MS spectrum of P3HT A and B; simulation of 30 monomer units, $C_{300}H_{420}S_{30}BrC_2H$: 5092 g mol⁻¹; simulation of 40 monomer units, $C_{400}H_{560}S_{40}BrC_2H$: 6756 g mol⁻¹

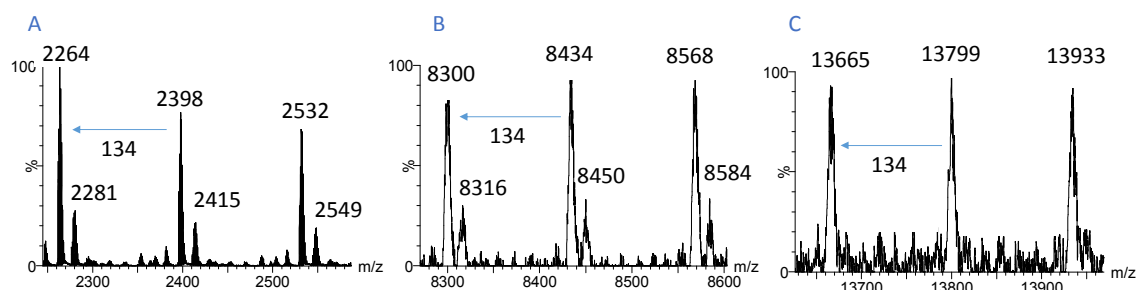


Figure S6 MALDI-(+)-ToF-MS spectrum of PPA₂₅ (A), PPA₇₀ (B), PPA₁₂₅ (C); simulations of 15 monomer units, $C_{120}H_{90}O_{30}C_{11}H_{22}ON_3C_3H_5ONBrNa$: 2398 g mol⁻¹ and $C_{120}H_{90}O_{30}C_{11}H_{22}ON_3C_3H_5ONBrK$: 2415 g mol⁻¹; simulations 60 monomer units, $C_{480}H_{360}O_{120}C_{11}H_{22}ON_3C_3H_5ONBrNa$: 8434 g mol⁻¹ and $C_{480}H_{360}O_{120}C_{11}H_{22}ON_3C_3H_5ONBrK$: 8450 g mol⁻¹; simulations 100 monomer units, $C_{800}H_{600}O_{200}C_{11}H_{22}ON_3C_3H_5ONBrNa$: 13799 g mol⁻¹.

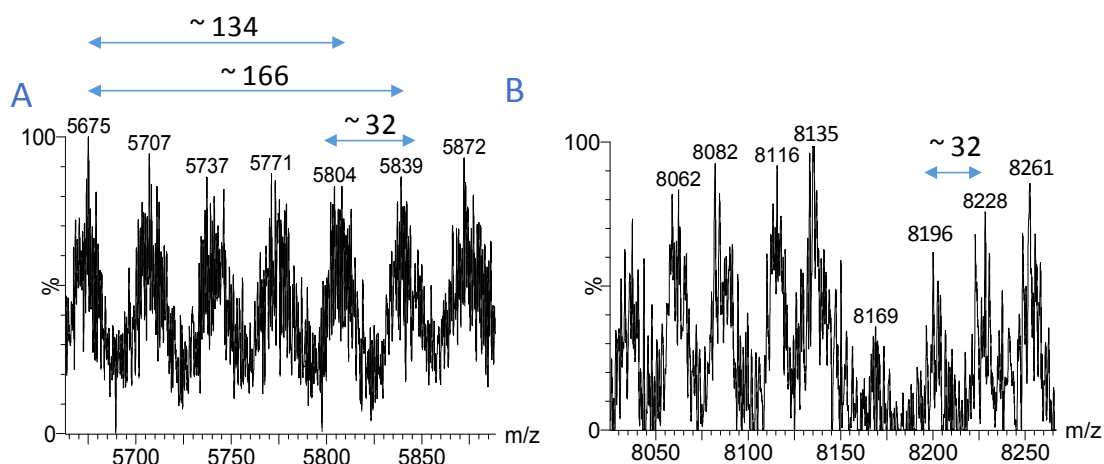


Figure S7 MALDI-(+)-ToF-MS analysis of P3HT₂₇-b-PPA₂₅ and P3HT₅₄-b-PPA₇₀

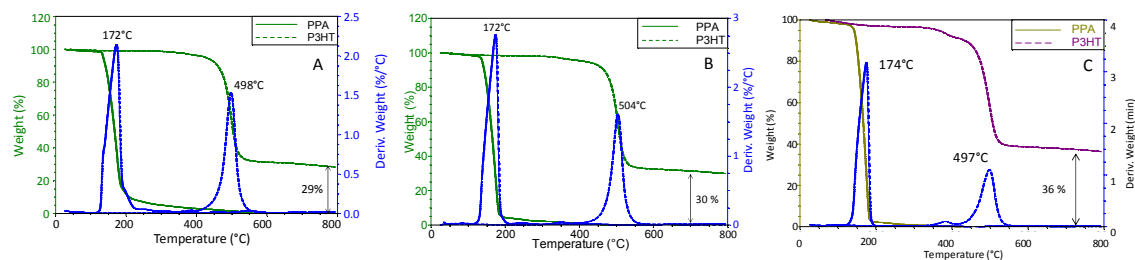


Figure S8 TGA of P3HT₂₇ and PPA₂₅, P3HT₅₄ and PPA₇₀ (B) and P3HT₇₈ and PPA₁₂₅ (C).

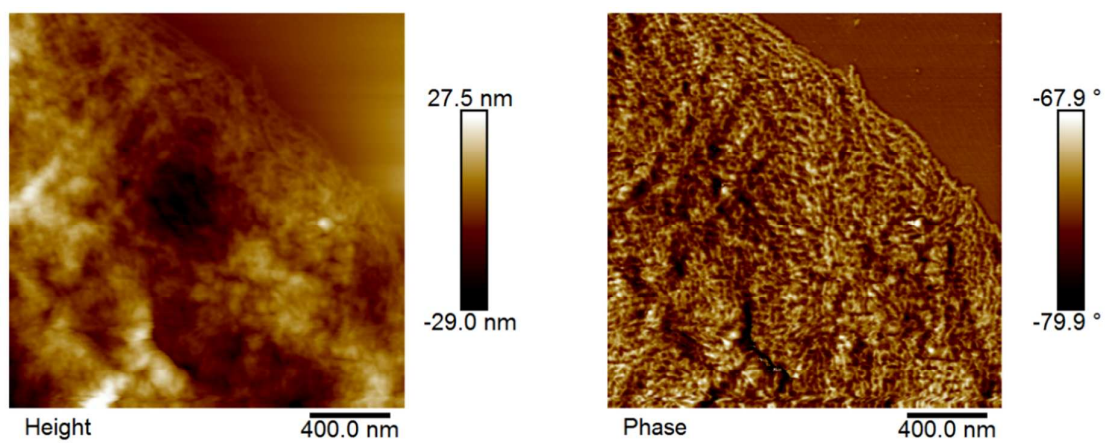


Figure S9 TM-AFM height (left) and phase (right) images of a thin film of P3HT₇₈ (13000 g.mol⁻¹).