

# Synthesis of amphiphilic rod-coil P3HT-*b*-P4VP carrying a long conjugated block using NMRP and Click Chemistry

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## Materials and Characterization

<sup>1</sup>H-NMR spectra were recorded in chloroform on a Bruker Avance 250 spectrometer at 300 MHz. Coupling constants are given in Hz. The spectra were calibrated according to the solvent signal at 7.26 ppm. Size exclusion chromatography measurements were performed utilizing a Waters 510 HPLC pump and stabilized THF with 0.25 wt% TBAB (tetrabutylammoniumbromide) as eluent at a flow rate of 0.5 mL/min. 100 µL of a solution was injected into a column setup comprising a guard column (PSS, 5 × 0.8 cm, SDV gel, particle size 5 µm, pore size 100 Å) and two separation columns (Varian, 30 × 0.8 cm, mixed C gel, particle size 5 µm). Polymer size distribution were monitored with a WATERS 486 tunable UV detector at 254 nm and a Waters 410 differential RI detector. Polystyrene was used as external standard and 1,2-dichlorobenzene as an internal standard for calibration. Matrix assisted laser desorption ionizations spectroscopy with time of flight detection mass spectroscopy (MALDI-TOF MS) measurements were performed on a Bruker Reflex III using dithranol as matrix and a mixture of 1000:1 (Matrix:Polymer). The Laser intensity was set to around 70%. Differential scanning calorimetry (DSC) measurements were done on a Perkin-Elmer Diamond DSC with a heating and cooling rate of 10 K/min. UV-vis measurements were performed with a U-3000 spectrometer from Hitachi. Sample for transmission electron spectroscopy were cut with a Ultramikrotom and measured on a Zeiss 9220mega. Dynamic light scattering measurements were done using an ALV DLS/SLS-SP 5022F compact goniometersystem with an ALV 5000/E cross correlator and a He-Ne laser (wavelength = 632.8 nm). The measurements were carried out in cylindrical scattering cells with a diameter of 10 mm at an angle of 90 ° and a temperature of 20 °C. The obtained correlation functions were analyzed with CONTIN algorithm and the apparent hydrodynamic radii were calculated according to the Stokes-Einstein equation. The samples were diluted before the measurement in a ratio of 1 to 3 with isopropanol to obtain good scattering intensity. It was controlled with UV-Vis that no change in the packing occurs by dilution.

The monomer 2,5-dibromo-3-hexylthiophene, the catalyst 1,3-bis(diphenylphosphino) propanenickel(II) chloride [Ni(dppp)Cl<sub>2</sub>] and 2,2,5-trimethyl-3-(10-p-azidomethylphenylethoxy)-4-phenyl-3-azahexane were synthesized according to the literature.<sup>1-3</sup> All glass apparatus for polymerization were heated and cooled down under argon. Dry THF was distilled over calcium hydride and potassium. Dry 1,2-dichlorobenzene, ethynylmagnesium chloride (0.6 M in THF/toluene) and *t*-BuMgCl (1.7 M in THF) were purchased from Acros and the Grignard reagents were titrated according to Krasovskiy and Knochel.<sup>4</sup> LiCl puriss p.a. water free was purchased from Fluka and dried prior to use. 4-Vinylpyridine (Aldrich, 95%) was dried over calciumhydride, distilled under reduced pressure, and degassed with nitrogen.

## Experimental Part

### Procedure for the Synthesis of P3HT-alkyne **4a** using LiCl

In a Schlenk flask LiCl was dried under vacuum at 140°C for 4h. After cooling to room temperature dry THF was added and stirred for 3 h to form at 0.5 M LiCl solution. In a dry schlenk flask 5.86 g (18 mmol) 2,5-dibromo-3-hexylthiophene was dissolved in 36 ml of 0.5 M LiCl solution and 13.1 ml (17.3 mmol) of *t*-BuMgCl were added with a syringe. After complete active Grignard monomer formation the solution was diluted with 129 ml dry THF. The polymerization was initiated with a suspension of 118 mg (0.22 mmol) Ni(dppp)Cl<sub>2</sub> in 1 mL THF. After 31 min the reaction was cooled with an ice bath and 9 ml (4.5 mmol) of ethynylmagnesium chloride were added with a syringe. After 11 min the reaction mixture was precipitated in MeOH. The polymer was dissolved two more times in CHCl<sub>3</sub>, filtrated and precipitated in MeOH. After filtration and drying under vacuum 1.98 g of the pure polymer were obtained.

SEC  $M_p = 23400 \text{ g mol}^{-1}$ ,  $M_n = 19200 \text{ g mol}^{-1}$ ,  $M_w = 21800 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.14$ ;

$\delta^1\text{H}$  (300 MHz;  $\text{CDCl}_3$ ) 6.98 (1 H, s,  $\text{H}_{\text{ar}}$ ), 3.52 (0.013 H, s, CH of alkyne end group) 2.80 (2 H, t,  $J_{\alpha\beta} 7.6$ ,  $\alpha\text{-CH}_2$ ), 1.82–1.60 (2 H, m,  $\beta\text{-CH}_2$ ), 1.50–1.10 (6 H, m), 1.0–0.75 (3 H, m,  $\text{CH}_3$ );

Procedure for the synthesis of P3HT-macroinitiator **6**

In a dry Schlenk flask 254 mg of 2,2,5-Trimethyl-3-(10--p-azidomethylphenylethoxy)-4-phenyl-3-azahexane was dried under vacuum and 638 mg of P3HT-Alkyne were added. Both were dissolved in 123 ml dry THF and 3 mL of *N,N*-diisopropylethylamine was added with a syringe. After three freeze, pump, thaw cycles 130 mg of Cu(I)I were introduced and the reaction mixture was stirred at 40°C for 2 days. The reaction mixture was precipitated in MeOH with small amounts of  $\text{NH}_3$ . To remove excess Cu the polymer was dissolved in  $\text{CHCl}_3$  and extracted with a 1:1 (v:v) mixture of  $\text{NH}_3$  and water. After precipitation in MeOH 642 mg of pure macroinitiator were obtained.

SEC  $M_p = 24200 \text{ g mol}^{-1}$ ,  $M_n = 19900 \text{ g mol}^{-1}$ ,  $M_w = 22700 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.14$ ;

Procedure for the synthesis of P3HT-*b*-P4VP **8a**

To a dry Schlenk tube 7.18 mg of 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl was added in chloroform and the solvent was evaporated under high vacuum. P3HT-macroinitiator **6** (202 mg, 0.016 mmol) was inserted and the tube was evacuated and flooded with argon for three times. The polymer was dissolved in 12 mL degassed *o*-dichlorobenzene (*o*-DCB) and 12 mL 4-vinylpyridine was added. The reaction mixture was degassed with three freeze, pump, thaw cycles and the polymerization was started by placing the mixture in a 125 °C hot oil bath. After 45 min the polymerization was stopped by cooling with liquid nitrogen. The raw polymer mixture was diluted with chloroform and precipitated in pentane. The polymer was filtered and washed with hydrochloric acid to protonate the P4VP block. In a Soxhlet apparatus the remaining macroinitiator was removed by hot extraction with toluene. After drying under high vacuum the polymer was deprotonated by washing with a one to one mixture of ammonia and water. The pure polymer (282 mg) was obtained by dissolution in chloroform, precipitation in pentane, filtration and drying under vacuum.

SEC  $M_p = 104100 \text{ g mol}^{-1}$ ,  $M_n = 57100 \text{ g mol}^{-1}$ ,  $M_w = 81700 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.43$ ;

$\delta^1\text{H}$  (300 MHz;  $\text{CDCl}_3$ ) 8.60-8.00 ( $m^*2\text{H}$ , m,  $\text{H}_{\text{ar}}$  P4VP), 6.98 ( $n^*1 \text{ H}$ , s,  $\text{H}_{\text{ar}}$ , P3HT), 6.70-6.00 ( $m^*2\text{H}$ , m,  $\text{H}_{\text{ar}}$  P4VP), 2.80 ( $n^*2 \text{ H}$ , t,  $J_{\alpha\beta} 7.6$ ,  $\alpha\text{-CH}_2$ , P3HT), 1.82–1.60 ( $n^*2 \text{ H}$ , m,  $\beta\text{-CH}_2$ , P3HT), 1.50–1.10 ( $n^*6 \text{ H}$ , m, P3HT and  $m^*2\text{H}$ , m,  $\text{CH}_2$  P4VP), 1.0–0.75 ( $n^*3 \text{ H}$ , m,  $\text{CH}_3$ );  $n$  = degree of polymerization of P3HT and  $m$  = degree of polymerization of P4VP.

Solution structures

For the formation of the solution structures 1 mg P3HT-*b*-P4VP was dissolved in 1 mL of  $\text{CHCl}_3$ . 4 mL of isopropanol were slowly added under stirring with a flow rate of 1 mL/h using a syringe pump from neMESYS. The remaining  $\text{CHCl}_3$  was removed and the samples were analyzed with UV-Vis and dynamic light scattering.

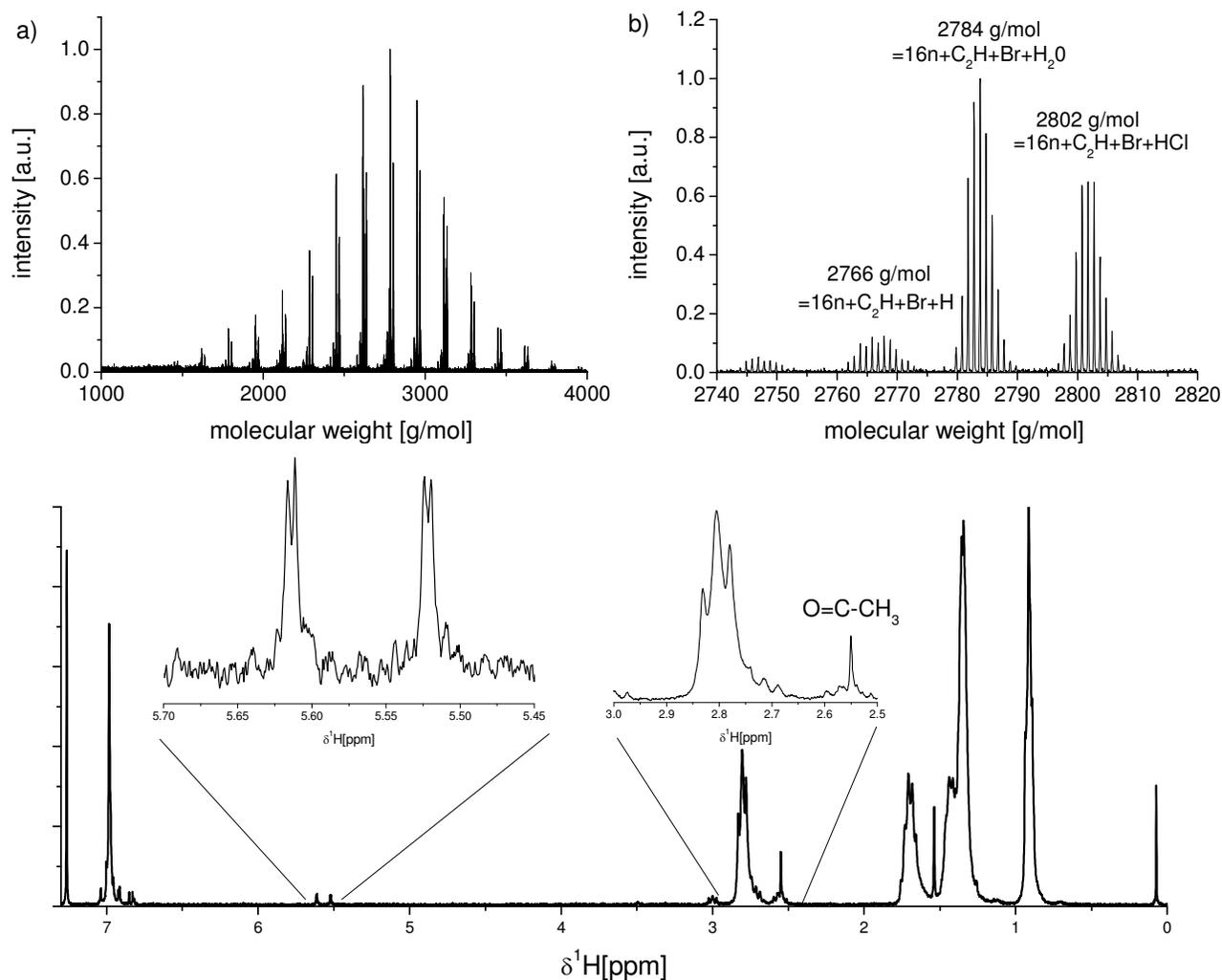


Figure SI 1: Spectra of P3HT obtained after quenching the end capping reaction of ethynylmagnesium chloride with hydrochloric acid at room temperature a) MALDI-ToF MS spectra b) magnified part in the range of 16 repeating units c)  $^1\text{H}$ -NMR spectrum. The respective end groups are indicated.

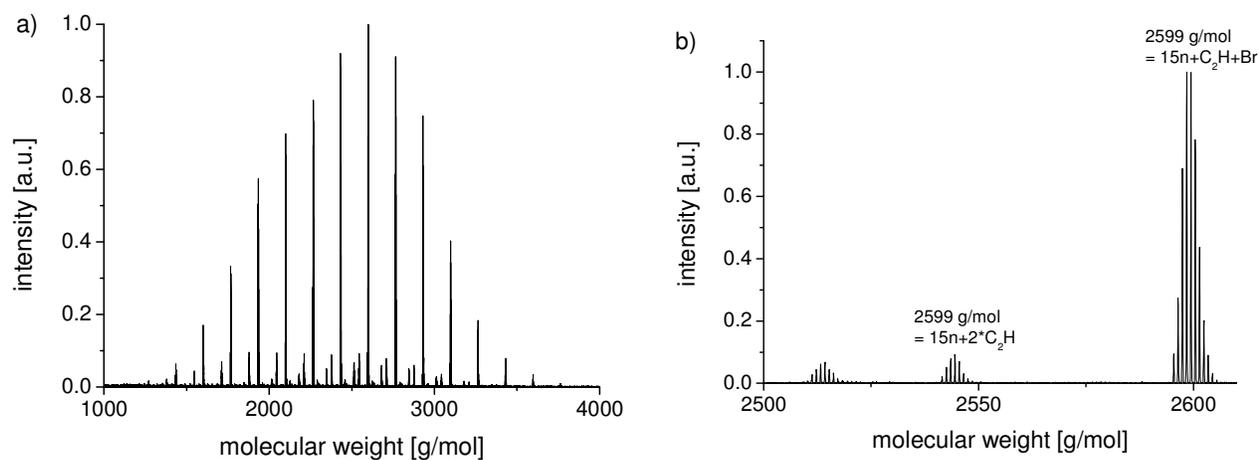


Figure SI 2: a) MALDI-ToF MS spectra of P3HT-alkyne quenched with methanol b) magnified part in the range of 15 repeating units. The main series belongs to alkyne and bromine terminated chain ends. Small amounts of alkyne alkyne terminated P3HT are visible.

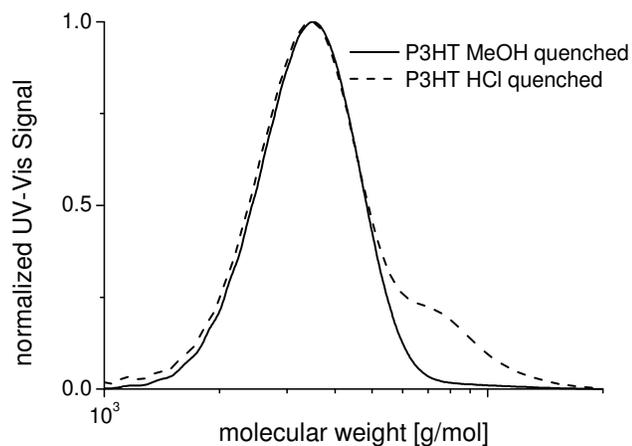


Figure SI 3: SEC curves of P3HT-alkyne quenched at 0°C with hydrochloric acid or methanol. Only for the sample quenched with hydrochloric acid small amounts of chain-chain coupling are visible.

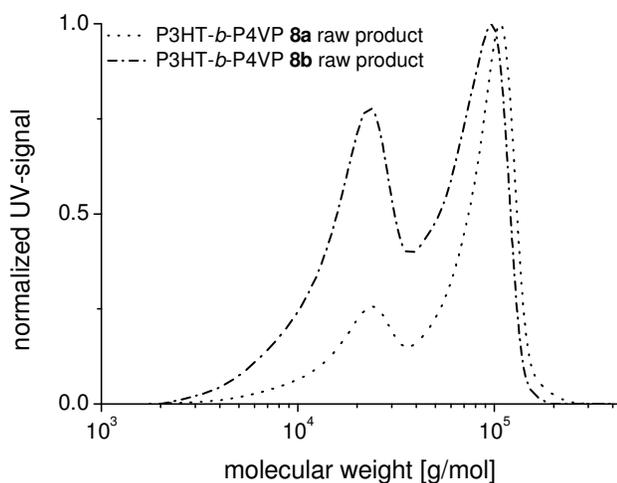


Figure SI 4: SEC curves of the raw products of P3HT-*b*-P4VP **8a** and **8b**.

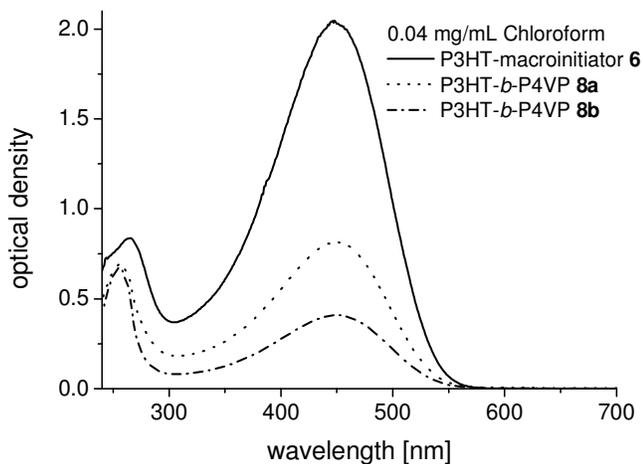


Figure SI 5: UV-Vis spectra of P3HT-alkoyamine **6** and P3HT-*b*-P4VP **8a** and **8b** in 0.04 mg/mL solution in chloroform.

#### Reference List

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- (4) Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, *5*, 890-891.