Supporting Information: Horner-Wadsworth-Emmons dispersion polymeriza-tion for the production of monodisperse conjugated polymer particles at am-bient conditions

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Materials and methods: Triethylphosphite, potassium tert-butoxide, PVPVA and Triton X-45 were purchased from Sigma Aldrich. 1,4-bischloromethy hexafluorobenzene from Santa Cruz Biotechnology and n-propanol from Fisher Chemicals. All other chemicals were purchased from TCI Chemicals. All chemicals were used as received.

1H NMR was recorded using Bruker DPX-400 FT Spectrometer. Chemical shifts were measured in ppm in CDCl3 with the internal reference at 7.26 ppm.

Electron microscopy: Field Emission scanning electron microscopy images were recored on a HITACHIS-4800 microscope. All samples were first purified by centrifugation, dispersed in fresh propanol, deposited on a Si wafer, dried and sputter coated with a 6 nm thin Pd-Au film. Average particle diameters were determined by image analysis while averaging over 200 particles. **STEM measurements** were carried out on a Hitachi SU-9000.

Fluorescence spectra were recorded with a Fluoromax-4P Spectrofluorometer with an excitation wavelength of λ = 410 nm. DLS measurements were recorded on a zeta sizer.

Differential Scanning Calorimetry (DSC) analysis was performed on a Perkin Elmer DSC 8500 under nitrogen atmosphere with a scan rate of 10 K·min–1. Ca. 5 mg of polymer particles were used for the measurement.

Gel permeation - size exclusion chromatography (SEC): Molecular weights and molecular weight distributions were determined by size-exclusion chromatography (SEC). SEC analyses were carried out

with chloroform as eluent using a HPLC pump (PU-2080plus, Jasco) equipped with a refractive index detector (RI-2031plus, Jasco) and an evaporative light scattering detector (PL-ELS-1000, Polymer Laboratories). The sample solvent chloroform) contained 250 mg·mL-1 3,5-di-tert-4-butylhydroxytoluene (BHT, \geq 99%, Fluka) as an internal standard. One pre-column (8 x 50 mm) and four SDplus gel columns (8 x 300 mm, MZ Analysentechnik) were applied at a flow rate of 1.0 mL·min-1 at 20 °C. The diameter of the gel particles measured 5 μ m, the nominal pore widths were 50, 102, 103 and 104 Å. Calibration was achieved using polystyrene standards (Polymer Standards Service).

Dynamic light scattering (DLS): The average diame-ter of the particles were determined via dynamic light scattering on a Zetasizer Nano ZS (Malvern in-struments) using non-invasive back-scatter technolo-gy. A He-Ne-Laser, operating at a wavelength of 633 nm is applied. All measurements are carried out at 20°C at an angle of 173°. Every sample is measured three times for 120 seconds.



Figure S1: Histograms of particle diameters from SEM image analysis of monomer concentrations of (a) 6.2 mM, (b) 8.2 mM, (c) 9.0 mM and (d) 10.1 mM. The concentration in (d) delivers bidisperse particles. The inset represents the particle size distribution of the second population of particles.



Figure S2: Representative SEM image bidisperse particles (10.1 mM). scalebar represents 10 $\mu m.$



Figure S3: Representative DLS traces for monodisperse (average diameter: 1024 nm, PDI: 0.056) (left) and (b) bidisperse (average diameter 1: 225 nm, diameter 2: 1457 nm) (right) batch of particles.



Figure S4: GPC measurement of the monomer (black) and polymer particles obtained by HWE dispersion polymerization at different conversions (see legend).



Figure S5: Probability P_i of finding a molecule composed of i monomer units versus the conversion p. Dark blue data points represent monomer, blue = dimer, cyan = trimer-hexamer, dark grey = hexameroctamer, grey = octamer-11-mer.



Figure S6: High resolution scanning electron microscopy images of nuclei particles after approximately 30 minutes (left) and 1 h (right). The scale bar represents 500 nm.



Figure S7: GPC trace of the final purified polymer particles dissolved in chloroform.



Figure S8: XRD measurement of particles with increasing crystallinity. Using the monomer M2 and M3 with the KO^tBu concentration of 0.8 M (dark grey), 0.7 M (grey), 0.4 M (cyan), and 0.2 M (blue). The peak are indexed according to our previous work.¹



Figure S9: Differential Scanning Calorimetry measurement of the platelet-like polymer particles indicates a melting event at ~ 95 °C.

Experimental Section:

Synthesis of Monomer M1:



The monomer M1 is synthesized in accordance with a previously described method (Michaelis-Arbuzov):^{2,3} In short we performed the reaction as follows: The reaction was performed in a nitrogen glove box. Triethyl phosphite (4.2 g, 23.9 mmol) was

added to 1,4-bischloromethyltetrafluorobenzene (1 g, 2.8 mmol). The reaction mixture was stirred at 120°C overnight. The crude product was recrystallized in n-hexane. The compound was received as white nee-dles (1.26 g, 80%).

¹H NMR (400 MHz, CDCl3) (ppm): 4.10 (q, J=7.35 Hz, 14.9 Hz, 8H), 3.70 (d, J= 21,4 Hz, 4H), 1.28 (t, J=6.76 Hz, 12H).

Synthesis of Monomer M2:



Monomer M2 was synthesized in analogy to the procedure for monomer M1 using 1,4bischloromethyltetrafluorobenzene (1 g, 2.8 mmol) and triethyl phosphite (4.2 g, 23.9 mmol) as reactants. The product was received as white crystals (1.053 g,84 %).

¹H NMR (400 MHz, CDCl3) (ppm): 4.16-4.06 (m, 8 H), 3.25 (d, J= 20.0 Hz, 4 H), 1.29 (t, J=7.07 Hz, 12 H).

Synthesis of the polymer particles

All dispersion polymerizations reactions were carried out following this general procedure: Equimolar amounts of the fluorene dialdehyde M3, and the tetrahalogenated phenylene bisphosphonate M1, M2 were dissolved in 1-propanol together with the stabilizers poly(1-vinylpyrolidone-co-vinlyacetate) and triton X-45. The Monomers and stabilizer mixture was brought to the reaction temperature (25, 40 or

60 °C). KOtBu in 1-propanol was added rapidly to initiate the reaction. The obtained polymer particles were purified by centrifugation and decantation (3 x propanol, 2 x water).

References

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