

Electronic Supplementary Information (ESI) for:

One-Pot Synthesis and Self-Assembly of Supramolecular Dendritic Polymers

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Experimental part

Materials

All the chemicals were purchased from Sigma-Aldrich or Alfa Aesar. *n*BuA was filtered prior to passing through a basic aluminium oxide column to remove inhibitors. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol.

Characterization methods

¹H NMR spectra were recorded on a Varian Unity Inova 500 (500 MHz) NMR spectrometer using CDCl₃ as solvent.

Polymers were analysed by size exclusion chromatography (SEC) running in THF at 35°C (flow rate: 1 mL·min⁻¹) and recorded on a GPCmax VE 2001 from Viscotek™, equipped with a column set of a H_{HR}-H Guard-17369 column, a CLM30111 column and a G2500H_{HR}-17354 column. The average molar mass of polymers were derived from calibration curve based on polystyrene.

Matrix-assisted laser desorption/ionization-time of flight mass (MALDI-TOF MS) spectra were obtained on a Bruker Autoflex III system (Bruker Daltonics) operating in the linear mode using flexAnalysis software (3.4). Ions were formed by laser desorption (smart beam laser at 355, 532, 808, and 1064 ± 5 nm; up to 50 Hz repetition rate), accelerated by a voltage of 20 kV detecting positive ions. The matrix solution was prepared by dissolving 1,8,9-anthracenetriol (dithranol) in THF (20 g/L), polymer and NaI in THF and acetone at a

concentration of 20 g/L, respectively. Solutions of the matrix, polymer and NaI were mixed in a volume ratio of 100 : 20 : 1, and 0.5 μ L of the resulting mixture were spotted on a MALDI sample plate, air-dried and subsequently subjected to measurements.

High performance liquid chromatography (HPLC) measurements were performed on Elite LaChrom HPLC, Hitachi VWR, equipped with an autosampler, a quaternary gradient pump, a degasser, a diode array detector (UV-DAD) operating at 190 – 900 nm and a column oven with temperature control (temperature = 25 °C). Temperatures were maintained constant (\pm 0.2 °C) throughout all experiments, and the injected sample volume was 10 μ L. Liquid chromatography at critical conditions (LCCC) was carried out on a non polar reversed-phase Atlantis-RP C18 column, 100 Å, 5 μ m, dimension 4.6 \times 250 mm using ACN/DCM = 11/89 as the mobile phase with a flow rate of 0.50 mL/min. The DAD signals were recorded on EZchrom Elite software version 3.3.2 SP2 with an operating wavelength from 190 to 900 nm at a sampling width of 200 ms to obtain sufficient data points across peaks.

Rheology experiments were conducted on Anton Paar (Physica) MCR MCR 301/SN 80753612. For all measurements a parallel plate with a diameter of 8 mm was used, the gap width used was in the range 0.20-0.40 mm. The sample temperature was regulated by thermoelectric cooling/heating in a Peltier-chamber under a dry oxygen atmosphere. All measurements were performed in the dynamic mode. Frequency sweep measurements were carried out within the linear visco-elastic (LVE) region.

Small angle X-ray scattering (SAXS) experiment was carried out in transmission geometry

with a laboratory setup consisting of a Rigaku rotating anode, a focusing X-ray optics device (Osmic confocal max flux), an evacuated flight path and a Bruker 2D-detector (HighStar). The optics served as monochromator for Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) as well. The sample holder consisting of an aluminium foil with a hole (diameter = $\sim 1 \text{ mm}$) in the centre was used. The sample was placed in the hole, and the aluminium foil was attached onto a Linkam hot stage TMS 94 by thermal conducting paste. The measurements took ~ 15 minutes.

For imaging their topography by atomic force microscopy (AFM), the Ba-(P*n*BuA-HW)₂ aggregates were immobilized on a Si solid support by spin coating films from a Ba-(P*n*BuA-HW)₂ solution in chloroform or toluene (1 g/L). AFM imaging was carried out with a Multimode V atomic force microscope with a Nanoscope VII controller (Bruker Instruments, Santa Barbara, USA) operating in intermittent contact mode in air and at room temperature. TESPA-type silicon cantilevers (NanoWorld, Neuchâtel, Switzerland) with nominal spring constants of about 42 N/m and tip radii of smaller than 10 nm were used. The images were recorded with an acquisition speed of 6 $\mu\text{m/s}$ (1 Hz line scan rate) and a resolution of 512 pixels \times 512 pixels. Prior to usage, the silicon substrates were freshly cleaned by piranha solution. Images were processed using the Nanoscope software or Gwyddion.

Solution polymerization of *n*BuA mediated by Ba-(RAFT)₂ (Figure S1)

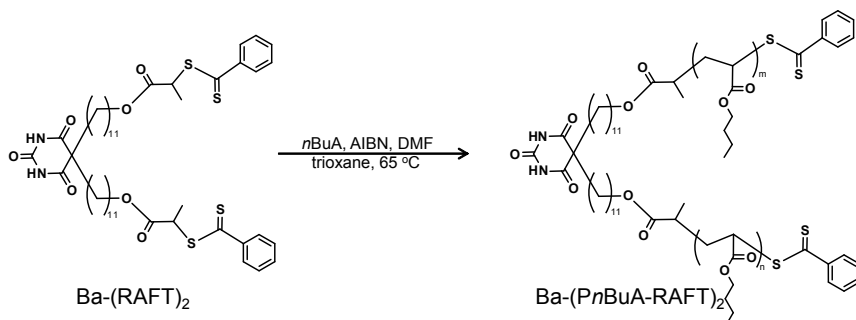


Figure S1: Solution polymerization of *n*BuA.

Solution polymerization of *n*BuA was carried out using Ba-(RAFT)₂^[1] as RAFT agent, and AIBN as initiator (**Figure S1**). Typically, solution polymerization of *n*BuA (0.28 mL, 2.0×10^{-3} mol) was carried out using AIBN (0.41 mg, 2.5×10^{-6} mol), Ba-(RAFT)₂ (22.1 mg, 2.5×10^{-5} mol), DMF (0.28 mL) and trioxane (32 mg, 3.5×10^{-2} mol) as an internal reference for the measurement of *n*BuA consumption via ¹H NMR. A stock solution was transferred into Schlenk tubes which were thoroughly deoxygenated by nitrogen bubbling for about 30 min at 0 °C, and then immersed into an oil bath thermostatted at 65 °C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into cold methanol/water (1/1, v/v) in order to eliminate residual monomer and trioxane. The polymer was dried under vacuum and characterized by ¹H NMR and SEC (**Figure S2**). The molar mass of pure mid-Ba functionalized poly(*n*-butyl acrylate) (Ba-(P*n*BuA-RAFT)₂) was finally evaluated by ¹H NMR (CDCl₃) from relative integration of the protons of P*n*BuA backbone (-O-CH₂-CH₂-, 2*n*H, $\delta=3.97$ ppm, with *n* being the degree of polymerization) and of two characteristic aromatic protons ortho to the dithio group (-S-

C(=S)Ph, 2H, $\delta=7.86$ ppm).

Synthesis of mid-Ba and α,ω -HW functionalized polymer Ba-(PnBuA-HW)₂

Ba-(PnBuA-HW)₂ was prepared according to literature method with slight modification.^[2, 3]

Ba-(PnBuA-RAFT)₂ ($Mn_{NMR} = 5.0$ kDa, $Mn_{SEC} = 4.8$ kDa, $\mathcal{D} = 1.25$, 50 mg, 0.01 mmol), Br-HW (32 mg, 0.04 mmol) and triethylamine (4.1 mg, 0.04 mmol) were dissolved in 0.5 mL acetonitrile and purged with nitrogen at room temperature. Hexylamine (2.4 mg, 0.024 mmol) dissolved in 0.5 mL of acetonitrile, was added slowly into above solution. After 1 hour, the solution was precipitated into cold methanol/water (1/1, v/v), then purified by silica column chromatography (dichloromethane/methanol, 40/1, v/v), the obtained product Ba-(PnBuA-HW)₂ was analysed by SEC (**Figure S2**), NMR, MALDI-TOF MS (**Figure S3**) and LC (main text).

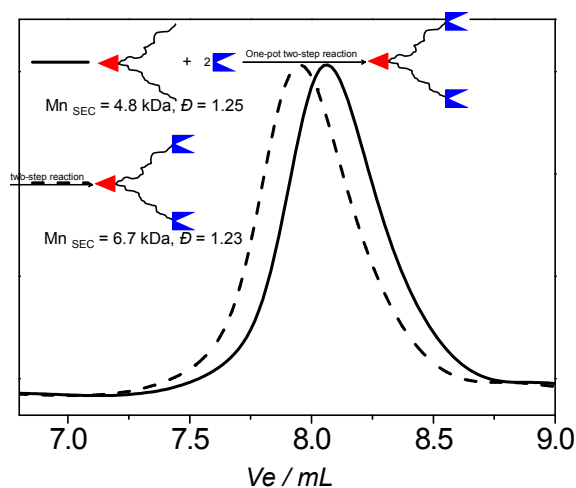


Figure S2: Evolution of SEC traces for Ba-P(nBuA-RAFT)₂ (solid line), and Ba-(PnBuA-HW)₂ (dash line), detector: refractive index, eluent: THF.

MALDI-TOF MS of Ba-(PnBuA-RAFT)₂ and Ba-(PnBuA-HW)₂ (Figure S3)

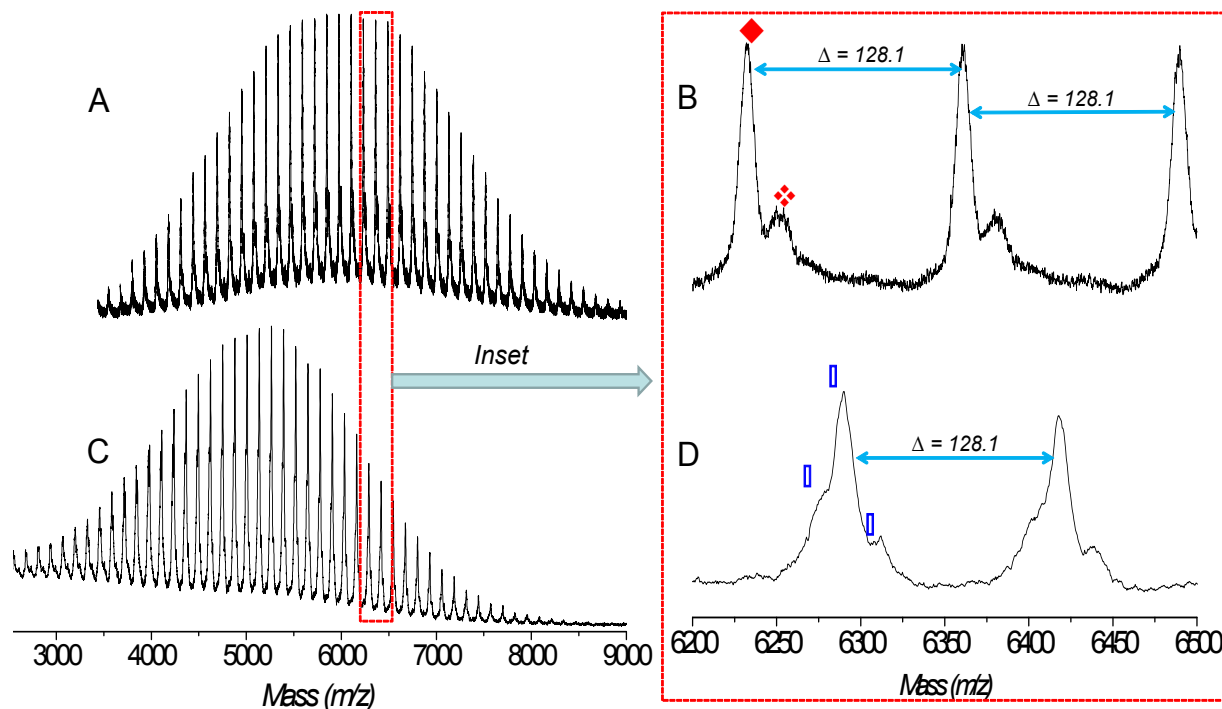


Figure S3: MALDI-TOF MS of Ba-(PnBuA-HW)₂ (A) full spectrum and (B) expansion, Ba-(PnBuA-RAFT)₂ (C) full spectrum and (D) expansion.

Temperature-dependent rheology of Ba-(PnBuA-RAFT)₂ and Ba-(PnBuA-HW)₂ (Figure S4)

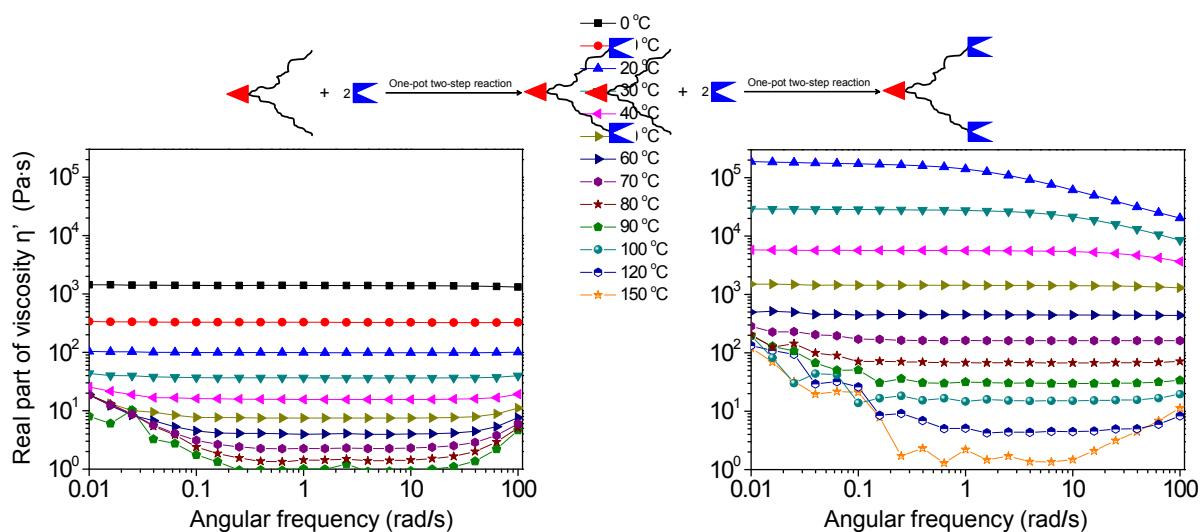


Figure S4: Real part of viscosity (η') of Ba-(PnBuA-RAFT)₂ (left) and Ba-(PnBuA-HW)₂ (right) at different temperatures based on a frequency sweep in the melt.

Shear modulus studies of Ba-(P*n*BuA-RAFT)₂ and Ba-(P*n*BuA-HW)₂

(Figure S5)

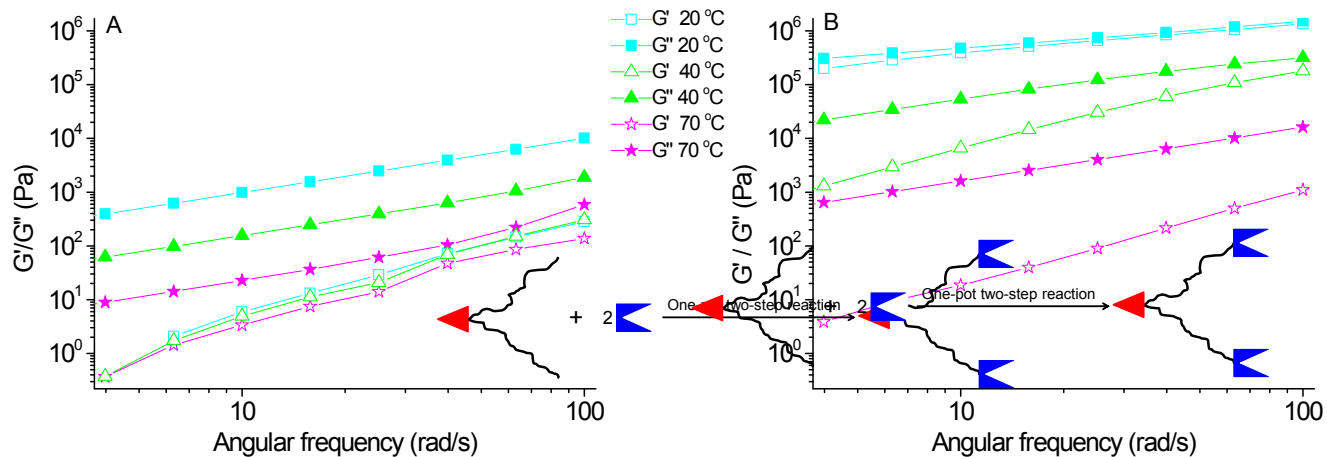


Figure S5: Rheological measurements of (A): Ba-P(*n*BuA-RAFT)₂ and (B): Ba-(P*n*BuA-HW)₂ at different temperatures.

SAXS profile of Ba-(P*n*BuA-HW)₂ (Figure S6)

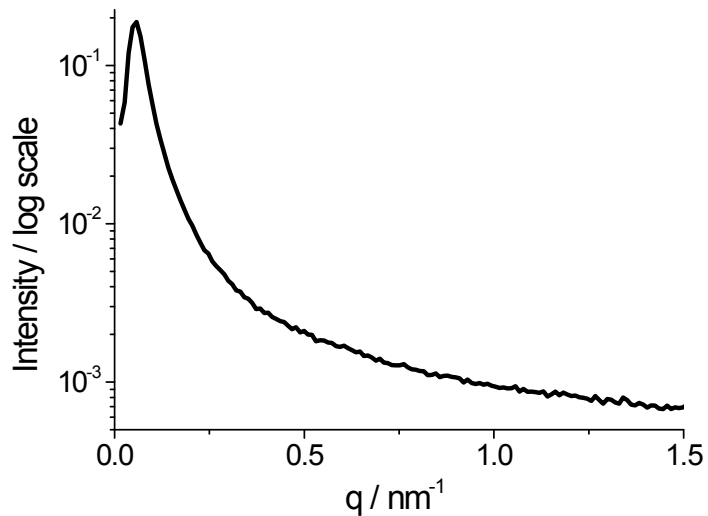


Figure S6: One-dimensional SAXS profile for Ba-(P*n*BuA-HW)₂ recorded at 20 °C.

AFM height images of Ba-(PnBuA-HW)₂

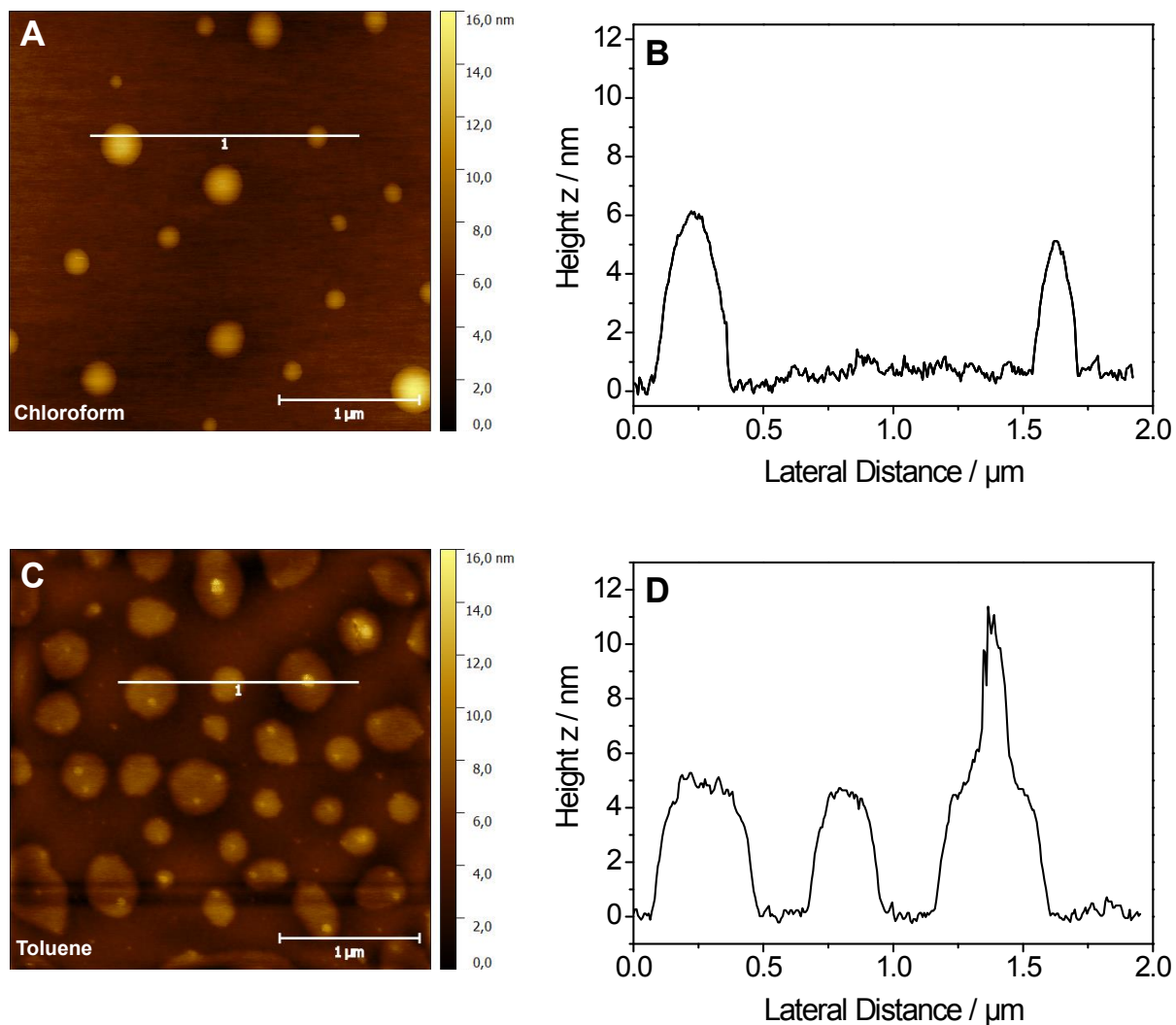


Figure S7: AFM height images (A&C refer, respectively, to **Figure 5A&C** in the main text) and cross section (B, D) at the marked white line of the immobilized supramolecular dendritic polymer self-assembled from Ba-(PnBuA-HW)₂.

DOSY NMR of Ba-(PnBuA-HW)₂ (Figure S8)

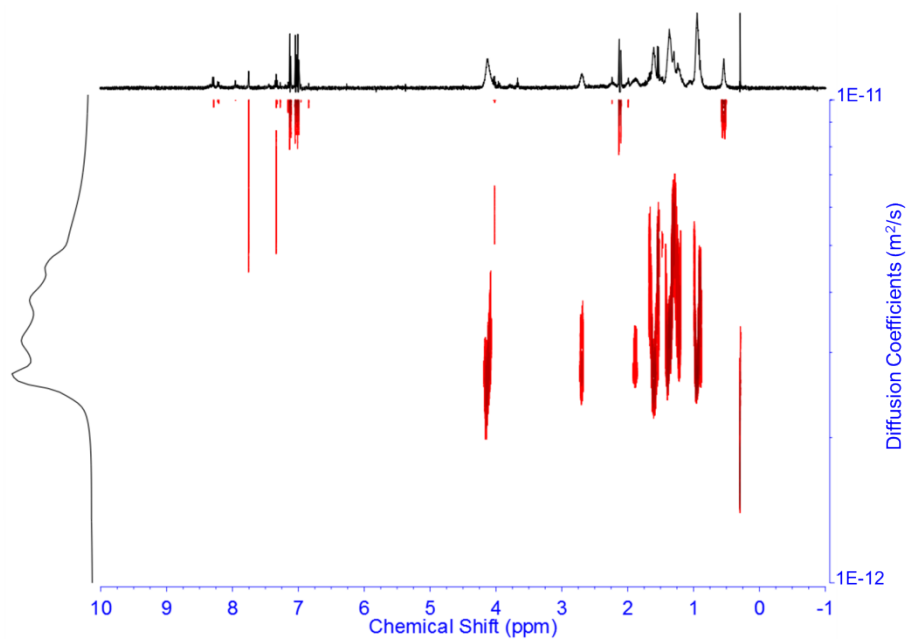


Figure S8: Diffusion coefficients distribution as a function of the chemical shift in toluene-d₈ at 27 °C.

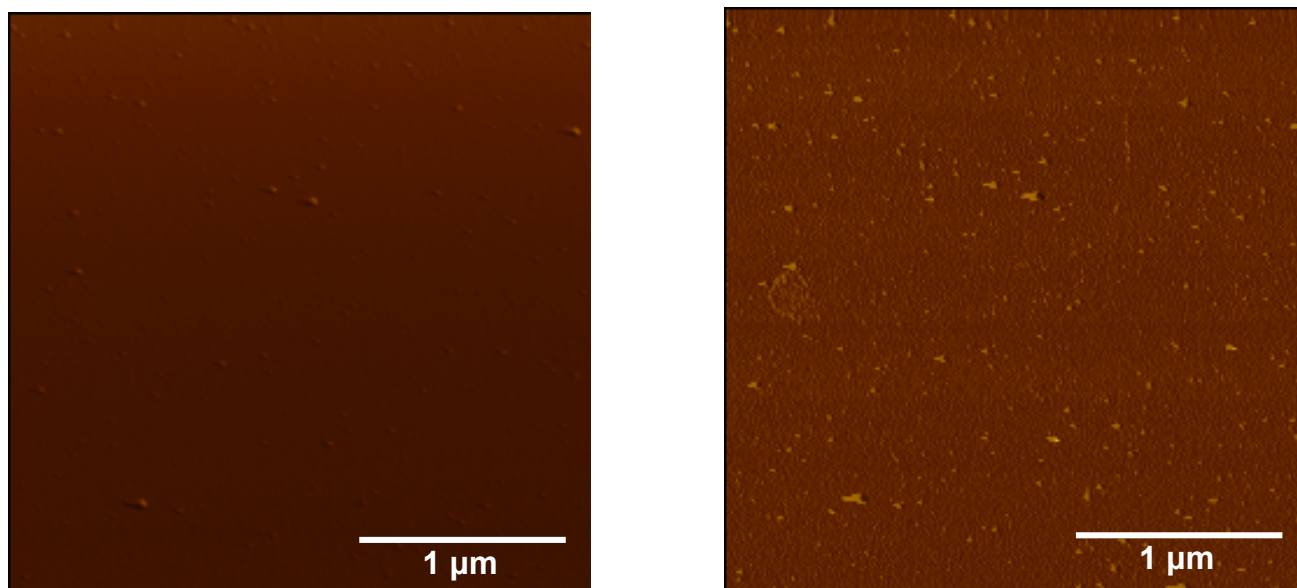


Figure S9: AFM height (left) and phase (right) images immobilized on a Si solid support by spin-coating from Ba-(PnBuA-HW)₂ solution using a mixture of chloroform and methanol (1/1, v/v) as solvent.

References

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- [2] J. Xu, L. Tao, C. Boyer, A. B. Lowe, T. P. Davis, *Macromolecules.* **2010**, *43*, 20-24.
- [3] S. Chen, D. Ströhl, W. H. Binder, *ACS Macro Lett.* **2015**, *4*, 48-52.