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

 Senbin Chen,<sup>a</sup> Matthias Schulz,<sup>a</sup> Bob-Dan Lechner,<sup>b</sup> Clement Appiah<sup>a</sup> and Wolfgang H. Binder\*<sup>a</sup>

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We report the design and synthesis of novel supramolecular dendrimers, formed by the association of X-Y<sub>2</sub> type single-chain polymeric building blocks Ba-(PnBuA-HW)<sub>2</sub>, with (poly(*n*-butyl acrylate) PnBuA) separating the two specific interacting supramolecular moieties X (barbiturate, Ba) and Y (Hamilton wedge, HW). Based on a one-pot two-step synthesis, the mid-Ba and α,ω-HW functionalized X-Y<sub>2</sub> type polymer, Ba-(PnBuA-HW)<sub>2</sub>, is generated via a direct thiol-bromo click reaction with Ba-(PnBuA-RAFT)<sub>2</sub>, (*M<sub>n</sub>*<sub>NMR</sub> = 5.0 kDa, *M<sub>n</sub>*<sub>SEC</sub> = 4.8 kDa, Đ = 1.25, prepared via reversible addition-fragmentation chain transfer (RAFT) polymerization), successfully attaching the heterocomplementary supramolecular moieties (HW) at both chain ends in a one-pot fashion at room temperature within one hour. The so obtained Ba-(PnBuA-HW)<sub>2</sub> (*M<sub>n</sub>*<sub>NMR</sub> = 7.1 kDa, *M<sub>n</sub>*<sub>SEC</sub> = 6.7 kDa, Đ = 1.23) assembles into supramolecular dendritic polymers via hydrogen-bonds (H-bonds), illustrating impressive viscosity enhancement in the bulk state (at 20 °C by a factor as high as ~1839). Atomic force microscopy (AFM) investigations reveal large but defined disc-like objects when spin-coated from a Ba-(PnBuA-HW)<sub>2</sub> solution, enabling to tune morphology at the mesoscale to generate hierarchical structures by choice of the solvent.

### Introduction

Taking advantage of hydrogen bonds as specific supramolecular interactions, impressive progress has been achieved in the construction of various supramolecular architectures during the last decade,<sup>1-7</sup> such as supramolecular block-copolymers,<sup>8-13</sup> (miktoarm) star,<sup>14-17</sup> H-shaped<sup>18</sup> and comb/brush-shaped<sup>19-22</sup> architectures or even more complex supramolecular aggregates.<sup>23-27</sup>

Among those, the design of supramolecular dendritic architectures is special, as they require appropriate design of the assembling components. Thus one widely investigated synthetic strategy relies on mixing two heterocomplementary components, namely X<sub>n</sub> and Y<sub>m</sub>, where n ≥ 2 and m ≥ 3,<sup>28</sup> or via self-organization of a X-Y<sub>n</sub> (n ≥ 2) type single-chain building block—an approach, where only few examples<sup>29-32</sup> have been reported, all of them focusing on low-molecular-weight compound systems. To the best of our knowledge, the preparation of X-Y<sub>n</sub> (n ≥ 2) type single-chain polymeric

macromolecules has not been exploited, presumably due to the tedious synthesis requiring a complete attachment of supramolecular entities—an issue which is often hampered by less robust chemistries and/or time-consuming complicated purification procedures, especially when applied onto polymers as the central scaffold.

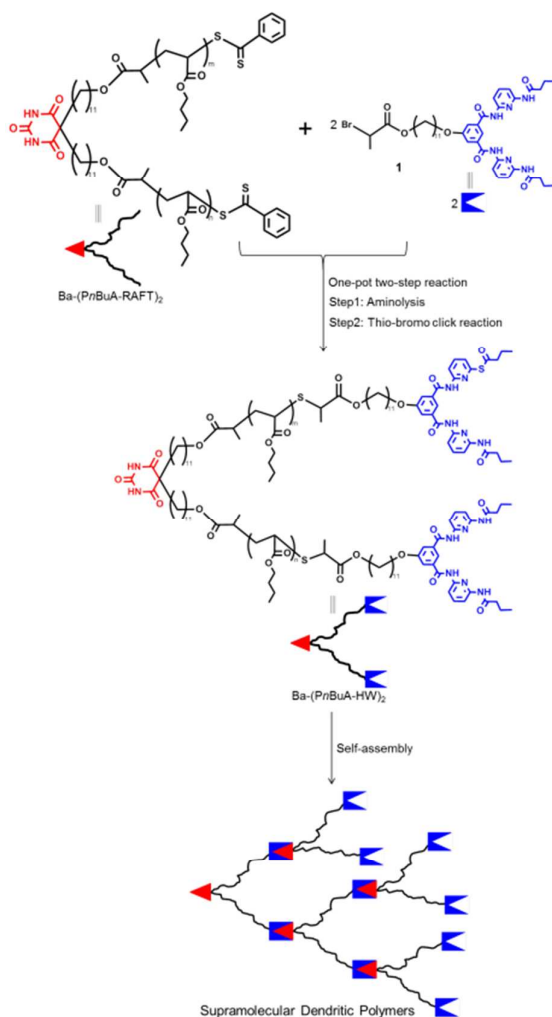
It is known that the advance of click reaction<sup>33,34</sup> has paved a way for new opportunities in the fabrication of supramolecular architectures based on polymeric macromolecules.<sup>4, 35-38</sup> In addition to the well-known copper-catalysed alkyne-azide cycloaddition click reaction,<sup>39</sup> metal-free thiol-based chemistries have been also identified as a highly robust synthetic approach recently.<sup>40, 41</sup> Compared to other thiol-based efficient coupling reactions, such as the thiol-ene, the thiol-yne, the thiol-isocyanate and the thiol-epoxy reaction, the investigation of the thiol-bromo click reaction still remains limited,<sup>42</sup> although several examples have been reported very recently.<sup>43-47</sup>

We here describe the synthesis of novel supramolecular dendritic polymer using X-Y<sub>2</sub> type heterotropic single-chain polymers, namely the mid-Ba and α,ω-HW functionalized polymer Ba-(PnBuA-HW)<sub>2</sub>, where PnBuA is separating the two specific interacting supramolecular moieties X (Ba) and Y (HW). We are using a one-pot two-step reaction, successfully linking the HW moieties onto both polymer chain ends directly after the polymerization reaction. From its design we target the generation of a X-Y<sub>2</sub> architecture, equipped with the Ba/HW moieties, displaying a high association constant of approximately 10<sup>5</sup> M<sup>-1</sup>,<sup>11</sup> in turn leading to the formation of a

<sup>a</sup> Chair of Macromolecular Chemistry, Faculty of Natural Science II (Chemistry, Physics and Mathematics), Martin-Luther University Halle-Wittenberg, von-Danckelmann-Platz 4, Halle (Saale) D-06120, Germany. Email: wolfgang.binder@chemie.uni-halle.de

<sup>b</sup> Physical Chemistry, Faculty of Natural Sciences II (Chemistry, Physics and Mathematics), Martin-Luther University Halle-Wittenberg, von-Danckelmann-Platz 4, Halle (Saale) D-06120, Germany.

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**Figure 1:** Synthetic route to the mid-Ba and  $\alpha,\omega$ -HW functionalized X-Y<sub>2</sub> type polymer Ba-(PnBuA-HW)<sub>2</sub> and its self-assembly to afford the supramolecular dendritic polymers.

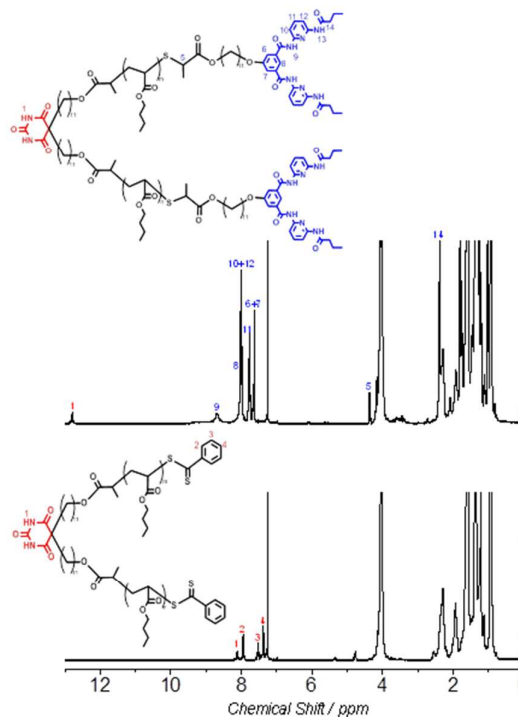
non-crosslinked, dendritic macromolecule via supramolecular specific association. The synthesis of the X-Y<sub>2</sub> type heterotropic single-chain polymer Ba-(PnBuA-HW)<sub>2</sub> relies on the combination of the thiol-bromo click reaction together with a PnBuA-polymer prepared by RAFT polymerization. The easy, yet complete conversion of the dithioester moiety of the RAFT-made polymer into a reactive thiol group via aminolysis facilitates the subsequent direct polymer functionalization relying on the above mentioned thiol-based efficient coupling reaction (Figure 1).<sup>40</sup> Subsequent association yields the expected supramolecular dendrimers, displaying large but defined disc-like nanoscopic structures spin-coated from a Ba-(PnBuA-HW)<sub>2</sub> solution in chloroform. Moreover, the disc-like structures can be tuned to generate hierarchical morphologies by changing the solvent from chloroform to less polar toluene.

## Results and discussion

### Design, synthesis and structure characterization of the X-Y<sub>2</sub> type polymer Ba-(PnBuA-HW)<sub>2</sub>

Aiming at fabricating the mid-Ba and  $\alpha,\omega$ -HW functionalized X-Y<sub>2</sub> type polymer Ba-(PnBuA-HW)<sub>2</sub> (Figure 1), we have first prepared mid-Ba functionalized polymer Ba-(PnBuA-RAFT)<sub>2</sub> ( $M_n$  NMR = 5.0 kDa,  $M_n$  SEC = 4.8 kDa,  $D$  = 1.25, ESI, Figure S1 and Figure S2).<sup>48</sup> Subsequently, the  $\alpha,\omega$ -dithiobenzoate end groups of the so prepared Ba-(PnBuA-RAFT)<sub>2</sub> are cleaved to thiols via an aminolysis reaction, directly reacting the *in situ* generated thiols with compound 1,<sup>49</sup> a bromoester bearing a Hamilton wedge, in one-pot fashion. Although acetonitrile is unable to fully dissolve Ba-(PnBuA-RAFT)<sub>2</sub>, the one-pot two-step reaction is completed at room temperature within one hour. The targeted X-Y<sub>2</sub> type polymer, Ba-(PnBuA-HW)<sub>2</sub>, is purified by precipitation into methanol/water (1/1, v/v) and then silica column chromatography (dichloromethane/methanol, 30/1, v/v), the obtained product Ba-(PnBuA-HW)<sub>2</sub> is analysed by size exclusion chromatography (SEC,  $M_n$  SEC = 6.7 kDa,  $D$  = 1.23, ESI, Figure S2).

Primary evidence of the successful synthesis of the mid-Ba and  $\alpha,\omega$ -HW functionalized X-Y<sub>2</sub> type polymer Ba-(PnBuA-HW)<sub>2</sub> is provided by <sup>1</sup>H NMR (Figure 2). Compared to the spectrum of



**Figure 2:** <sup>1</sup>H NMR spectra of Ba-(PnBuA-RAFT)<sub>2</sub> (bottom), and Ba-(PnBuA-HW)<sub>2</sub> (top) at 27 °C in CDCl<sub>3</sub> ([Ba-(PnBuA-RAFT)<sub>2</sub>] = [Ba-(PnBuA-HW)<sub>2</sub>] = 2 mM). The second imide peak of Hamilton wedge is overlapping with the aromatic protons in the top spectrum.

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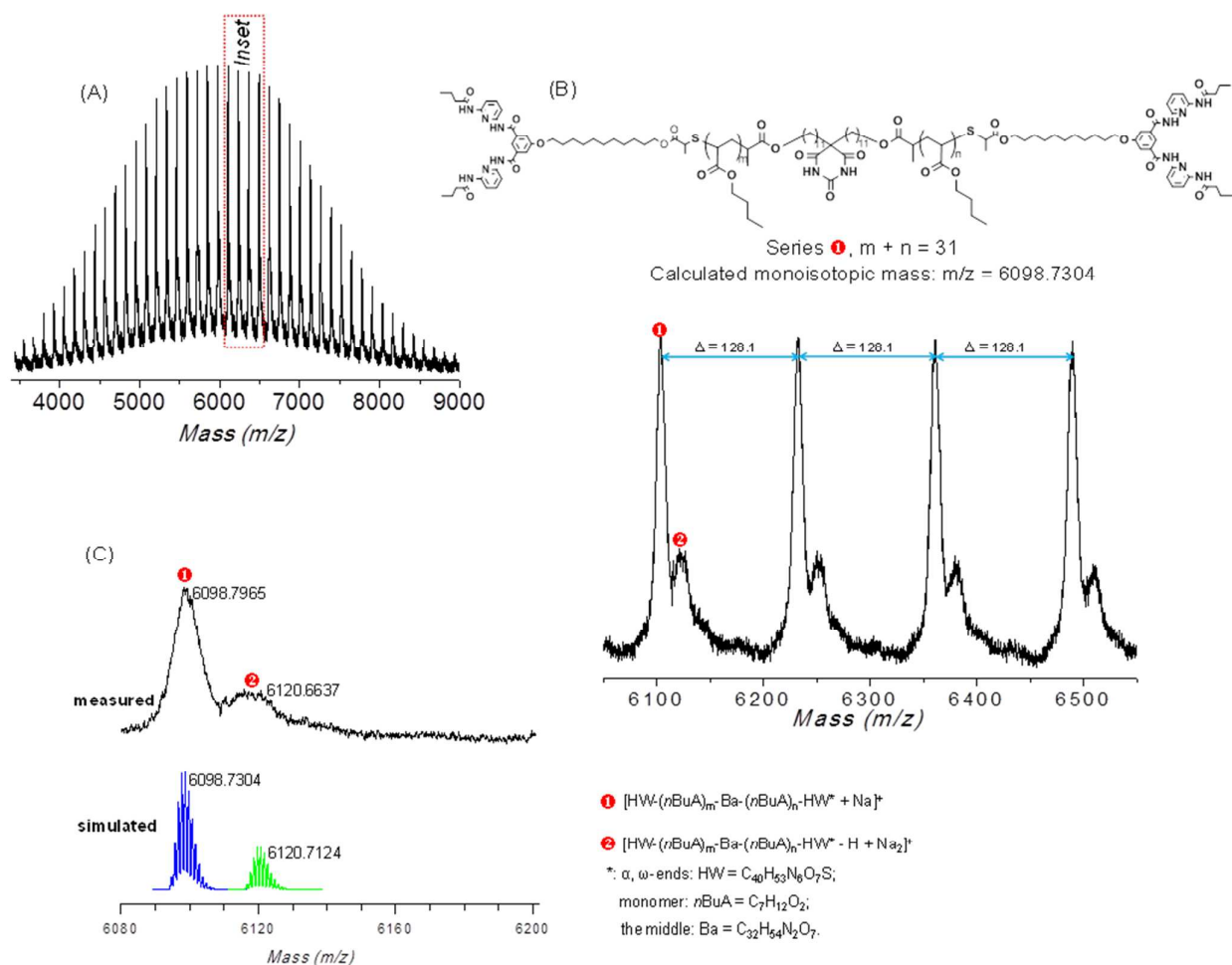


Figure 3 : MALDI-TOF MS of  $\text{Ba}-(\text{PnBuA-HW})_2$  (A) full spectrum, (B) expansion and (C) simulation of the isotope pattern.

the starting material,  $\text{Ba}-(\text{PnBuA-RAFT})_2$ , the complete disappearance of the characteristic phenyl protons (7.95, 7.53 and 7.39 ppm in **Figure 2**, bottom) *ortho* to the dithiobenzoate group, along with the emergence of the Hamilton wedge imide protons (8.68 ppm in **Figure 2**, top), as well as the pyridyl and phenyl protons (8.02, 7.77 and 7.63 ppm in **Figure 2**, top) indicates the successful linking of HW moieties onto polymer chain ends.

Furthermore, matrix-assisted laser desorption/ionization-time of flight mass (MALDI-TOF MS) spectrometry has been used to prove the attachment of two HW moieties via the thiol-bromo

click reaction. Mass spectra of the starting material  $\text{Ba}-(\text{PnBuA-RAFT})_2$  and final product  $\text{Ba}-(\text{PnBuA-HW})_2$  are shown in the linear mode, (see **Figure S3A&C** (ESI)) obtained by ionization of polymer chains assisted with dithranol as matrix and sodium iodide as the cationization agent. As seen in **Figure S3** (ESI), comparing the MALDI-TOF spectrum of  $\text{Ba}-(\text{PnBuA-HW})_2$  (ESI, **Figure S3A**) to the initial starting material  $\text{Ba}-(\text{PnBuA-RAFT})_2$  (ESI, **Figure S3C**), the shift towards high mass clearly indicates the successful attachment of both HW moieties via the thiol-bromo-click reaction. Both MALDI-TOF spectra (ESI, **Figure S3B&D**) underline the presence of a main series (1 and 2)

refer, respectively, to Ba-(PnBuA-HW)<sub>2</sub> and Ba-(PnBuA-RAFT)<sub>2</sub>, along with other minor series (②, ②&③): each set of ions is separated by 128.1 Da, reflecting the repeating unit of the nBuA monomer (calculated 128.08 Da). The detailed simulation of MALDI-TOF MS spectrometry for Ba-(PnBuA-HW)<sub>2</sub> (Figure 3A, corresponding to Figure S3A in the ESI) is subsequently accomplished, proving the assignment of the main series (①), located at 6098.7965 Da (Figure 3C), to a mid-Ba, α,ω-HW functionalized species [Ba-(nBuA<sub>15.5</sub>-HW)<sub>2</sub> + Na]<sup>+</sup>, i.e., [C<sub>32</sub>H<sub>54</sub>N<sub>2</sub>O<sub>7</sub>-((C<sub>7</sub>H<sub>12</sub>O<sub>2</sub>)<sub>15.5</sub>-C<sub>40</sub>H<sub>53</sub>N<sub>6</sub>O<sub>7</sub>S)<sub>2</sub> + Na]<sup>+</sup>, which matches well with the simulated pattern (*m/z*<sub>average</sub> = 6098.7304 Da). The observed isotopic patterns of the minor series (②), illustrated in Figure 3B&C, also agree well with the simulated structure, proving that the one-pot two-step reaction proceeded efficiently, thus further ascertaining the successful macromolecular modification, also showing no residual trace of an only mono- or non-functionalized polymer.

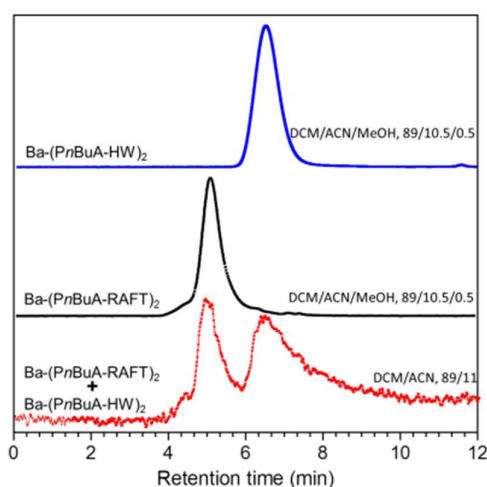
However, to fully establish a complete end-group transformation from Ba-(PnBuA-RAFT)<sub>2</sub> to Ba-(PnBuA-HW)<sub>2</sub>, liquid chromatography at critical conditions (LCCC) is conducted (Figure 4). To this end, Ba-(PnBuA-RAFT)<sub>2</sub> and Ba-(PnBuA-HW)<sub>2</sub> are subsequently characterized by LC at near-critical conditions (dichloromethane/acetonitrile, DCM/ACN, 89/11, v/v at 25 °C) reported for PnBuA.<sup>50</sup> Ba-(PnBuA-HW)<sub>2</sub> under these conditions is however partially retained on the reversed phase Atlantis column. Thus, overcoming this retention-effect is accomplished by adding 0.5% methanol (MeOH) to the mobile phase (i.e. DCM/ACN/MeOH, 89/10.5/0.5, v/v/v). As seen in Figure 4 (bottom) for the mixed sample (Ba-(PnBuA-RAFT)<sub>2</sub> + Ba-(PnBuA-HW)<sub>2</sub>), no major changes in the retention time compared to the pure Ba-(PnBuA-RAFT)<sub>2</sub> (Figure 4, middle) is observed, indicating that the 0.5 % methanol addition does not have

any negative effect on the LCCC conditions, but rather helped in solubilising the polar end-group to enhance a better movement of the polymer in the column. Most importantly, the results from the LC show different retention times for Ba-(PnBuA-RAFT)<sub>2</sub> (4.65 min, Figure 4, middle) and Ba-(PnBuA-HW)<sub>2</sub> (6.26 min, Figure 4, top). The signal of the starting polymer Ba-(PnBuA-RAFT)<sub>2</sub> is not present in the spectrum of final pure Ba-(PnBuA-HW)<sub>2</sub> (see Fig 4/top), which undoubtedly confirms the successful macromolecular conversion via the thiol-bromo click reaction.

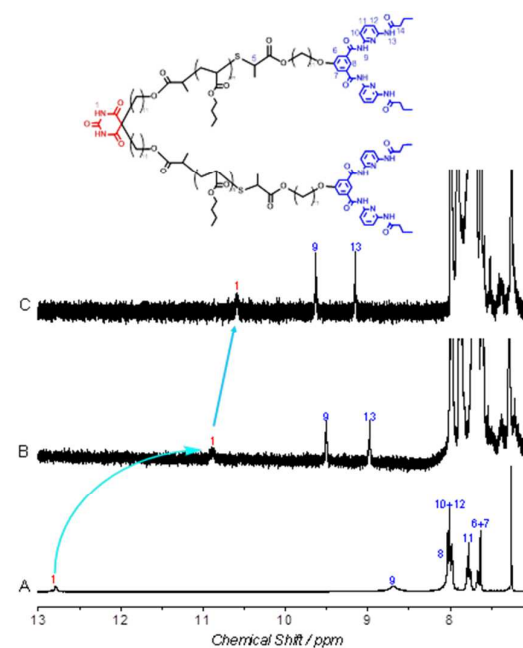
#### Characterization of Ba-(PnBuA-HW)<sub>2</sub> self-assembly

Upon confirming the expected structure and purity of Ba-(PnBuA-HW)<sub>2</sub> prepared via the one-pot two-step reaction, we subsequently question the self-assembly behaviour, both in solution and in the bulk state.

A first indication of self-assembly of Ba-(PnBuA-HW)<sub>2</sub> is provided by <sup>1</sup>H NMR studies (Figure 2). Compared to the spectrum of Ba-(PnBuA-RAFT)<sub>2</sub> (Figure 2, bottom), in addition to the appearance of Hamilton wedge protons in the expected stoichiometric amounts, a considerable downfield shift of the barbiturate imide protons from 8.12 to 12.79 ppm is observed: a strong indication for the formation of the expected H-bonded complex (Figure 2, top). In order to prove the effect of H-bonding more clearly, the addition of small amounts of a polar solvent MeOD-d<sub>4</sub> into the CDCl<sub>3</sub> solution is performed (Figure 5), which leads to a significant upfield shift of the barbiturate NH protons to



**Figure 4:** LC chromatograms for a defined 1/1-mixture of Ba-(PnBuA-RAFT)<sub>2</sub> with Ba-(PnBuA-HW)<sub>2</sub> (bottom), Ba-(PnBuA-RAFT)<sub>2</sub> (middle) and pure Ba-(PnBuA-HW)<sub>2</sub> (top) showing separation based on their functionality.



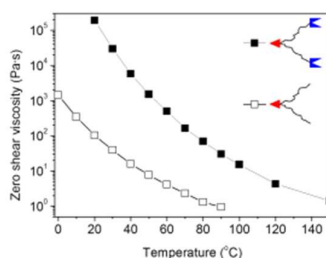
**Figure 5:** Partial <sup>1</sup>H NMR spectrum of Ba-(PnBuA-HW)<sub>2</sub> recorded in different solvents at 27 °C, [Ba-(PnBuA-HW)<sub>2</sub>] = 2 mM. (A): CDCl<sub>3</sub>, (B): CDCl<sub>3</sub>/MeOD-d<sub>4</sub> (10/1, v/v), (B): CDCl<sub>3</sub>/MeOD-d<sub>4</sub> (10/2, v/v).



10.89 and 10.54 ppm in **Figure 5B** and **C**, respectively, revealing the partial dissociation of the supramolecular structures by action of the hydrogen breaking solvent. It is also noteworthy that the barbiturate NH protons are difficult to be detected in the mixed solvent of  $\text{CDCl}_3/\text{MeOD-d}_4$  (**Figure 5B, C**).

Rheological measurements have been subsequently performed in the bulk state to achieve more insight into the relaxation dynamics of supramolecular structures. Thus  $\text{Ba-(PnBuA-RAFT)}_2$  and  $\text{Ba-(PnBuA-HW)}_2$  are investigated by frequency-dependent measurements at different temperatures (ESI, **Figure S4**). The zero shear viscosities ( $\eta_0$ ) are then plotted as a function of temperature (**Figure 6**). As expected, the absolute values of  $\eta_0$  decrease with increasing temperature in both cases. In comparison to the starting material  $\text{Ba-(PnBuA-RAFT)}_2$ , the supramolecular polymer self-assembled from  $\text{Ba-(PnBuA-HW)}_2$  demonstrates impressive viscosity enhancements (at 20 °C by a factor as high as  $\sim 1839$ ). In comparison our recently developed supramolecular linear structures<sup>49</sup> display viscosity enhancements only by a factor of  $\sim 42$  at 20 °C: such striking differences in viscosity enhancements (1839 vs 42) undoubtedly prove the generation of three-dimensional supramolecular dendritic structures by  $\text{Ba-(PnBuA-HW)}_2$ , compared to the one-dimensional supramolecular linear structures generated from same polymer with similar molar mass.

In order to further prove the formation of dendritic associates, we have conducted frequency-dependent melt rheology of  $\text{Ba-(PnBuA-RAFT)}_2$  and  $\text{Ba-(PnBuA-HW)}_2$  in the temperature ranging from 20 to 70 °C (ESI, **Figure S5**). In all cases,  $\text{Ba-(PnBuA-HW)}_2$  exhibits much higher storage ( $G'$ ) and loss ( $G''$ ) moduli than  $\text{Ba-(PnBuA-RAFT)}_2$  under same conditions (frequency and temperature). Moreover, no intersection of the storage and the loss modulus is observed (ESI, **Figure S5**), indicating the viscous property of the sample, together with small angle X-ray scattering (SAXS) profile which doesn't show any clusters (**Figure S6**), we can exclude supramolecular



**Figure 6:** Zero shear viscosity ( $\eta_0$ ) vs temperature for  $\text{Ba-(PnBuA-RAFT)}_2$  (open square), and  $\text{Ba-(PnBuA-HW)}_2$  (closed square).

aggregation or crosslinking (gelation) and thus can prove the formation of nonclustered dendritic supramolecular polymers. A final insight into the morphology and size of the supramolecular dendrimers formed by  $\text{Ba-(PnBuA-HW)}_2$  is corroborated by AFM investigations (intermittent contact

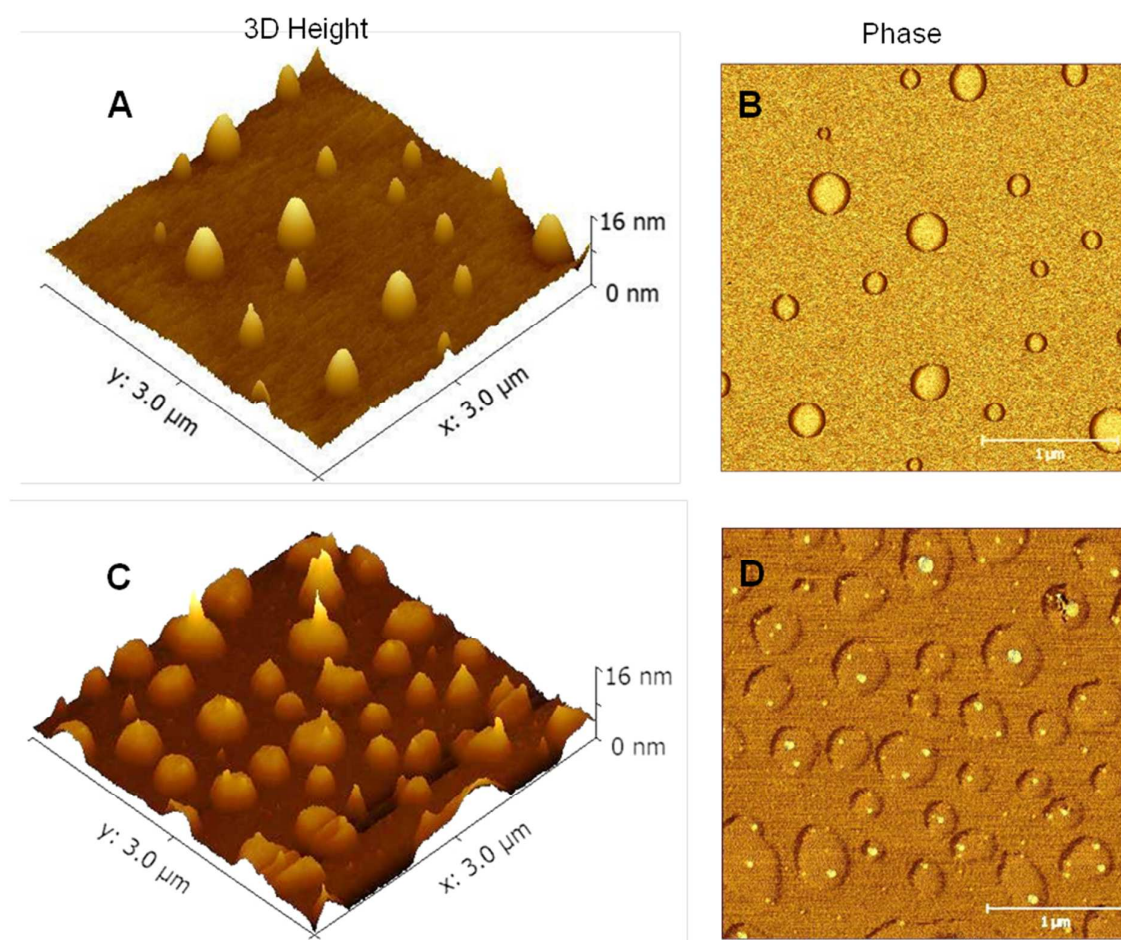
mode in air) exerted from solution. **Figure 7** shows typical AFM images of aggregates, obtained by spin-coating on a silicon wafer from a  $\text{Ba-(PnBuA-HW)}_2$  solution in chloroform or toluene. The presence of supramolecular nanostructures is firstly evidenced using chloroform as solvent (**Figure 7A&B**,  $c = 1 \text{ g/L}$ ): the images show defined disc-like objects predominately with diameters ( $d$ ) of  $\sim 180$  and  $310 \text{ nm}$ , but all of the disc-like objects are remarkably uniform in height ( $5\text{--}6 \text{ nm}$ , **Figure 7A**, ESI, **Figure S7A&B**). In fact, recent reports have demonstrated that the discontinuity in diameter of objects is a striking feature for the presence of high-generation supramolecular dendrimers.<sup>31,32</sup> While using less polar toluene as solvent at the same concentration, the AFM results exhibit even larger ( $d = \sim 250, 340$  and  $430 \text{ nm}$ ) disc-like objects (**Figure 7C**) with again uniform heights ( $\sim 5 \text{ nm}$ , ESI, **Figure S7C&D**), but a denser surface coverage, explainable by the expected higher degree of association. In addition, diffusion-ordered NMR (DOSY NMR) spectroscopy of a  $\text{Ba-(PnBuA-HW)}_2$  solution in toluene- $d_8$  demonstrates discrete diffusion coefficients which further confirm the differences in the homogeneous size of the self-assembled dendritic supramolecular polymers (ESI, **Figure S8**). Interestingly, we also observe elongated nanodomains at the top the discs (**Figure 7C&D**, ESI, **Figure S7C&D**), which are harder than the surrounding materials (**Figure 7D**, brighter in the corresponding phase image). This interesting hierarchical morphology can be ascribed to the stiff H-bonding aggregates being surrounded by a soft  $\text{PnBuA}$  polymer matrix. Altogether, the large size of nanoscopic structures observed clearly confirms the presence of dendritic supramolecular polymers formed by the  $\text{Ba-(PnBuA-HW)}_2$ . In order to study the influence of polar solvent on the morphology of  $\text{Ba-(PnBuA-HW)}_2$ , a mixed solvent system (chloroform/methanol, 1/1, v/v) is used, as seen in **Figure S9**. The addition of polar methanol result in the complete disappearance of previously obtained disc-like morphology, clearly demonstrating the at least partial dissociation of the supramolecular structures, thus being in agreement with the expected solvent-dependent characteristics of H-bonds.

## Conclusions

Striving to generate supramolecular dendrimers via self-assembly of polymeric building blocks, we have designed X- $Y_2$  type polymers with appropriate supramolecular endgroups. Benefitting from RAFT-made polymers, the easily available reactive thiol group generated by the aminolysis reaction of dithioester moiety is employed to attach two Hamilton wedges (Y) via a thiol-bromo click reaction in a one-pot two-step synthesis at room temperature within 1 hour. As a result, the mid-barbiturate and  $\alpha,\omega$ -Hamilton wedge functionalized X- $Y_2$  type polymer  $\text{Ba-(PnBuA-HW)}_2$  is successfully prepared from  $\text{Ba-(PnBuA-RAFT)}_2$ . Subsequently, supramolecular dendritic polymers are formed through H-bonding self-assembly,

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**Figure 7:** AFM 3D height (first column) and phase images (second column) of supramolecular aggregates immobilized on a Si solid support by spin-coating from a Ba-(PnBuA-HW)<sub>2</sub> solution in CHCl<sub>3</sub> (upper row) or toluene (lower row).

illustrating remarkable viscoelastic properties. AFM investigations reveal defined disc-like objects spin-coated from a Ba-(PnBuA-HW)<sub>2</sub> solution, indicative of the formation of dendritic aggregates. Most importantly, the morphologies of the supramolecular associates have been tuned at the mesoscale by changing the solvent from chloroform to the less polar toluene. The current work expands the scope of the thiol-bromo click reaction, aiding the further construction and potential applications of supramolecular complex structures and hierarchical morphologies.

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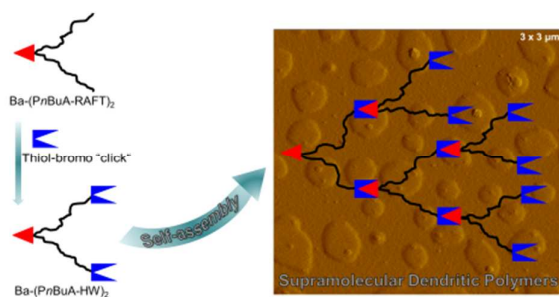
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Table of contents entry:



A X-Y<sub>2</sub> type heterotropic single-chain polymer, Ba-(PnBuA-HW)<sub>2</sub>, is prepared in a one-pot two-step reaction, subsequently self-assembling into supramolecular dendrimers, which are displaying solvent-dependent disc-like hierarchical nanoscopic structures as evidenced by AFM.