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Authors: Binbin Xu, Hongyu Qian, Ling Zhang, and Shaoliang Lin

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Branched Aggregates with Tunable Morphology via Hierarchical Self-Assembly of Azobenzene-Derived Molecular Double-Brushes

Binbin Xu, Hongyu Qian, Ling Zhang, and Shaoliang Lin*

[*] Dr. B. Xu, H. Qian, Prof. Dr. L. Zhang, Prof. Dr. S. Lin

Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrafine Materials of Ministry of Education, Frontiers Science Center for Materiobiology and Dynamic Chemistry, School of Materials Science and Engineering, East China University of Science and Technology Shanghai 200237 (China) E-mail: slin@ecust.edu.cn

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Abstract: Hierarchical self-assembly has been one of the most effective approach to fabricate nature-inspired materials with subtle nanostructures and variable functions. Herein, we report a distinct hierarchical self-assembly process of azobenzene-derived Janus molecular double-brushes (MDBs) with each graft site carrying a poly(azobenzene-acrylate) (PAzo) chain and a poly(ethylene oxide) (PEO) chain. Asymmetric tapered-worm (ATW) nanostructures with chain-end reactivity assembling from the azobenzene-derived MDBs serve as primary subunits to prepare branched supermicelles by increasing water content (Cw) in THF/water, which is predominantly facilitated by the distinctive molecular brush architecture and the intermolecular interaction of PAzo brushes. Various natural antedonshaped multiarm worm-like aggregates (MWAs) can be created depending on Cw via the particle-particle connection of ATWs. Intriguingly, the azobenzene moieties undergo trans-cis isomerization upon UV irradiation and further promote a morphology evolution of MWAs, leading the formation of starfish-shaped aggregates. Subsequently, multiscale luidia ciliaris and crossaster papposusshaped supermicelles with different features of central body and arms are prepared by manipulating irradiation time.

Introduction

Branched architectures are ubiquitous in nature, which have received considerable attention owing to their unique geometries and functionalities.^[1] For example, sea urchins, antedon, starfish and other echinoderms are well recognizable by their radial symmetry. There is a great variability of branched features between different classes of echinoderms, which is concomitant with their individually distinctive biological processes. Antedon consists of a tiny central body circled by 1-200 slender, feathery arms, whereas in starfish the multiple fairly broad arms have been incorporated into the relatively large body. The phenotypic differences between closely related species may take thousands of years during the evolution of species. Mimicking the naturally occurring diverse structures and shape transformations/ evolutions would be a remarkably effective and feasible approach to design nanomaterials with subtle nanostructures and variable functions.^[2]

In the past decade, tremendous efforts have been made to create sophisticated branched supermicelles through the hierarchical assembly of artificial molecules.^[3] Manners and co-

workers realized various "cross" and multidimensional superstructures based on living crystallization-driven selfassembly (CDSA).^[4] Du *et al.* created multipod polymersomes with precisely defined spatial structures by utilizing fusion-induced particle assembly strategy.^[5] Zhou *et al.* prepared hierarchical sea-urchin-like aggregates via emulsion-assisted polymerization-induced self-assembly.^[6] Despite of these great achievements, it is still challenging to build branched supermicelles with abundant hierarchical structures and stimuli-responsive morphology deformability, which restricts their potential applications.

Molecular brushes (MBs),^[7] or bottlebrush polymers, are branched macromolecules^[8] which graft polymeric chains onto a linear polymeric backbone densely. The high concentration of polymeric brushes, distinct worm-like features, and tunable architecture of MBs provide a new avenue for creating novel and distinct nanostructures that are difficult to achieve for linear amphiphiles, which endow them with lots of applications, such as sensors, supersoft elastomers, drug delivery, and photonic crystals.^[9] In particular, MBs-based nanostructures possess active chain ends that are not fully shielded by the corona chains.^[10] The chain-end reactivity renders the nanostructures more accessible and exposes their internal functionalities, which can be utilized to direct the hierarchical assembly of primary nanostructures into higher-order structures. Similar to CDSA, the end-to-end self-assembly of MBs-based nanostructures as an alternative route to form the multidimensional supramolecular assemblies with great designability and tunability is particularly appealing. On the other hand, azobenzene-containing nanoparticles are fascinating due to their strong noncovalent $\pi\text{-}\pi$ interactions and the ability to exhibit morphology deformation upon alternative UV/vis light irradiation driven by trans-cis reversible isomerization process.[11] Therefore, combining the feature of azobenzene molecules with the properties of MBs, azobenzene-containing MBs-based hierarchical supermicelles with morphology deformability could be achieved.

Aiming at creating diverse branched nanostructures with morphology deformability through hierarchical solution self-assembly, herein, we design molecular double-brushes (MDBs),^[12] a Janus type of MBs, with two statistically distributed side chains attached to each repeat unit of the backbone, wherein photoresponsive hydrophobic azobenzene and hydrophilic PEO brushes are simultaneously introduced into the backbone in order to increase attractive forces between the reactive chain ends, as

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Scheme 1. Left: chemical structures of PA-g-PAzo/PEO MDBs. Right: the schematic representations and typical TEM images of ATWs and MWAs self-assembled from Janus-type MDBs, and the evolution of MWAs from antedon to starfish-like branched architectures upon UV irradiation. Scale bars: 200 nm.

well as to trigger photo-induced changes of the molecular shape. Primary asymmetric tapered-worms (ATWs) are formed by amphiphilic Janus MDBs of polyacrylate-g-poly(6-(4-butyl-4'oxyazobenzene) hexyl acrylate)/poly(ethylene oxide) (PA-g-PAzo/PEO) with each graft site carrying PAzo and PEO hetero double-brushes, which was synthesized by simultaneous atom transfer radical polymerization (ATRP) and click reaction in one pot based on a bifunctional macro-agent of poly(Br-acrylatealkyne) (PBAA), as our previously reported.^[13] The detailed syntheses and characterizations of PBAA₃₄ and PA₃₄-g-PAzo₂₅/PEO₁₇ MDBs are provided in Supporting Information (Table S1 and Scheme S3). We demonstrate multiarm worm-like aggregates (MWAs) with branched architectures could be obtained via the hierarchical assembly of original ATWs with active chain-end as the water content increased and the ATWs were connected together (Scheme 1). More interestingly, the evolution of artificial echinoderm-like MWAs from antedon to starfish-shaped architectures was achieved (Scheme 1 and Scheme S5) by taking advantage of the photo-responsive morphology transformation of azobenzene-containing micelles via trans-cis isomerization.

Results and Discussion

In the first step, primary ATWs were prepared by using the selective solvent addition method. Deionized water, a poor solvent for PAzo brushes, was added slowly into the THF solution of PA-g-PAzo/PEO MDBs under stirring. The volume percentage of the added water relative to the whole volume (C_w) was 45%. Then, nanoparticles in THF/H₂O with various initial concentration (C_{ini}, in THF) were kinetically trapped by addition of excess water (100 times) to retain the original morphological sizes and geometries. Figure 1 and Figure S7 show a set of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the obtained tapered-worm structures as functions of initial polymer concentration at 45% water content. At a low C_{ini} of 0.05 mg mL⁻¹, the aggregates are asymmetric tapered worm-like nanoparticles with unobvious end caps (defined as ATW 1, Figure 1B). As C_{ini} increased to 0.1 mg mL⁻¹, asymmetric worm-like nanoparticles developed and further evolved to extended tapered-worm morphology (ATW 2, Figure 1C). At a Cini of 0.2 mg mL⁻¹, as shown in Figure 1D, the asymmetric taperedworm structures (ATW 3) can still be observed. However, the length of the ATW 3 becomes increasingly long (several micrometers) due to ordered packing of more MDBs in aggregates with the increase of C_{ini}. Figure 1A shows the schematic models of ATWs, which typically consist of an initiation site, a tapered cylinder and a hemispherical end cap. We hypothesize that the special tapering behavior of ATWs is a result of PAzo brushes stretching to various extension levels along the axis of the tapered assembly by considering the interfacial energy of PAzo and PEO brushes and the interaction of intermolecular PAzo brushes.^[14] In other words, the intermolecular association of pendant PAzo brushes within the tapered assembly varies systematically along the tapered worms (Figure 2A).



Figure 1. (A) Simple models of ATWs consisting of an initiation site, a tapered cylinder, and an end cap. TEM images of ATWs formed by PA-g-PAzo/PEO MDBs at different conditions: (B) ATW **1**, $C_{ini} = 0.05$ mg mL⁻¹ and $C_w = 45\%$ (Inset scale bar: 100 nm); (C) ATW **2**, $C_{ini} = 0.1$ mg mL⁻¹ and $C_w = 45\%$ (Inset scale bar: 200 nm); (D) ATW **3**, $C_{ini} = 0.2$ mg mL⁻¹ and $C_w = 45\%$ (Inset scale bar: 500 nm).

In the current work, the most important factors affecting the tapered-worm formation are the chain mobility and Janus-type structure of MDBs. It is well known that changing the environmental medium can change the conformational degrees of freedom and mobility of individual molecules. In our case, the slow addition of water caused the different mobility of PAzo brushes at different stage. In the early assembly stage, the mobile PAzo brushes of PA-g-PAzo/PEO with relative short backbone promoted interactions among them under the condition of high ratio of THF (good solvent for PAzo brushes) and the intermolecular PAzo brushes adopted a chain-interlaced structure, which would result in a smaller core segment at the initial site of assemblies (Figure 2A). Once sufficient water was added, continuously increasing interfacial energy between dense PAzo and PEO brushes would drive brushes to stretch away from the interface so as to limit the interactions of the immiscible doublebrushes.^[4a,15] Notably, the stretching of PEO and PAzo brushes is a much faster process than intermolecular interactions of PAzo brushes in relatively poor solvent. Thus, the internal extension of PAzo brushes occurred at the end of assemblies and the asymmetric tapered-worms were observed. Moreover, the inner hydrophobic cores are fully surrounded by hydrophilic shells to

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minimize exposure to the selective solvent due to the existence of hemispherical caps at the ends of ATWs (Figure 1A).



Figure 2. (A) Schematic illustration for the preparation of ATW 2 and symmetric worms: different association of intermolecular PAzo brushes in cores. (B, C) TEM images of symmetric worms formed by fast addition of water to a 0.1 mg mL⁻¹ initial MDBs solution in THF ($C_w = 45\%$ after addition). (D) Schematic representation for the fusion of symmetric worms. (E, F) TEM images of vine-like aggregates (inset: a photograph of vine) formed by the symmetric worms after dialysis ($C_w = 100\%$) without a quench process.

To better understand the role of Janus double-brushes in such ATWs, we investigated the self-assembly behaviors of amphiphilic poly(acrylic acid)-*g*-poly(6-(4-butyl-4-oxyazobenzene) hexyl acrylate) (PAA-*g*-PAzo) MBs consisting of PAA backbone and PAzo brushes at the same condition, which is chemically similar to PA-*g*-PAzo/PEO apart from the absence of PEO brushes (Scheme S4). As shown in Figure S9, PAA-*g*-PAzo exhibited the self-assembly into symmetric worms, suggesting that PAzo brushes stretching of PAzo brushes at the large end of ATWs is caused by strong stretching of PEO brushes because of the immiscibility of Janus double-brushes. These results indicate that the slow rate of adding selective solvents and unique Janus-type conformation are essential for the tapered-worm structures.

To further investigate the effect of the chain mobility of the PAzo brushes in tapered-worm conformations, we examined the self-assembly behaviors of MDBs by adding the selective solvent quickly to generate kinetic morphologies. We started with a system that had 0.1 mg mL⁻¹ initial concentration of PA-g-PAzo/PEO in THF. Then deionized water was added at a fast rate of 5 mL h⁻¹ to reach a water concentration of 45%. Interestingly, the kinetically trapped morphology of homogeneous symmetric worms was observed in the rapid manner (Figure 2 and Figure S10). As estimated from the TEM images, the diameter of the symmetric worms is approximately 16 nm (Figure 2A and Figure S11), which is different from the dimensions of the corresponding ATW 2 range from 22 nm at the large end and 11 nm at the small initiation site. The fast addition of water had a combined effect of quickly aggregating the hydrophobic PAzo brushes into aggregate cores while concurrently stretching the hydrophilic PEO brushes. Considering the poor mobility of PAzo brushes during the fast water addition process, the formation of symmetric worms is based on the relatively uniform chain stretching and weak chain-interlaced structure of intermolecular PAzo brushes along the axis (Figure 2A). Additionally, we carried out dialysis experiments without quench process to monitor whether these kinetically generated aggregates transform to the thermodynamically stable morphology. Intriguing self-assembled structures were expected to be created during dialysis because of the active ends of the symmetric worms. As expected, the obtained images show that vine-like nanostructures with many branching sites were observed (Figure 2E, F and Figure S12), which facilitated by more than two fusion sites between one symmetric worm and its neighbors. The vine-like nanostructures revealed that the primary aggregates formed by MDBs could be readily used to access sophisticated branched supermicelles through the hierarchical assembly process.

Similar to symmetric worms, the initiation sites of ATWs are not fully shielded by the corona PEO brushes (Figure 1A), which endows the initiation sites with sufficient activity to induce second self-assembly of the ATWs through the strong noncovalent aromatic-aromatic interactions of PAzo brushes. It should be noted that the hemispherical end-caps with a dense corona of hydrophilic PEO brushes render the core face inaccessible and efficiently inhibit hierarchical assembly at the chain ends (Figure 1A). To explore the possibility of this second self-assembly approach of ATWs, we first attempted to disassemble the ATWs by strong sonication of their solutions. It was found that the ATWs were replaced by "seed" entities (Figure S13A), indicating that disassembly of the worm nanostructures had occurred. As shown in Figure S13B-C, end-to-end fusion of "seed" entities occurred and the length of seed continuously increased as a function of the aging time, demonstrating a relatively greater accessibility of the seed terminus. Interestingly, we found that a part of seed clusters appeared to be branched and interconnected with each other (Figure S13D), which may reflect that the interactions between seed entities were not necessarily unidirectional. Therefore, the hierarchical self-assembly of the ATWs is expected to selfassemble into higher-order aggregates with branched architectures.

As shown in Figure 3, the second assembly/connection of ATWs can be induced by increasing C_{w} .^[3a,5,16] ATW 1 was fused to form di- or tri-arm worm-like aggregates (defined as MWA 1, Figure 3A and Figure S14A-C) when the C_{w} increases from 45% to 50%. Then more ATW 1 were interconnected with each other

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to form multiarm worm-like aggregates (MWA 2, Figure 3B and Figure S14D-G) at a C_w of 55%. Finally, worm clusters appeared by usage of a C_w of 60% (MWA 3, Figure 3C and Figure S14H-I). Interestingly, MWAs have both tiny central body and slender arms, and such a branched structure is similar to the natural antedon (Scheme S5, inset of Figure 3D). In order to clarify the C_w of the mixture solvent driving the assembly, UV-Vis spectroscopy was performed to monitor the changes of the turbidity of the solution during the self-assembly. As shown in Figure S6, a sharp increase in turbidity was observed at Cw of 40%, indicating the primary selfassembly process. The turbidity kept steady changing until the C_w reached 50% where the reactive initiation sites of ATWs were activated. To reduce the unfavorable ends and high-energy defects, the ATWs tend to fuse together by physical connecting PAzo brushes on the initiation sites of ATWs at $C_{\rm w}$ > 50%. Together with the TEM results, these data demonstrate the successful preparation of the MWAs with branched structures which evolved from particle-particle connection of individual ATW 1 via hierarchical self-assembly.



Figure 3. TEM images of MWAs hierarchical assembled from original ATWs: (A) MWA **1**, $C_{ini} = 0.05$ mg mL⁻¹ and $C_w = 50\%$, (B) MWA **2**, $C_{ini} = 0.05$ mg mL⁻¹ and $C_w = 55\%$, (C) MWA **3**, $C_{ini} = 0.05$ mg mL⁻¹ and $C_w = 60\%$, inset scale bar: 200 nm. (D) Schematic illustration of the connection process of ATWs by increase of C_w (inset: simple model of natural antedon). (E) TEM image of MWA **4**, $C_{ini} = 0.2$ mg mL⁻¹ and $C_w = 60\%$. (F) CLSM image of MWA **4** encapsulated with Nile Red. (G) OM image of MWA **5**, $C_{ni} = 0.2$ mg mL⁻¹ and $C_w = 67\%$.

Afterwards, the connection of ATW 2 and ATW 3 was also studied by TEM measurements upon addition of various amounts of water. Figure S15 shows the increase of water content causes ATW 2 and ATW 3 to fuse to longer-branched structures of MWAs. Interestingly, when the Cw increases to 60%, asymmetric taperedworm clusters (MWA 4, Figure 3E), which can be defined as multiple tapered-arm branched supermicelles, were obtained via the fusion of multiple ATW 3. To enable direct characterization of the tapered-worm clusters in solution, Nile Red was blended with tapered-worm clusters to form fluorescent-containing aggregates. The resulting aggregates were readily visualized in solution by means of confocal laser scanning microscopy (CLSM). CLSM images (Figure 3F and Figure S16) show that tapered-worm clusters consisting of many radiating arms stretching out from the central site indicates the antedon-shaped architectures. Upon further increasing the water content, given that the diameter of

Owing to the advantage of photoresponsive behavior of PAzo brushes (Figure S4), the morphology evolution of as-prepared ATWs and MWAs can be achieved through trans-cis photoisomerization. To test this hypothesis, we first examined the morphology deformation of ATWs under the irradiation of 365 nm light (70% light density, see experimental details in Supporting Information). As shown in Figure 4 and Figure S17, ATWs expanded resulting from trans-cis transformation upon UV irradiation.^[17] We propose that the photo-induced trans-cis isomerization generates a change in azobenzene molecular geometry and destroys the original ordered arrangement resulting in a distinctive hydrophilicity and random configuration for the cisazobenzene. Therefore, azobenzene-containing ATWs expanded when they converted to *cis* state upon UV irradiation. Conversely, the diameter and hydrophilicity of PAzo core decreased upon visible light irradiation, leading to the shrinkage of the ATWs (Figure S21A). Once the photoresponsive properties of the ATWs were investigated, the possibility of encapsulation and controlled release of Nile Red was assessed.^[18] As shown in Figure 4B, a gradual decrease of the fluorescence intensity of Nile Redencapsulated ATWs was observed upon irradiation, suggesting that controlled release of Nile Red from the aggregates to the aqueous media.



Figure 4. (A) Schematic illustration of the expansion of ATWs upon UV light irradiation. (B) Emission spectra of the Nile Red encapsulated ATW **2** recorded at different UV light irradiation times. TEM images of the expanding worms formed by (C) ATW **1** and (D) ATW **2** after UV light irradiation.

Subsequently the photo-induced evolution of MWAs was assessed to study the effect of *trans-cis* isomerization on the branched nanoparticle morphology. SEM and TEM analysis show that expanding and merged MWAs (Figure 5 and Figure S19) were obtained after UV light irradiation. For example, after irradiation, MWA **1** were transformed to the expanding and merged tri-arm worm-like aggregates (Figure 5B). Expanding and merged multiarm worms (Figure 5C and Figure S18A) and worm clusters (Figure 5D and Figure S18D) were observed which evolved from MWA **2** and MWA **3**, respectively. By analogy with the expanding behaviors of ATWs under the irradiation of UV light, the morphology evolution of branched MWAs can be explained by the same rationale. The isomerization of PAzo brushes generates an increase of the hydrophilicity and destroys the ordered align-

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Figure 5. (A) Schematic illustration of the evolution of MWAs from natural antedon to starfish-like branched architectures over different irradiation periods. Simple models and photographs of luidia ciliaris and crossaster papposus, two types of starfish. TEM images of expanding and merged (B) MWA 1, (C) MWA 2, and (D) MWA 3 after UV light irradiation (luidia ciliaris shape). TEM images of expanding and merged (E) MWA 2 and (F) MWA 3 after a longer period of UV light irradiation (crossaster papposus shape).

ment, leading to a certain expansion and fusion of the multiarms. Particularly, it is noteworthy to emphasize that expanding and merged MWAs exhibit a unique shape of central site and arms, which multiple fairly broad arms fuse in the central bodies. In contrast to the antedon-shaped MWAs as described in Figure 3, such high-branched structure (Figure 5C, D) agrees well with the natural luidia ciliaris, one type of starfish (Figure 5A and Scheme S5C).

Given the observation that antedon-shaped MWAs evolved to luidia ciliaris-shaped multiarm worms after UV irradiation, we further evaluated the effect of irradiation time on the branched morphology evolution. Considering the weak and unordered loose structures of *cis*-state azobenzene-containing aggregates, the typical intermediate morphologies were captured at low light density (50%) over different irradiation periods. The TEM image of MWA 2 taken at 1.5 h (Figure 5E and Figure S18B, C) was featured by another type of starfish-shaped aggregates. It can be clearly seen that multiple arms stretched out from the obvious central body radially like rays shining out from the sun, which is very similar to the structures of natural crossaster papposus (Figure 5A and Scheme S5D). Meanwhile, a similar crossaster papposus-shaped structure (Figure S18E, F) evolving from worm clusters was also observed in the MWA 3 system after irradiation for 1.5 h, in which the central body was fully covered by multiple broad arms. When the irradiation time was increased to 2 h (Figure 5F and Figure S20B, C), more crossaster papposusshaped aggregates were found in both MWA 2 and MWA 3 system. However, nano-fragments appeared around the aggregates at this stage, indicating the dissociation of polymer aggregates upon long time UV irradiation. Therefore, all of these observations suggest that diverse branched supermicelles can be prepared by the particle-particle connection of primary azobenzene-containing PA-*g*-PAzo/PEO MDB aggregates via hierarchical self-assembly, which further enables the morphology evolution from antedon to starfish-shaped architectures upon UV irradiation.

Conclusion

In summary, we describe the effective formation of multiarm branched supermicelles by utilizing the hierarchical self-assembly of PA-g-PAzo/PEO MDBs. The topological polymer chemistry of MDBs, π - π interaction and photoisomerization of PAzo brushes guarantee the reactive sites of hierarchical self-assembly process, enhanced noncovalent association and photo-induced morphology deformability of PA-g-PAzo/PEO aggregates. We found that PA-g-PAzo/PEO first self-assembled into ATWs that can serve as the basic building block by taking advantage of active initiation site. The primary ATWs were connected with each other to form di- or tri-arm worms, multiarm worms, and worm clusters upon increasing C_{w} . Interestingly, the obtained MWAs could be expanded and fused gradually upon UV light irradiation, leading to the morphological evolution of MWAs from antedon to starfish-shaped architectures. Additionally, by manipulating the irradiation time, the starfish-shaped aggregates displayed accordingly variable branched features in their central body and arms. The hierarchical assembly and morphology evolution of MDBs-based nanostructures provide a new avenue for fabricating extremely complex and deformable assemblies with diverse geometries.

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Keywords: Azo compounds • Branched supermicelles • Hierarchical assembly • Molecular double-brushes • Photoresponsiveness

- a) E. Ye, M. D. Regulacio, S.-Y. Zhang, X. J. Loh, M.-Y. Han, *Chem. Soc. Rev.* 2015, *44*, 6001-6017; b) Q. Luo, C. Hou, Y. Bai, R. Wang, J. Liu, *Chem. Rev.* 2016, *116*, 13571-13632; c) P. A. Rupar, L. Chabanne, M. A. Winnik, I. Manners, *Science* 2012, *337*, 559-562; d) X. Cui, P. Xiao, J. Wang, M. Zhou, W. Guo, Y. Yang, Y. He, Z. Wang, Y. Yang, Y. Zhang, Z. Lin, *Angew. Chem. Int. Ed.* 2017, *56*, 4488-4493; *Angew. Chem.* 2017, *129*, 4559-4564.
- [2] a) X. Li, J. locozzia, Y. Chen, S. Zhao, X. Cui, W. Wang, H. Yu, S. Lin, Z. Lin, Angew. Chem. Int. Ed. 2018, 57, 2046-2070; Angew. Chem. 2018, 130, 2066-2093; b) G. M. Whitesides, B. Grzybowski, Science 2002, 295, 2418-2421; c) Y. Mai, A. Eisenberg, Chem. Soc. Rev. 2012, 41, 5969-5985; d) S. Mann, Nat. Mater. 2009, 8, 781-792; e) H.-J. Kim, T. Kim, M. Lee, Acc. Chem. Res. 2011, 44, 72-82; f) K. Zhang, M. Jiang, D. Chen, Prog. Polym. Sci. 2012, 37, 445-486; g) Y. Liu, Y. Zhang, Z. Wang, J. Wang, K. Wei, G. Chen, M. Jiang, J. Am. Chem. Soc. 2016, 138, 12387-12394; h) P. Xu, L. Gao, C. Cai, J. Lin, L. Wang, X. Tian, Angew. Chem. Int. Ed. 2020, 59, 14281-14285; Angew. Chem. 2020, 132, 14387-14391.
- a) J. Chen, S. Wang, G. Shi, R. Wang, S. Cai, J. Zhang, X. Wan, Macromolecules 2018, 51, 7500-7508; b) T. Zhao, L. Chen, P. Wang, B. Li, R. Lin, A. A. Al-Khalaf, W. N. Hozzein, F. Zhang, X. Li, D. Zhao, Nat. Commun. 2019, 10, 4387; c) C. V. Synatschke, T. Nomoto, H. Cabral, M. Fortsch, K. Toh, Y. Matsumoto, K. Miyazaki, A. Hanisch, F. H. Schacher, A. Kishimura, N. Nishiyama, A. H. E. Müller, K. Kataoka, ACS Nano 2014, 8, 1161-1172; d) M. Yanagisawa, M. Imai, T. Taniguchi, Phys. Rev. Lett. 2008, 100, 148102.
- [4] a) H. Qiu, Y. Gao, V. A. Du, R. Harniman, M. A. Winnik, I. Manners, J. Am. Chem. Soc. 2015, 137, 2375-2385; b) X. Li, Y. Gao, C. E. Boott, D. W. Hayward, R. Harniman, G. R. Whittell, R. M. Richardson, M. A. Winnik, I. Manners, J. Am. Chem. Soc. 2016, 138, 4087–4095; c) X. Li, Y. Gao, R. Harniman, M. A. Winnik, I. Manners, J. Am. Chem. Soc. 2016, 138, 12902-12912.
- [5] J. Xiao, J. Du, J. Am. Chem. Soc. 2020, 142, 6569-6577.
- [6] Q. Xu, T. Huang, S. Li, K. Li, C. Li, Y. Liu, Y. Wang, C. Yu, Y. Zhou, Angew. Chem. Int. Ed. 2018, 57, 8043-8047; Angew. Chem. 2018, 130, 8175-8179.
- a) T. Pelras, C. S. Mahon, M. Müllner, Angew. Chem. Int. Ed. 2018, 57, 6982-6994; Angew. Chem. 2018, 130, 7100-7113; b) G. Xie, M. R. Martinez, M. Olszewski, S. S. Sheiko, K. Matyjaszewski, Biomacromolecules 2019, 20, 27-54; c) J. Rzayev, ACS Macro Lett. 2012, 1, 1146-1149; d) X. Pang, Y. He, J. Jung, Z. Lin, Science 2016, 353, 1268-1272; e) Y. Liu, J. Wang, M. Zhang, H. Li, Z. Lin, ACS Nano 2020, 14, 12491-12521.
- [8] X. Pang, L. Zhao, W. Han, X. Xin, Z. Lin, *Nat. Nanotechnol.* 2013, *8*, 426-431.
- [9] a) W. F. M. Daniel, J. Burdyńska, M. Vatankhah-Varnoosfaderani, K. Matyjaszewski, J. Paturej, M. Rubinstein, A. V. Dobrynin, S. S. Sheiko, *Nat. Mater.* 2016, *15*, 183-189; b) Y. Xia, V. Adibnia, R. Huang, F. Murschel, J. Faivre, G. Xie, M. Olszewski, G. D. Crescenzo, W. Qi, Z. He, R. Su, K. Matyjaszewski, X. Banquy, *Angew. Chem. Int. Ed.* 2019, *58*, 1308-1314; *Angew. Chem.* 2019, *131*, 1322-1328; c) Y.-L. Li, X. Chen, H.-K. Geng, Y. Dong, B. Wang, Z. Ma, L. Pan, G.-Q. Ma, D.-P. Song, Y.-S. Li, *Angew. Chem. Int. Ed.* 2021, *60*, 3647-3653; *Angew. Chem.* 2021,

133, 3691-3697; d) H. Luo, M. Szymusiak, E. A. Garcia, L. L. Lock, H. Cui, Y. Liu, M. Herrera-Alonso, *Macromolecules* **2017**, *50*, 2201-2206.

- [10] a) J. C. Foster, S. Varlas, B. Couturaud, Z. Coe, R. K. O'Reilly, *J. Am. Chem. Soc.* 2019, *141*, 2742-2753; b) Z. Li, J. Ma, N. S. Lee, K. L. Wooley, *J. Am. Chem. Soc.* 2011, *133*, 1228-1231; c) Y. Xia, Y. Li, A. O. Burts, M. F. Ottaviani, D. A. Tirrell, J. A. Johnson, N. J. Turro, R. H. Grubbs, *J. Am. Chem. Soc.* 2011, *133*, 19953-19959.
- [11] a) W. Wang, D. Shen, X. Li, Y. Yao, J. Lin, A. Wang, J. Yu, Z. L. Wang, S. W. Hong, Z. Lin, S. Lin, Angew. Chem. Int. Ed. 2018, 57, 2139-2143; Angew. Chem. 2018, 130, 2161-2165; b) W. Wang, C. Du, X. Wang, X. He, J. Lin, L. Li, S. Lin, Angew. Chem. Int. Ed. 2014, 53, 12116-12119; Angew. Chem. 2014, 126, 12312-12315; c) B. Xu, H. Qian, S. Lin, ACS Macro Lett. 2020, 9, 404-409; d) R. Dong, B. Zhu, Y. Zhou, D. Yan, X. Zhu, Angew. Chem. Int. Ed. 2012, 51, 11633-11637; Angew. Chem. 2012, 124, 11801-11805; e) N. Corrigan, J. Yeow, P. Judzewitsch, J. Xu, C. Boyer, Angew. Chem. Int. Ed. 2019, 58, 5170-5189; Angew. Chem. 2019, 131, 5224-5243; f) G. Liu, J. Sheng, W. L. Teo, G. Yang, H. Wu, Y. Li, Y. Zhao, J. Am. Chem. Soc. 2018, 140, 16275-16283.
- [12] a) Z.-H. Guo, A. N. Le, X. Feng, Y. Choo, B. Liu, D. Wang, Z. Wan, Y. Gu, J. Zhao, V. Li, C. O. Osuji, J. A. Johnson, M. Zhong, *Angew. Chem. Int. Ed.* 2018, *57*, 8493-8497; *Angew. Chem.* 2018, *130*, 8629-8633; b) A. N. Le, R. Liang, M. Zhong, *Chem. Eur. J.* 2019, *25*, 8177-8189; c) B. Xu, C. Feng, Y. Lv, S. Lin, G. Lu, X. Huang, *ACS Appl. Mater. Interfaces* 2020, *12*, 1588-1596; d) T. Palacios-Hernandez, H. Luo, E. A. Garcia, L. A. Pacheco, M. Herrera-Alonso, *Macromolecules* 2018, *51*, 2831-2837.
 [13] B. Xu, C. Feng, X. Huang, *Nat. Commun.* 2017, *8*, 333.
- [14] a) H. Cui, Z. Chen, S. Zhong, K. L. Wooley, D. J. Pochan, *Science* 2007, 317, 647-650; b) X. Wang, K. Hong, D. Baskaran, M. Goswami, B. Sumpter, J. Mays, *Soft Matter* 2011, 7, 7960-7964.
- [15] a) M. W. Matsen, F. S. Bates, *J. Chem. Phys.* **1997**, *106*, 2436-2448; b)
 S. Jain, F. S. Bates, *Macromolecules* **2004**, *37*, 1511-1523; c) N.-K. Lee,
 A. Johner, T. A. Vilgis, *Macromolecules* **2002**, *35*, 6043-6054.
- [16] H. Chen, E. Zhang, G. Yang, L. Li, L. Wu, Y. Zhang, Y. Liu, G. Chen, M. Jiang, ACS Macro Lett. 2019, 8, 893-898.
- [17] S. Guan, Z. Deng, T. Huang, W. Wen, Y. Zhao, A. Chen, ACS Macro Lett. 2019, 8, 460-465.
- [18] a) E. Blasco, B. V. K. J. Schmidt, C. Barner-Kowollik, M. Piñol, L. Oriol, *Macromolecules* 2014, 47, 3693-3700; b) J. del Barrio, L. Oriol, C. Sánchez, J. L. Serrano, A. Di Cicco, P. Keller, M.-H. Li, *J. Am. Chem.* Soc. 2010, 132, 3762-3769.

RESEARCH ARTICLE

Entry for the Table of Contents



Diverse branched supermicelles can be prepared by particle-particle connection of primary tapered worm-like aggregates from azobenzene-containing Janus molecular double-brushes (MDBs), which further enables biomimetic morphology evolution from antedon to starfish-shaped architectures upon UV irradiation.