Hierarchical Assembly

Simulation-Assisted Self-Assembly of Multicomponent Polymers into Hierarchical Assemblies with Varied Morphologies**

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Self-assembly of two or more components simultaneously into defined hierarchical structures is ubiquitous in nature. Understanding this natural phenomenon could enhance the power of supramolecular chemistry for the development of novel functional materials.[1] Based on developed block copolymer supramolecular chemistry, solution self-assembly of block copolymers with a second component, including nanoparticles,[2] small molecules,[3] metallic and organometallic species,[4] and macromolecules,[5] has been experimentally explored and has led to a variety of interesting nanostructures and functional materials.

Synthesis of defined nanostructures using concurrent self-assembly of multiple components is a great challenge, but may offer more opportunities for the creation of novel nanostructures. A good example is the discovery of multicompartment cylindrical micelles with phase-separated cores by co-assembly of a linear poly(acrylic acid)-*b*-poly(methyl acrylate)-*b*-polystyrene triblock copolymer in the presence of organic diamines.[3a] Stupp et al. investigated the self-assembly of peptide amphiphiles in the presence of dumbbell molecules containing hydrophobic oligo(*p*-phenylene ethylene) segments with bulky hydrophilic end caps, resulting uniform nonspherical supramolecular aggregates with the peptide amphiphiles coated on the rigid-rod dumbbell molecules.[5e] This early research developed a concept for possible nanostructure design by self-assembling amphiphilic molecules using molecular templates.

Very recently, we have discovered that poly(γ-benzyl-L-glutamate)-*b*-poly(ethylene glycol) (PBLG-*b*-PEG) rod–coil block copolymers and rigid PBLG homopolymers were able to co-assemble into virus-like superhelical rods and rings with uniform diameter and screw pitch.[6] It is believed that the hierarchical structures were formed with PBLG bundles as cores wrapped by PBLG-*b*-PEG block copolymers. Obviously, the structure of this system, as a result of the co-assembly of the two macromolecules, is quite different from other previously reported helical structures self-assembled from single polymers.[3b,7] It is therefore worth carrying out further studies to understand the system for possible designed synthesis. However, because the system involves many possible interactions between the two polymers, including hydrophobic, dipolar π–π interactions and an ordered packing tendency of α-helical polypeptide segments, it is a daunting task for us to understand exactly how the observed structures were formed. In fact, many other studies in the area face the same challenge.

Computer simulation, such as Brownian dynamics (BD), has emerged as a powerful method for the investigation of self-assembly behavior of amphiphilic block copolymers. Recent research has confirmed that simulations are capable of capturing the essential feature of the experimental findings, including multicomponent complex self-assembly systems.[8] What particularly important is that the simulation can provide microscopic information about the self-assembled aggregates, which could not to be discerned using currently available experimental techniques. Combining the experimental and simulation work is therefore an effective strategy for the investigation of polymer self-assembly.[8g]

Herein, we present the Brownian dynamics (BD) simulation-assisted, designed self-assembly of a binary system containing rod–coil (or coil–coil) block copolymers and rod-like (or coil) homopolymers. The simulation results suggest that a number of parameters, including interpolymer association forces, rigidity of polymers, and mixture ratio of the two polymers, influence the self-assembly behavior. By adjusting these parameters, the morphologies of the self-assembled objects can be systematically varied from abacus-like (beads-on-wire) structures to superhelices and plain fibers. Instructed by these simulation results, we have synthesized an array of block copolymers (for example PBLG-*b*-PEG and PS-*b*-PEG) and homopolymers (such as PBLG and PS), from which a number of binary systems were composed, allowing the simulated parameters to be investigated experimentally. The results follow the simulation predictions, allowing us understand the assembling behavior of the investigated

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system and synthesize hierarchical supramolecular polypeptide nanostructures in a predictable fashion.

The simulation system contains rigid homopolymers A_{150} and rod–coil block copolymers A_7B_3, where the rigid **A** segments are solvophobic and the coil **B** segments are solvophilic. The coarse-grained molecular dynamics program (COGNAC) of OCTA was employed for the simulations.[9] During the simulation, the amphiphilicity existed in the multicomponent systems was defined by setting different interaction potentials. The interactions between **A** and **A** (**A**–**A** interactions), which is considered as a major parameter dominating the cooperative self-assembly, were modeled with a potential containing an attractive component. Such selection makes **A** blocks perform as a solvophobic part for the formation of the cores of the aggregates. The interactions between **B** and **B** blocks (**B**–**B** interactions) were modeled with a purely repulsive potential, thus accounting for a solvophilic nature of the block. Furthermore, the incompatibility between **A** and **B** blocks was also modeled with a purely repulsive potential. The simulation details, including choices of parameters, can be found in the Supporting Information.

The strength of **A**–**A** interactions (ε_{AA}) was varied from 2.4 to 2.1 to 1.6. The effect of ε_{AA} on the simulation results are presented in Figure 1a–c; three distinctive hierarchical mor-

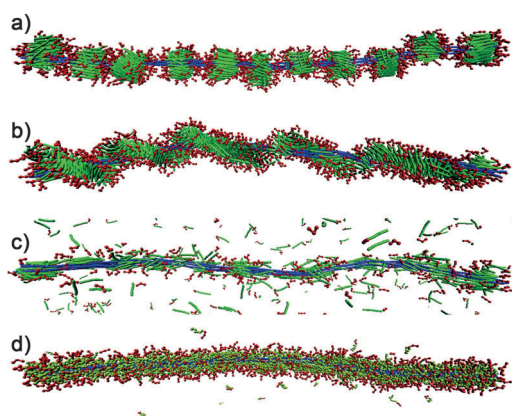***Figure 1.*** Simulation predictions for hierarchical structures self-assembled from rod–coil block copolymer/rigid homopolymers (A_7B_3/A_{150}): a) With higher interactions, $\varepsilon_{AA} = 2.4$; b) with moderate interactions, $\varepsilon_{AA} = 2.1$; c) with lower interactions, $\varepsilon_{AA} = 1.6$, and d) self-assembled from coil–coil block copolymers/rigid homopolymer (C_7B_3/A_{150}), $\varepsilon_{AA} = \varepsilon_{AC} = \varepsilon_{CC} = 2.1$. The molar ratio of block copolymer to homopolymer is 660. The blue, green, red and olivine beads correspond to the homopolymers **A**, **A** block, **B** block, and **C** block of block copolymers, respectively.

phologies with A_7B_3 coating on A_{150} bundles are revealed. As can be seen, the block copolymers and homopolymers cooperatively associate into a large-length-scale fiber structure with the block copolymers forming small-length-scale structure on the homopolymer bundles. When ε_{AA} is higher (2.4), an abacus-like structure (beads-on-wire) is observed with A_7B_3 aggregated into separating beads around A_{150} bundles (Figure 1a). As ε_{AA} decreases to 2.1, A_7B_3 become helically wrapping on the A_{150} bundles (Figure 1b). While

further decreasing the ε_{AA} to 1.6, full integration of the two components cannot be achieved. As shown in Figure 1c, although the bundles of A_{150} are randomly coated with A_7B_3, many A_7B_3 chains are freely dispersed in the simulation cell. This set of simulation emphasizes the important role of interaction strength of the rod blocks for the synthesis and variation of hierarchical nanostructures. Furthermore, the mixture ratio of A_7B_3 to A_{150} has a prominent effect on the formed hierarchical structures (see the Supporting Information). For example, by decreasing molar ratio (MR) of A_7B_3 to A_{150} at the condition $\varepsilon_{AA} = 2.1$, the helical structure becomes gradually less apparent owing to less A_7B_3 coated on the A_{150} axis (Supporting Information, Figure S1). The simulations also revealed that a long rigid homopolymer is essential for the formation of hierarchical structures. Mixture systems with shorter rigid homopolymers self-assembled into spheres or short helical rods (Supporting Information, Figure S2).

To understand the importance of the rigidity of **A** block in the assembly, coil–coil block copolymers of C_7B_3 were used to replace the rod–coil block copolymers of A_7B_3 for the study. The interaction parameter between **A** and **C** ($\varepsilon_{AC} = 2.1$) was set to be equal to ε_{AA} and ε_{CC}. As shown in Figure 1d, despite the high ratio of C_7B_3 with respect to A_{150} that was used, the simulated assembling only leads to plain fibers with C_7B_3 smoothly coating on the surfaces of A_{150} bundles. Increasing ε_{AC} does not change the morphology obviously (Supporting Information, Figure S3). These simulation results stress the point that the rigidity of the polymer blocks is essential in determining the fine structure of the assemblies.

As we learned from the simulation results, self-assembly of the binary systems can be influenced markedly by the interaction strength of hydrophobic blocks. To experimentally explore such a parameter, a set of experiments on the same pair of polymers (PBLG-*b*-PEG/PBLG) at various temperatures was designed. It is well-known that PEG is water-soluble and its solubility decreases with increasing solution temperature.[10] Therefore, at higher temperatures, the block copolymers are less hydrophilic, which induces a relatively stronger attraction between hydrophobic PBLG segments; at lower temperatures, increased hydrophilicity of PEG segments in the block copolymers renders the interaction between PBLG segments relatively weaker. Indeed, a drastic influence of solution temperature on the self-assembled structures has been observed.

Self-assembly of the $PBLG_{31000}$-*b*-$PEG_{5000}/PBLG_{528000}$ binary system (the subscripts denote the molecular weight for each segments) was first performed at 20 °C. The weight ratio of block copolymer to homopolymer is 4:1 (when converted into molar ratio, it is ca. 58). Figure 2a is a TEM image of self-assembled structures. As can be seen, uniform superhelical structures, including fibers and rings, are clearly observed, which is consistent with our previous report.[6] The supramolecular structures have PEG-rich corona, as determined by ¹H NMR analysis (Supporting Information, Figure S4). The inset in Figure 2a is the simulation prediction of the superhelical structure in which homopolymer bundles form the inner axis and block copolymers form screws through ordered packing of the rod segments. The experimental results combined with simulation predictions indicate
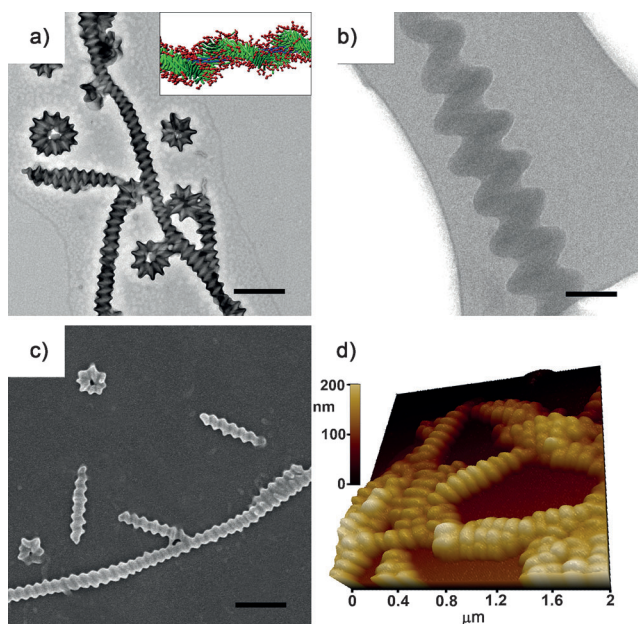
Figure 2. a) HRTEM, b) cryo-TEM, c) SEM, and d) AFM images of superhelices prepared at 20 °C. MR = 58. Inset in (a): simulation prediction of the superhelical structure. Scale bars: 500 nm (a, c), 100 nm (b). Samples for (a, c, and d) were prepared from aqueous solution; the sample for (b) was prepared from vitrification of aqueous solution using liquid ethane.

Figure 3. SEM images of aggregates self-assembled from the PBLG-*b*-PEG/PBLG binary system at various temperatures: a) 10 °C, b) 5 °C, c) 30 °C, and d) 40 °C. Inset in (d): simulation prediction of the abacus-like structure. Scale bars: 200 nm. Samples were prepared from aqueous solution.

that the superhelical structure is formed from hydrophobic PBLG homopolymer inner bundles wrapped by the PBLG rod segments from the PBLG-*b*-PEG block copolymers. The superhelical feature of the aggregates is confirmed using cryo-TEM (Figure 2b). As the cryo-TEM reveals the same morphology as conventional TEM testing, possible drying effect for the formation of observed helical structure can be ruled out. The diameter and screw-pitch of the superhelices, as estimated from the cryo-TEM image (Figure 2b), are about 140 and 95 nm, respectively. The self-assembled structure was further examined using SEM (Figure 2c) and AFM (Figure 2d), from which three-dimensional shapes of superhelical fibers and rings are clearly observed. Moreover, the images show that all these helices are right-handed.

In a separate experiment, we have examined the influence of chirality of polypeptides by replacing PBLG with poly(γ-benzyl-D-glutamate) segments (PBDG; takes opposite chirality to PBLG). Right-handed superhelices were also observed from PBDG-*b*-PEG/PBDG mixtures. However, when the handedness of polypeptides in the block copolymer and homopolymer is opposite, such as PBLG-*b*-PEG/PBDG and PBDG-*b*-PEG/PBLG mixtures, the helical structures become less regular (Supporting Information, Figure S5). These results suggest that the same handedness of polypeptides in block copolymer and homopolymer is essential for the formation of ordered hierarchical structures.

To investigate the effect of self-assembling temperature, the same experiments were further carried out at lower temperatures of 5 and 10 °C, and higher temperatures of 30 and 40 °C. Figure 3a,b shows SEM images of the aggregates prepared at lower temperatur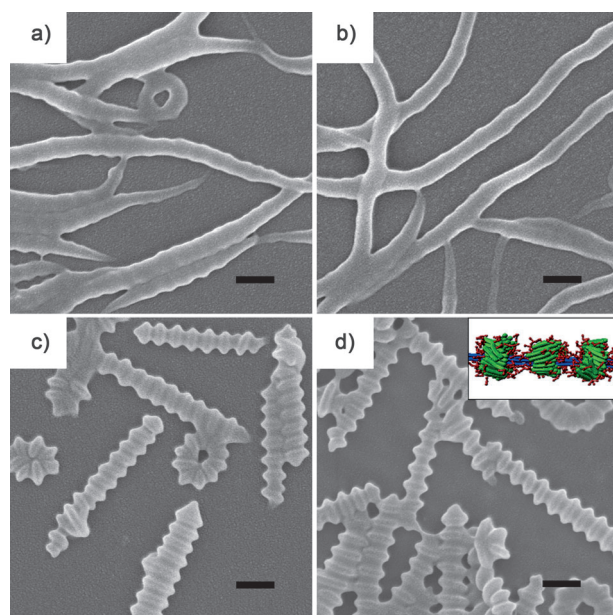es. As shown in Figure 3a, fibers with rough surface or irregular helical sense are observed when the preparation temperature is 10 °C. For the samples prepared at 5 °C, plain fibers are obtained (Figure 3b). Figure 3c,d shows the SEM images of the aggregates prepared at higher temperatures: a new morphology appears, namely an abacus-like structure. For the sample prepared at 30 °C, the abacus-like structures coexist with helical structures (Figure 3c). Upon increasing the experimental temperature to 40 °C, the abacus-like structures become the predominant morphology (Figure 3d). As indicated by simulated structures (see Figure 1a and the inset in Figure 3d), the abacus-like structures are formed with block copolymers aggregating into separated beads around the homopolymer bundles. These nanostructures are also confirmed using TEM (Supporting Information, Figure S6) and Cryo-TEM (Supporting Information, Figure S7).

Apart from temperature, the effects of other factors on the self-assembled structures were also briefly investigated. The helical feature becomes less apparent upon decreasing the mixture molar ratio (MR) of block copolymer to homopolymer from 58 to 14. When further decreasing the MR to 6, fibers with smooth surface were obtained (Supporting Information, Figure S10). These results are in agreement with the simulation results (Supporting Information, Figure S1). Moreover, a relatively higher molecular weight of PBLG homopolymer is essential to obtain a helical structure (Supporting Information, Figure S11); for PBLG-*b*-PEG block copolymers, both the PBLG and PEG block lengths should be moderate (Supporting Information, Figures S12, S13). Finally, the initial polymer concentration in organic solvents is found to have some influence on the self-assembled structures. Similar superhelical structures have

been observed with the initial polymer concentrations ranging from 0.05 to 0.9 gL^{-1}. However, upon increasing the initial polymer concentrations, the diameter increases, and the screw of the helices becomes relatively tighter (Supporting Information, Figure S14).

Based on simulation and experimental results, the supramolecular morphology variation from plain fiber to superhelix and then to abacus-like morphologies can be attributed to gradually increased PBLG–PBLG interactions as a function of temperature. The strong association of PBLG–PBLG facilitated an ordered packing (side-by-side) of PBLG rods on the surface of PBLG bundles, leading to abacus-like morphologies (Figure 3 d). As estimated from Figure 3 d, the width of ridge regions in the abacus is about 30 nm, which is only slightly larger than the length of PBLG rods (ca. 22 nm),[11] indicating that PBLG rods are packed in a relatively highly ordered fashion. By decreasing the interactions between PBLG–PBLG (experimentally achieved by dropping self-assembly temperatures), the packing order of PBLG rods decreased and gradually transform from side-by-side to dislocated and to random fashion (Figure 1). Consequently, the widths of ridge assembled from PBLG blocks gradually increases from 30 nm for abacus-like structure to 35 nm for helix structure, and finally become indistinguishable in the plain fibers (Figure 3 b) as a result of random packing of PBLG-b-PEG block copolymer on the surface of PBLG homopolymer bundles. Detailed discussions of the mechanism for the formation of these abacus-like structures, superhelices, and plain fibers are given in the Supporting Information, Section S2.14.

To experimentally explore the effect of rigidity of hydrophobic segments on the self-assembled structures, we prepared polystyrene-b-poly(ethylene glycol) (PS-b-PEG) coil–coil block copolymers and PS homopolymers for our investigation. In contrast to PBLG, PS is a hydrophobic coil polymer. The interaction between PBLG and PS segments was considered to be comparable to that between PBLG and PBLG because both hydrophobic interaction and π–π stacking of phenyl groups existed in both PBLG–PS and PS–PS pairs.[12] Through selectively pairing up the block copolymers and homopolymers, the effect of rigidity of polymer chains on self-assembly behavior of the binary systems can be evaluated.

First, PS-b-PEG was used to self-assemble with PBLG homopolymers at 20 °C. TEM image reveals plain fibers and rings without helical or abacus-like features (Figure 4 a). This result is consistent with simulated structures (Figure 1 d), emphasizing the importance of rod–coil block copolymers required for small-length-scale features (helical or abacus-like). Furthermore, we do not observe the effect of temperature on the self-assembled morphology for such a system. These control experiments verified the theoretical results that the rigidity of hydrophobic segment in block copolymer is necessary for the formation of ordered packing of the block copolymer on the surface of PBLG bundles.

To test the importance of rigidity of core-forming homopolymers, the self-assembly of the PBLG-b-PEG/PS binary system was investigated. Although we could not simulate the system owing to the limitation of current
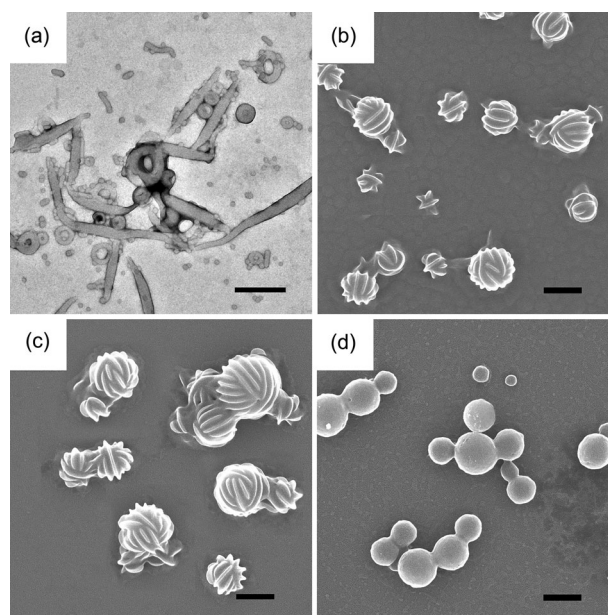

Figure 4. Images of aggregates self-assembled from: a) PS-b-PEG/PBLG, 20 °C, HRTEM; b) PBLG-b-PEG/PS, 20 °C, SEM; c) PBLG-b-PEG/PS, 40 °C, SEM; d) PBLG-b-PEG/PS, 5 °C, SEM. The weight ratio of block copolymer to homopolymer is 4:1 (a); 1.5:1 (b–d). Scale bars: 500 nm. Samples were prepared from aqueous solution.

simulation technique,[13] experimental studies follow our intuition that spherical rather than one-dimensional structures are obtained as a result of using PS homopolymers. Moreover, we have discovered a new morphology that is like that of a ball of wool. As shown in the SEM image (Figure 4 b), spheres with stripes on the surface are observed from the system assembled at 20 °C. Based on the knowledge developed from above investigation on superhelical and abacus-like structures, it is possible that the balls of wool consist of PS homopolymers cores covered by PBLG-b-PEG block copolymers. Owing to the rigidity of PBLG, the block copolymers are able to pack into ordered structures, leading to the formation of the stripes on the surface of the balls. To test this hypothesis, we performed the same experiment but at higher and lower temperatures, respectively. At the higher temperature (40 °C), larger spheres with regular stripes were obtained (Figure 4 c). However, the lower temperature (5 °C) leads to the formation of smooth spheres without stripe-patterned surfaces (Figure 4 d). Obviously, the morphology varying from balls of wool to smooth spheres can be explained by a decrease in association forces between the block copolymers at lower temperature as we discussed above.

In conclusion, with the assistance of computer simulation, we systematically investigated the self-assembling behavior of block copolymer/homopolymer binary systems, leading to a better understanding of supramolecular chemistry on such systems. As a result, we were able to rationally synthesize a number of hierarchical superstructures, including fibers, helices, abacus-like structures, spheres, and balls of wool, by varying a few parameters, such as temperature, ratio of the two polymers, and rigidity of polymer blocks. The work has demonstrated the possibility to vary nanostructures of multi-

component assemblies in a designed fashion and to create novel morphologies. Furthermore, the obtained hierarchical superstructures resemble viruses in structure, which consists of proteins spontaneously assembled around a DNA/RNA template. The information gained from the present work may provide useful guidance for construction of model viruses and subsequently facilitate the investigation of the physiological behavior of viruses, for example, cell penetration.

Experimental Section

To prepare self-assemblies, block copolymers of PBLG-*b*-PEG and PS-*b*-PEG and homopolymers of PBLG and PS were first dissolved in a tetrahydrofuran (THF)/*N,N'*-dimethylformamide (DMF) (3:7 v/v) solvent mixture. The polymer concentration of the stock solutions was typically 0.3 g L^{-1}. Block-copolymer and homopolymer solutions were first mixed with the intended volume ratio, typically 8 mL of PBLG$_{31000}$-*b*-PEG$_{5000}$ block copolymer solution and 2 mL of PBLG$_{528000}$ homopolymer solution. For the study of the effect of the mixing ratio of block copolymer to homopolymer on the self-assembly, the initial total polymer concentrations are fixed at 0.3 g L^{-1}, and the feeding ratio of block copolymer to homopolymer was varied for the study. Deionized water (2.5 mL), a selective solvent for PEG, was added to the system at a rate of ca. 1 mL min^{-1} with vigorous stirring. Upon the addition of water, the colorless solution gradually took on a blue tint, which indicates the formation of self-assembled aggregates. Finally, the solution was dialyzed against deionized water for at least 3 days to remove organic solvents.

All experimental procedures, including the processes of adding water and dialysis, were performed at a constant temperature. The polymer solutions, water for micellization, and water for dialysis were stored at a corresponding temperature for more than 12 h before use. The self-assembling experiments were conducted at temperatures of 5, 10, 20, 30, or 40 °C. The aggregate morphologies were characterized by TEM (JEM-2100F, 200 kV), Cryo-TEM (JEM-2200FS, 200 kV, −174 °C), SEM (S4800, 10 kV), and AFM (XE-100, tapping mode). Detailed experimental information is available in the Supporting Information.

The self-assembled structures are equilibrium under the initial self-assembly conditions (water/organic solvent = 1:5 v/v). The aggregates of superhelices and abacus-like structures are reversible when temperature varies; for example, the superhelices transform to abacus-like structures when the temperature is increased, and the abacus-like can be reversibly transformed back to the superhelices by decreasing the temperature (Supporting Information, Figure S8). After dialysis against water, the hierarchical structures are frozen. The store temperature has negligible effect on the morphologies of the frozen aggregates. For example, no morphology transformation was observed even the aggregates were aged at various temperature up to 40 °C for more than 3 months (Supporting Information, Figure S9).

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