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The histidine-coated fibrillar nanoprobe response to Ag$^+$ with fluorescence enhancement was developed through a rational design based on the aqueous self-assembly of peptide amphiphiles for potential use as cell-imaging and antimicrobial agents.
“Light-up” 1D supramolecular nanoprobe for silver ion based on an assembly of pyrene-labeled peptide amphiphiles: Cell-imaging and antimicrobial activity

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We prepared pyrene-labeled peptide amphiphiles (PAs) consisting of a hydrophobic linear- or branched-alkyl chain (for 1 or 2, respectively) and a hydrophilic histidine-rich peptide of HGGGHGHGGGHG (HG12). Both peptides have a strong tendency to form nanofibrils (NFs) in aqueous media. The resulting histidine-coated NFs show a great binding affinity to Cu²⁺ as a fluorescence “light-off” sensor. Interestingly, the emission spectra of the pyrene probe show that the different supramolecular assemblies between 1 and 2 can significantly affect the binding affinity to specific metal ions. In particular, “light-up” fluorescent Ag⁺ detection of NFs of 2 through the inhibition of photoinduced electron transfer (PET) was observed even at a low concentration of PA solution. As a means to determine the biological responsibility of 2 to Ag⁺, intracellular detection using the “turn-on” response was performed. A considerable enhancement of fluorescence in NF-loaded HeLa cells was observed. In addition, the NFs were used as a template scaffold for the production of Ag nanoparticles (AgNPs) with high monodispersity and stability. The NFs decorated with AgNPs are shown to possess highly effective and long-term antibacterial activity against both Gram-negative and -positive bacteria.

Introduction

The self-assembly of peptide-conjugated amphiphiles (PAs) can lead to a variety of nanoarchitectures such as micelles, barrels, vesicles, nanofibrils (NFs), ribbons and tubes, in aqueous media.¹ It has been recognized as one of the most attractive biomaterial scaffolds due to its inherent properties including good biodegradability, biocompatibility and bioactivity.² Understanding the self-assembly process of naturally and rationally designed PAs and the resulting well-organized nanostructures at the molecular level has created new opportunities for developing novel functional materials for applications such as tissue engineering,³ regenerative medicine,⁴ targeted therapeutic delivery⁵ and diagnosis.⁶ For instance, among the PA-based nanostructures, one-dimensional (1D) β-sheet rich fibrillar assemblies of PAs have been known to play a central role in neurodegenerative disease which give rise to not only a functional motif for biomaterials,⁷,⁸ but also a structural diversity for the 1D assembly of nanomaterials.⁹ In addition, the intrinsic propensity of PAs to form core-shell aggregates in aqueous solutions allows for the easy addition of desired chemical and biological activities to the specific region of the nanostructure by incorporating a functional building block into the molecular architecture.¹⁰-¹³ However, NFs with optical responses to the physiological environment, as a result of changing the molecular packing within the fibrillar core, have rarely been investigated.¹⁴,¹⁵ Meanwhile, the molecular systems used to capture metal ions with biological interests have been intensively investigated and applied in many fields, including diagnosis and clinical toxicology.¹⁶,¹⁷ Among the peptide building blocks, histidine-rich peptides have attracted much attention as molecular recognition scaffolds for binding metal ions in the active sites of proteins due to a very efficient imidazole-nitrogen donor atom in the histidyl residue.¹⁸ In particular, it has been reported that an HGGGHGHGGGHG (HG12) consisting of histidine and glycine immobilized on the pre-assembled nanotube can complex with Cu²⁺ and Ni²⁺,¹⁹ leading to the formation of metal nanoparticle-coated nanotubes in the presence of a reducing agent.²⁰,²¹ This result stimulated us to investigate whether the introduction of HG12 into a hydrophilic block of PA would facilitate the utilization of self-assembled NFs as supramolecular platforms for the selective and sensitive detection of metal ions as well as for the nucleation and growth of metal crystals in aqueous solutions. It might ultimately be used to control the optoelectronic, magnetic, and biological properties of organic-inorganic NF-hybrids mimicking biomineralization.²²,²³
Along this line, HG12-conjugated PA 1 was simply designed, which contains a linear alkyl chain (Scheme 1). The pyrene moiety was attached to the N-terminus of 1 as a fluorescent probe to monitor the self-organization process of the PAs. It has been well-known that the emission spectra of pyrene represent the relative spatial proximity between neighboring pyrene chromophores, which leads to the formation of a monomer or excimer, enabling the interpretation of the molecular packing of the hydrophobic core in self-assembled nanostructures. In order to promote the robust assembly of PA through the enhanced hydrophobic interaction, a branched alkyl chain with a pyrene pendant was incorporated into PA 2.

Interestingly, although both 1 and 2 self-assembled into 1D NFs in an aqueous solution, they showed different molecular packing modes for the pyrene (Fig. 1). The ability of the NFs to bind the specific metal ions was shown to work differently with respect to the spatial constraint of HG12 imposed by the molecular packing in the core of the NFs. More interestingly, the NFs of 2 exhibited a significant fluorescence “light-up” response to Ag⁺. In general, efficient fluorescent chemosensors for metal ions were designed and developed based on various photoinduced processes, but most of the pyrene fluorophore-containing supramolecular systems have shown fluorescence quenching via electron or energy transfer, leading to low sensitivity. In addition, silver-containing nanomaterials have been of special interest due to their low toxicity toward mammalian cells, strong antimicrobial activity against bacteria, and unique optical properties. For this reason, one can envision that the supramolecular fibrils decorated with Ag⁺ by fluorescence “light-up” molecular recognition in an aqueous solution can act as both a multifunctional nanoplateform for developing a highly sensitive supramolecular probe for metal ion detection in live cells and an antimicrobial agent leading to potent long-lasting activity.

Herein, we report the unique self-assembling characteristics of PAs to form NFs depending on the nature of alkyl chains (i.e., a linear or branched structure of the chains). The NFs are coated with a metal-binding peptide that showed a great binding affinity to Cu²⁺, leading to the fluorescence “light-off” response. Remarkably, the ability of the NFs to bind Ag⁺ enables the intracellular imaging of HeLa cells by the fluorescence “turn-on” response and the fabrication of Ag nanoparticles (AgNPs) on the surface of NFs by the reduction of Ag⁺ with NaBH₄. The resulting AgNPs-NFs hybrid system shows an effective antimicrobial effect against both Gram-negative and -positive bacteria. Most chemo sensors for Ag⁺ exhibit a limitation in practical biomedical applications due to the small molecule-based development, low sensitivity from the “turn-off” response, and low water solubility. To the best of our knowledge, this report is the first example of supramolecular 1D nanoprobes showing dual functions: a “light-up” response for Ag⁺ in an aqueous solution, and growth templates for AgNPs, leading to cell imaging and an antibacterial effect. It may provide a useful strategy for the fabrication of biomedical nanomaterials for sensing and imaging, and it could have special value in terms of comprehending the biological functions of the metal-peptide system.

**Results and Discussion**

**Synthesis and self-assembly behavior of PAs in water**

The PAs were synthesized on Rink amide MBHA resin using standard Fmoc (9-fluorenylmethoxycarbonyl) protocols (Scheme S1,2). Pyrene butyric acid was covalently linked to the N-terminus of the HG12 peptide segment through linear- or branched-dodecanoic acid (C₁₂) tails. The resulting crude product was purified to produce pure PAs (>95% as determined by analytical HPLC, Fig. S1). The molecular weight was confirmed using matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy, and it was consistent with the theoretical value (Fig. S1).

To investigate the self-assembly behaviors of the PAs, transmission electron microscopy (TEM) experiments were performed on the aqueous solutions of PAs 1 and 2 (Fig. 2a-d). Direct visualization of the aggregates of PA 1 containing a linear-alkyl chain revealed micrometer-long NFs with regular diameters of 9.5 ± 1.0 nm (Fig. 2a,S4a). Cryogenic TEM (cryo-TEM) experiments confirmed the presence of aqueous NFs with an average diameter of 4.2 nm (Fig. 2b,S4b). Normally, as the solvated hydrophilic block is invisible, the hydrophobic core appears to be dark in a cryo-TEM image. Considering the extended molecular length of the hydrophobic block (ca. 2.8 nm by CPK modeling), the diameter of 4.2 nm is in reasonable agreement with the formation of interdigitated bilayer packing of 1 (Fig. S4c).

Although 2 with a dibranched-alkyl chain is shown to form...
the NFs, the average diameters and lengths of the NFs decrease compared to those of 1 (Fig. 2c,d), which is consistent with the DLS data (Fig. 2e). The average hydrodynamic diameters ($R_d$) of 1 and 2 were 6.6 μm and 4.9 μm, respectively. Interestingly, the diameters of the NFs of 2 in TEM decreased to $8.2 \pm 0.6$ nm as compared with those in 1 (Fig. S4c), whereas those in cryo-TEM increased to $5.7 \pm 0.4$ nm (Fig. S4d), averaged over 100 NFs. This unexpected increment in the diameter of the hydrophobic core, including the pyrenyl moiety and alkyl chains, is considered to be attributed to the change in the internal molecular packing with regard to the incorporation of the branched-dodecanoic tails. The fluorescence spectroscopy was first carried out to study the fine organization in the molecular packing with regard to the incorporation of Cu$^{2+}$ to 1 and 2 (0.1 mM in water, $\lambda_{ex}$ = 340 nm).

Fluorometric “turn-off” sensing of the NFs for Cu$^{2+}$ and the growth of CuNPs on the surface of the NFs

The metal ion recognition event of histidine-rich peptide (HG12) coated-NFs was first examined with Cu$^{2+}$. The fibrillar structure with a high aspect ratio was kept, while the fluorescence was significantly quenched following the addition of the paramagnetic d$^9$ Cu$^{2+}$ (Fig. 2f). In particular, $\lambda_{max}$ of 2 was blue-shifted from 478 nm to 455 nm, indicating a conversion of an excimer fashion from a sandwich-like dynamic excimer to a partially overlapped static excimer. This means that a closer molecular interaction between the pyrenyl groups was induced by capturing of Cu$^{2+}$ with the HG12. TEM images of the NFs of both 1 and 2 after the addition of Cu$^{2+}$ reveal a remarkable enhancement of mass contrast even without staining (Fig. 3a,b). Indeed, the
After the addition of Cu^{2+}, the association between Cu^{2+} and the NFs was confirmed by MALDI-TOF mass spectra of Cu^{2+}-PA complexes. (d) FTIR spectra before and after the addition of Cu^{2+} (inset, N-H stretching vibrations in the imidazole of the histidine). TEM images of the NFs decorated with CuNPs of (e) 1 and (f) 2, respectively (inset, selected area diffraction patterns confirming the formation of Cu nanocrystals).

Supramolecular fluorescent nanoprobes of PAs to metal ions

To corroborate the metal-binding affinity of the aqueous NFs in detail, a variety of metal ions, including Ag^{+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}, were employed. These investigations may provide an opportunity to find interesting characteristics of the NFs. We first measured the critical micellar concentration (CMC) of 1 and 2 in water using a fluorescence spectrometer to systematically investigate the ability of the NFs as metal binders in a dilute solution. The intensity ratio of the two emission peaks (I_{396}/I_{378}) of the pyrene pendant were highly sensitive to the medium polarity, which was calculated and plotted against the concentration. The CMCs of the 1 and 2 were determined to be 7.5 μM and 6.1 μM, respectively (Fig. S10). These low CMC values suggest that PAs can act as supramolecular 1D nanoprobes in a dilute condition. As expected, both PAs 1 and 2 were shown to self-assemble into NFs even at low concentrations closed to the CMC (Fig. S11-13). The selectivity of probe 1 towards various metal ions was investigated at a concentration of 11.8 μM (Fig. S14). The fluorescence emission of 1 decreased with an increase in the amount of metal ions via the photoinduced stabilization of spherical NPs with a dark contrast on NFs with a grey contrast was observed in the TEM images (Fig. 3e,f). The average diameters of the CuNPs on both NFs 1 and 2 are 11.9 ± 2.6 nm and 21.6 ± 3.7 nm, respectively (Fig. S9). The selected area electron diffraction (SAED) pattern of the resulting NPs shows (111), (200), (220), and (311) planes corresponding to a face-centered cubic crystal (inset of Fig. 3e,f). Based on these results, we figure that the biocompatible hybrid NFs can be easily generated via the rational design of self-assembling PAs containing a metal-binding peptide segment to form the NFs template, mimicking biominalization.

Fig. 3 The unstained TEM images of Cu^{2+}-NFs (0.1 mM) of (a) 1 and (b) 2 with enhanced contrast, respectively (inset, negatively stained images). (c) MALDI-TOF mass spectra of Cu^{2+}-PA complexes. (d) FTIR spectra before and after the addition of Cu^{2+} (inset, N-H stretching vibrations in the imidazole of the histidine). TEM images of the NFs decorated with CuNPs of (e) 1 and (f) 2, respectively (inset, selected area diffraction patterns confirming the formation of Cu nanocrystals).

Fig. 4 (a) Fluorescence intensity of 2 (7.6 μM) upon the addition of various metal ions in water. (b) Fluorescence intensity ratios (F_{metal}/F_{metal free}) for 2 at 396 nm in the presence of 20 equiv. of specified metal ions. (c) Fluorescence spectra of 2 in response to the Cu^{2+} ions in the presence of various coexistent metal ions (λ_{ex}=340 nm). (d) TEM image of AgNPs generated on the NFs of 2 (inset, fluorescence Job’s plot for the determination of the stoichiometry of the NFs 2-Ag^{+} complex).
electron transfer (PET) mechanism.\textsuperscript{43} In particular, Cu\textsuperscript{2+}, Ni\textsuperscript{2+}, and Fe\textsuperscript{2+}, according to the Irving-Williams series considerations,\textsuperscript{44} caused a significant chelation-enhanced quenching effect (CHEQ),\textsuperscript{45} which limits their application in sensing of the metal ions.

Remarkably, the fluorescence intensity of 2 in water (7.6 μM) progressively increased upon addition of Ag\textsuperscript{+} (Fig. 4a). Cu\textsuperscript{2+} was the strongest quencher of fluorescence, whereas Ag\textsuperscript{+} was the only metal ion that caused a significant emission enhancement in 2 (Fig. 4b). By adding Cu\textsuperscript{2+} to each metal solution, competition experiments clearly revealed that Ag\textsuperscript{+} interferes with the binding and fluorescence quenching of 2 to Cu\textsuperscript{2+} (Fig. 4c).

The stoichiometric ratio of 2:Ag\textsuperscript{+} was found to be 2:1 (inset of Fig. 4d). The incubation of PA 2 with AgNO\textsubscript{3} and the subsequent reduction with NaBH\textsubscript{4} led to the nucleation and growth of AgNPs along with the NFs, as shown in the TEM image in Fig. 4d. No negative staining was used, so the dark contrast of the spherical aggregates was due to the AgNPs. Averaged over 50 AgNPs within the hybrid NFs, a diameter of 10.3 ± 1.7 nm was determined from the TEM images (Fig. S9). These results demonstrated that the supramolecular fibril nanoprobe of 2 shows a selective fluorescence “light-up” detection of Ag\textsuperscript{+} and the capability to transform into AgNP-incorporated hybrid NFs.

It is noted that the fluorescence emission spectrum of 2 changed at a low concentration to near the CMC of the PA solution, in contrast to 1 (Fig. S11). When decreasing the concentration of 2 from 0.1 mM to 7.6 μM, the pyrene monomer-like emission appeared with excimer emission. The packing mode of the hydrophobic core with a centrally closed stack of pyrenyl groups seems to change to the interdigitation mode with the alkyl chains and pyrenyl groups facing each other, which satisfies the fibrillar thickness of ~6.5 nm in the TEM and the monomer emission formation (Fig. S11). It can be considered a plausible model for the hydrophobic cores in the NFs from 2. Nevertheless, the NFs of 2 reveal an ability to form hybrid nanowires with AgNPs at both low and high concentrations (7.6 μM and 0.1 mM, Fig. S15), indicating that the HG12 of NFs 2 can well-recognize to Ag\textsuperscript{+}. Therefore, the selective response of the NFs of 2 to Ag\textsuperscript{+} can be understood by considering the packing arrangements of the PAs imposed by the molecular architecture. The PAs of 1 contains a hydrophobic block with a linear geometry, which are fully interdigitated with each other to avoid contact between the hydrophobic block and the water, resulting in dense packing of the core. The incorporation of a bulky-branch shaped hydrophobic block into PA 2 frustrates the dense packing within the core of the NF. These distinct differences were identified by FTIR spectroscopy (Fig. S16). The IR bands at 2850 cm\textsuperscript{-1} and 2918 cm\textsuperscript{-1}, which are corresponding to symmetric and asymmetric stretching vibrations of CH\textsubscript{2}, respectively, are sensitive to the crystalline packing of alkyl chain.\textsuperscript{15,46} The thin films of 1 cast from an aqueous solution show strong and sharp bands whereas the films of 2 represent weak and broad bands, indicating that the core of NFs of 2 has the less ordered “liquid-like” structure of alkyl chains.\textsuperscript{15} As a result, the alleviation of the steric constraint between the HG12 blocks covalently attached to the end of the bulky branched alkyl chains, which results in loose distribution of HG12, offers enough space responsible for the binding of large metal ions on the exterior of the NFs. In conjunction with the fact that the radii of Cu\textsuperscript{2+}, Ni\textsuperscript{2+} (0.72 Å), and Fe\textsuperscript{2+} (0.76 Å) are comparable and that the radius of Ag\textsuperscript{+} is larger (1.26 Å, Fig. S15),\textsuperscript{40} the binding affinity of the NFs of 2 to Ag\textsuperscript{+} can be rationalized by a great dependence on the packing density of HG12 and the space-filling requirement to metal ions in an aqueous solution. Consequently, the PAs with fluorophore-spacer-metal ion binding site architecture provide a fluorescence enhancement upon the binding event of Ag\textsuperscript{+} to HG12 via the efficient inhibition of the PET process between the pyrene groups and HG12 (Fig. 1).\textsuperscript{33a,47}

**Dual functional fibrillar nanoprobe with Ag\textsuperscript{+} detection: cell-imaging and antimicrobial activity**

![Fig. 5 Schematic representation of dual-functional hybrid PA-NFs for cell imaging and antimicrobial effects.](image)

The formation of biocompatible PA-based NFs enables the pursuit of potential biomedical applications. Indeed, 10 μM of NF shows high cell viability (93%), which was evaluated by a standard live-dead assay of HeLa cells (Fig. S19).\textsuperscript{58} In particular, the selective response of NFs to Ag\textsuperscript{+} with fluorescence emission enhancement stimulated the investigation into the abilities of PAs in cell-imaging.\textsuperscript{49} The presence of Ag\textsuperscript{+}-immobilized nanofibers led to the investigation of whether the fabrication of hybrid NFs has the potential to induce antimicrobial effects (Fig. 5).\textsuperscript{29,50} However, since it has proven that AgNPs are more suitable antibacterial agents than substances based on the Ag\textsuperscript{+} ion due to significantly lower toxicity toward mammalian cells,\textsuperscript{51} the reduction process of Ag\textsuperscript{+} attached to the surface of NFs was further performed.

Intact HeLa cells were incubated with 10 μM of 2 for 1 h in the absence of Ag\textsuperscript{+} at 37 °C and then washed with 20 mM HEPES buffer solution (pH 6.8) containing NaNO\textsubscript{3} instead of NaCl, and they exhibited a weak intracellular fluorescence when monitored using fluorescence microscopy (Fig. 6b). It should be noted that the presence of Cl\textsuperscript{−} in the solution promotes the formation of AgCl\textsubscript{3+} which interferes with the sensing of Ag\textsuperscript{+}.\textsuperscript{52} The pH influence was considered because the
protonation of the imidazole groups (pKa, ~6.1) in the histidine residue prevents the interaction with metal ions. After incubation with 150 μM of AgNO₃ for 30 min at 37 °C, a considerable enhancement (~4.1 fold) of fluorescence was observed in the cells (Fig. 6c). These results indicate that 2 can penetrate cells and yield a signal for intracellular Ag⁺ through the “turn-on” response. Although PA 2 did not include the cell-penetrating peptides, such as TAT, arginine- and lysine-rich peptides, the presence of HG12 on the exterior of the NFs led to cellular uptake of 2 in this condition. It has been reported that the histidine containing peptides can interact with cell membrane via electrostatic interactions and permeabilize it at slightly acidic conditions (pH 6.0-7.0). Therefore, the precise mechanism of cell penetration of HG12-containing PAs is being investigated by replacing histidine or glycine with other amino acids. At this stage, we consider that the delicate balance of the characteristic of cationic HG12 located at the corona of NFs and the extent of hydrophobicity of lipid-like alkyl chains may contribute to cellular uptake of NFs of 2.

The antimicrobial activities of the AgNPs-NFs against both Gram-negative Escherichia coli (E. coli) O157:H7 and Gram-positive Bacillus subtilis (B. subtilis) were investigated using growth inhibition assays. The AgNPs, NFs, and AgNPs incorporated NFs (AgNPs-NFs) were stored in air for several days and then added to the culture medium, and the turbidity measurements of cell suspension were taken over a time course (Fig. 7). The bacterial growth rates in the Luria-Bertani (LB) liquid media were determined by measuring the optical density at 600 nm (OD₆₀₀). Compared to the growth curve of the control bacteria, the presence of AgNPs-NFs showed a strong inhibition of the growth of E. coli O157:H7. On the contrary, AgNPs showed a lag phase of 10 h for E. coli O157:H7. The bare NFs did not show a noticeable antimicrobial activity against E. coli O157:H7, as the curve was similar to that of the control bacteria. After a week, the mixture medium containing the AgNPs-NFs remained pellucid (Fig. 7b), suggesting that few bacteria proliferated in the presence of AgNPs-NFs. These results indicate that the AgNPs decorated on the NFs show potent long-lasting antibacterial activity, since neither the AgNPs nor the NFs inhibited bacterial growth. The assembled microchip device with four unit modules was prepared to further visualize the antimicrobial ability of the AgNPs-NFs (Fig. 7c). The green fluorescent protein (GFP)-expressing E. coli O157:H7 solution (OD₆₀₀ = 0.1) suspended in the LB media was introduced into the inlet port in the microchannel using a syringe pump. Four types of microchannels were adopted for loading the control, AgNPs, NFs, and AgNPs-NFs solutions, respectively. Fluorescence optical images corresponding to the GFP expression were obtained over time. The innate fluorescence of the NFs was excluded from analysis since the excitation was performed at 488 nm. After incubation for 12 h, the GFP fluorescence appeared in the microchannels loaded with the control and the NFs solutions. After 24 h, in all the channels except one channel for the AgNPs-NFs solution, strong fluorescence emission was observed. These data indicate that AgNPs-NFs exhibit more effective antibacterial activity than AgNPs against Gram-negative bacteria, which is consistent with the results of the turbidity measurements as shown in Fig. 7a. Remarkably, the growth of Gram-positive B. subtilis was completely inhibited by the AgNPs-NFs solution, similar to Gram-negative E. coli O157:H7 (Fig. 7d). The observed long-term antibacterial activity of the AgNPs-NFs against both Gram-negative and -positive bacteria is due to their higher stability when compared to the AgNPs. The use of the NFs template to guide the growth of the AgNPs and the subsequent formation of hybrid NFs prevent the oxidation and aggregation of AgNPs in air which usually leads to a substantial reduction of antibacterial activity. The demand for novel antibacterial agents has grown significantly in recent years, as the number of infections associated with antibiotic-resistant bacteria has increased. Therefore, the design and fabrication of AgNPs-hybrid 1D NFs based on the aqueous self-assembly of biocompatible PAs may provide a useful approach for the development of antimicrobial nanomaterials as well as for the practical application of supramolecular nanotechnology in health care.
Conclusion

The histidine-rich peptide (HG12)-coated NFs were prepared by the self-assembly of pyrene-labeled PAs in an aqueous solution. As molecular scaffolds, PAs containing linear- or bulky branched alkyl chains were synthesized (for 1 and 2). The resulting fibrils were similar only outwardly, as they were actually very different. Depending on the number of alkyl chains, different molecular packing arrangements within the NFs appeared, which led to distinct emission modes for the pyrene probe. Even though a monomer-like pyrene emission was expressed, the existence of self-assembled NFs enabled the interpretation of the molecular packing within the hydrophobic core in which the pyrene moiety was intercalated between the linear-alkyl chains. Interestingly, the incorporation of branched-alkyl chains into the PA architecture allowed for the loose packing of HG12 on the exterior of the NFs of 2 in an aqueous solution. These molecular packing differences between 1 and 2 resulted in their specific binding affinities to metal ions. The imidazole group of the histidine residue of HG12 acted as a metal ion-decorated NFs. Both fibrils showed a great affinity to metal binding site, providing a strategy for the fabrication of metal ion decoration. The loose packing distribution of HG12 in the aqueous NFs resulted in their enhanced stability of AgNPs in an aqueous solution, which contributed to the response to the metal ion size requirement.

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Notes and references


