

Mixed-Valent Click Intertwined Polymer Units Containing Biferrocenium Chloride Side Chains Form Nanosnakes that Encapsulate Gold Nanoparticles

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Supporting Information

ABSTRACT: Polymers containing triazolylbiferrocene are synthesized by ROMP or radical chain reactions and react with HAuCl₄ to provide class-2 mixed-valent triazolylbiferrocenium polyelectrolyte networks (observed *inter alia* by TEM and AFM) that encapsulate gold nanoparticles (AuNPs). With triazolylbiferrocenium in the side polymer chain, the intertwined polymer networks form nanosnakes, unlike with triazolylbiferrocenium in the main polymer chain. By contrast, simple ferrocenecontaining polymers do not form such a ferricenium network upon reaction with Au^{III}, but only small AuNPs, showing that the triazolyl ligand, the cationic charge, and the biferrocenium structure are coresponsible for such network formations.

G old nanoparticles (AuNPs) have attracted considerable interest because of their applications in optics, nanoelectronics, nanomedicine, and catalysis depending on their size, shape and stabilizer.¹ Therefore, the way into which specific macromolecules direct such NP formation and assembly including size, shape, and organized network is of paramount importance toward nanoscience applications.² Ferrocene-containing macromolecules³ may be biocompatible candidates for AuNP stabilization owing to the suitably matching redox potentials of ferrocenes and Au^{III} precursors⁴ and the antitumoral properties of various ferrocene derivatives,⁵ although such a strategy has not yet been envisaged. An engineered approach to biferrocene polymer-mediated stabilization and encapsulation of AuNPs is presented here together with the intriguing properties of these new nanomaterials.

A simple way to construct ferrocene polymers is to branch ferrocene to polymerizable monomers by click Cu(I)-catalyzed Azide Alkyne Cycloaddition (CuAAC) reaction using commercial ethynylferrocene 1.⁶ A ferrocenyl-containing poly-(norbornene) polymer 4 was synthesized using the ring-opening metathesis polymerization (ROMP) of monomer 2 using the third-generation Grubbs catalyst 3.⁷ The reaction of 4 with HAuCl₄ leads to a triazolylferricenium polymer, but this product rapidly decomposes due to the instability of the ferricenium group under these conditions. Therefore, we subsequently addressed the possibility of using biferrocene, because the mixedvalent biferrocenium cation⁸ is much more robust than ferricenium (Scheme 1). Thus, low-dispersity biferrocene analogues 7 and 8 of 6 were synthesized identically with 30

Scheme 1. Synthesis of Biferrocene Polymers 7 and 8 Involving ROMP Initiated by the Ru Metathesis Catalyst "Grubbs III"



and 60 triazolylbiferrocene units, respectively. These polymers were characterized by ¹H and ¹³C NMR including HSQC 2D, HMBC 2D, and NOESY 2D NMR (Supporting Information (SI)) and cyclic voltammetry showing only the two chemically and electrochemically reversible waves of the biferocenyl units at 0.42 and 0.75 V⁸ due to the absence of intramolecular electronic interaction among the multiple biferrocenyl units.

The reactions of these biferrocene polymers with $HAuCl_4$ in dichloromethane—methanol provided the formation of Au^0NP -containing nanostructures 7a and 8a that were stabilized by the green mixed-valent triazolylbiferrocenium polymer 7⁺,Cl⁻ or 8⁺,Cl⁻ (Scheme 2) according to the stoichiometry of eq 1:

$$3Fe^{II}Fe^{II} + H^{+}Au^{III}Cl_{4}^{-}$$

$$\rightarrow 3[Fe^{II}Fe^{III}]^{+}Cl^{-}, Au^{0}, H^{+}Cl^{-} \qquad (1)$$

IR spectroscopy of 7a and 8a shows the presence of both Fe^{II} (ferrocene C–H bending, 813 cm⁻¹) and Fe^{III} (ferricenium C–

Received: August 2, 2014 Published: September 25, 2014 Scheme 2. Formation of Biferrocenium Chloride Polymer-Encapsulated AuNPs upon Reaction of 7, 8, or 9 with HAuCl₄



H bending, 834 cm⁻¹), near-infrared spectroscopy shows the presence of the intervalent charge-transfer band at $\lambda_{max} = 1558$ nm, characteristic of class-II mixed valency,⁹ and CV shows the same waves as the precursor polymers 7 and 8 (SI).

Incubation for 1 week progressively led to the formation of polymer nanosnakes 7**b** and 8**b** (Scheme 2). After only 3 days, the nanosnakes are not yet formed, but their nanostructuration appears in progress by TEM (SI, p S74). Finally, the isolated nanosnakes shown in Figure 2a presents a thickness of 8.7 nm ± 1.5 nm, a length of 210 ± 15 nm, and encapsulated 11 spherical AuNPs of 13.5 ± 1.5 nm size observed by transmission electron microscopy (TEM) with inter-AuNP distances of 5.2 ± 3 nm. The formation of polymer nanosnakes is taken into account by the electrostatic repulsion between the cationic biferrocenium units that is characteristic of polyelectrolytes.¹⁰

At this point, it was necessary to investigate the relationship between the polymer structure and the morphology of the AuNPs that are formed upon reaction with HAuCl₄. Lengthening the polymer by increasing the number of biferrocene units from 30 in 7 to 60 units in 8 did not provoke a significant morphology change.

The polymer framework was modified otherwise by designing another monosubstituted polymer **9** containing biferrocenyl units in the side chain. The CuAAC "click" reaction with ethynylbiferrocene **5** and a polystyrene core with an azido terminus catalyzed by $[Cu^{I}tren(benzyl)_{6}]$, **10**,¹¹ provided the triazolylbiferrocene polymer **9** (Figure 1).

Upon treatment of **9** (containing approximately 30 biferrocene units; see SI, pp S48, S53, and S56) with HAuCl₄ followed by incubation for 1 week under the same conditions as those with 7 and **8**, the isolated biferrocenium-containing



Figure 1. Polystyrene-derived polymer containing the biferrocene units in the side chain synthesized by "click" CuAAC reaction.

polymer nanosnake **9b** presented in TEM a length of 269 ± 10 nm, a thickness of 8.5 ± 2 nm and contained 14 AuNPs of 14.5 ± 1.5 nm size with inter-AuNP distances of 13.5 ± 1.5 nm (Figure 2b). Thus, the similarity of nanosnakes **7b**, **8b**, and **9b** that



Figure 2. TEM of (a) 8b, (b) 9b, (c) 13b, and (d) 9c.

encapsulate spherical AuNPs obtained with the two very distinct types of polymerization and distinct polymer length showed that the nanosnake formation does not significantly depend on these parameters. Reduction of **9b** by NaBH₄ to its neutral biferrocenyl form **9c** leads to flocculation, and TEM (Figure 2d) shows AuNPs of the same size as in the case of **9b**, but the network is destroyed due to the absence of electrostatic contribution to the AuNPs stabilization.

Another drastic structural modification is the incorporation of the biferrocenyl unit in the main polymer chain instead of the side chain. Thus, such a disubstituted biferrocene-diyl polymer 13 was prepared by CuAAC polycondensation of bis(azido) triethylene glycol 11 with bis(ethynyl)biferrocene 12 (Scheme 3).^{4b}

Reactions of these polymers with $HAuCl_4$ were carried out analogously and also provided AuNPs that are stabilized and encapsulated by mixed-valent biferrocenium chloride polymers **13a** (Scheme 4). Incubation showed that the polymer containing bis(triazolylferrocenium) in the main chain led to a wellorganized non-nanosnake network **13b** (TEM, Figure 2c). It can be concluded that the nanomaterial containing biferrocenium Scheme 3. "Click" CuAAC Synthesis of Biferrocene Polymers Containing the Biferrocene Units in the Main Chain^{4b}



Scheme 4. Reaction of the Biferrocene Polymer 13 with HAuCl₄ Giving Biferrocenium Chloride Polymer-Encapsulated AuNPs in the Polymer Network 13b after Incubation



chloride in the main chain lacks the driving force for nanosnake formation. The much larger distance between the biferrocenium units than in the nanomaterials containing biferrocenium choride in the side chain considerably weakens the electrostatic repulsion between the cationic charges of all biferrocenium units that is a key parameter for the nanosnake formation.

The large thickness of the nanosnakes in **7b**, **8b**, and **9b** indicates that more than a single polymer unit is involved in each nanosnake and that a group of several biferrocenium chloride polymer units are intertwined. Likewise, the length of the nanosnakes is much larger than that of a single polymer unit, which confirms the requirement of intertwining several polymer units in order to reach the nanosnake length.

Although trz-ferrocene polymers decompose upon oxidation by $HAuCl_4$, comparison of these nanosnakes with a related ferricenium polymer can be done upon using an amidoferrocene polymer 14 (Figure 3). Indeed, oxidation of 14 by $HAuCl_4$ yields a stable ferricenium nanostructure 14b in which only small



Figure 3. (a) Homopolymer 14 synthesized by ROMP and (b) its oxidation product 14a by reaction with HAuCl₄.

AuNPs are observed by TEM without an apparent network (SI, p S81). This points out the importance of the triazole in the AuNP network formation that originates from the complexation of precursor Au^{III} ions by the triazole moiety.

Atomic force microscopy studies of AuNPs 8 and 8b were performed on a graphite surface by peak force tapping mode where adhesion is mapped simultaneously with topography. The topography images of 8 showed the polymer with an average height of 7 ± 1.5 nm that did not form nanosnakes (SI, p S43). In the case of 8b however very long nanosnakes on the order of 200–300 nm were observed with a height of 18–35 nm. Adhesion of 8b was mapped providing qualitative mechanical information on the sample. Figure 4a shows an adhesion image of



Figure 4. AFM adhesion images of biferrocenium chloride polymerencapsulated AuNPs **8b**: (a) at 2 μ m scale, (b) at 270 nm scale at which the force curves of A, B, and C were recorded.

8b, and Figure 4b shows a zoom of one of the nanosnakes. The force curves were obtained while the two images were recorded which allowed examining the nature of the nanomaterial. In all cases three different regions A, B, and C were observed corresponding to three different force curves (Figure 4b).

The force curves of region A show that the round black zones belong to a less elastic and stiffer part of material that would belong to the AuNPs. On the other hand the force curves of region C show a larger adhesion of the white zones presenting a softer and more flexible nanomaterial that would correspond to the organic part of polymer **8b**. At last brown zones B (surrounding regions A) show intermediate force curves with a different adhesion from regions A and C, presumably due to the electrostatic forces of the biferrocenium chloride units that are stabilizing the AuNPs. These three different kinds of force curves A, B, and C are similar in all recorded adhesion images of the sample of **8b**.

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In conclusion, it has been shown that the first metallopolymers containing biferrocene in the side chain synthesized with various structures by ROMP with the Grubbs-III metathesis catalyst or radical chain form, upon oxidation with HAuCl₄ in dichloromethane-methanol followed by one-week incubation, class-II mixed-valent biferrocenium chloride nanosnake polymers that encapsulate AuNPs. With biferrocene in the main polymer chain, a non-nanosnake network that encapsulates AuNPs also forms, but only small AuNPs without a polymer network are observed by TEM when polyferrocene without a triazolyl substituent synthesized by ROMP is oxidized by HAuCl₄. This shows that the combination of the triazole ligand and the positive charge of the biferrocenium polymer are responsible for the AuNP encapsulation. The nanosnake formation by intertwining polymers is specific to electrolyte metallopolymers with triazolylbiferrocenium in the side chain. This nanoengineering strategy involving structural and electrostatic parameter variations shows that AuNP wrapping and encapsulation by metallopolymers can control networks eventually forming nanosnakes. Applications are forecasted for the control and visualization of polymers and nanostructures.

ASSOCIATED CONTENT

Supporting Information

Experimental methods, 1D and 2D (1 H) and (13 C) NMR spectroscopy, infrared, UV–vis, and mass spectra, SEC, DLS, cyclic voltammograms, TEM and AFM data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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