

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

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**S** Supporting Information

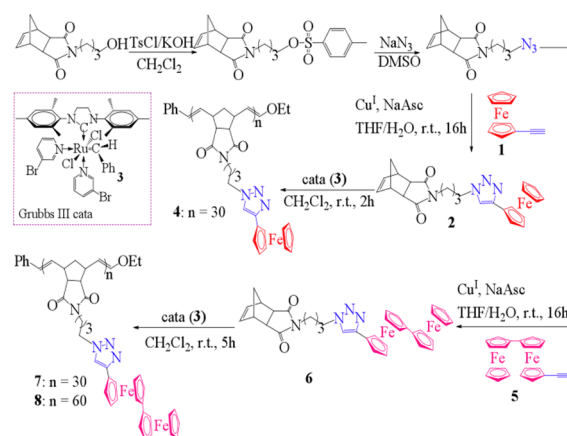
**ABSTRACT:** Polymers containing triazolylbiferrocene are synthesized by ROMP or radical chain reactions and react with HAuCl<sub>4</sub> to provide class-2 mixed-valent triazolylbiferrocenium polyelectrolyte networks (observed *inter alia* by TEM and AFM) that encapsulate gold nanoparticles (AuNPs). With triazolylbiferrocenium in the side polymer chain, the intertwined polymer networks form nanosnakes, unlike with triazolylbiferrocene in the main polymer chain. By contrast, simple ferrocene-containing polymers do not form such a ferricenium network upon reaction with Au<sup>III</sup>, but only small AuNPs, showing that the triazolyl ligand, the cationic charge, and the biferrocenium structure are coresponsible for such network formations.

Gold nanoparticles (AuNPs) have attracted considerable interest because of their applications in optics, nano-electronics, nanomedicine, and catalysis depending on their size, shape and stabilizer.<sup>1</sup> 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.<sup>2</sup> Ferrocene-containing macromolecules<sup>3</sup> may be biocompatible candidates for AuNP stabilization owing to the suitably matching redox potentials of ferrocenes and Au<sup>III</sup> precursors<sup>4</sup> and the antitumoral properties of various ferrocene derivatives,<sup>5</sup> 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**.<sup>6</sup> 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**.<sup>7</sup> The reaction of **4** with HAuCl<sub>4</sub> 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 mixed-valent biferrocenium cation<sup>8</sup> is much more robust than

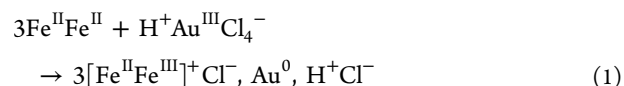
ferricenium (Scheme 1). Thus, low-dispersity biferrocene analogues **7** and **8** of **6** were synthesized identically with **30**

## 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 <sup>1</sup>H and <sup>13</sup>C 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 biferrocenyl units at 0.42 and 0.75 V<sup>8</sup> due to the absence of intramolecular electronic interaction among the multiple biferrocenyl units.

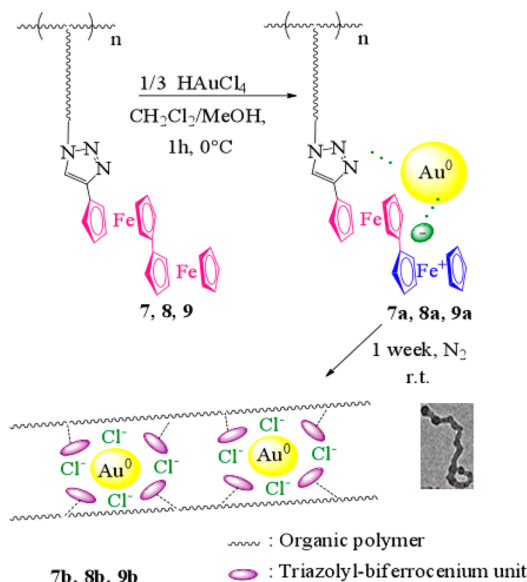
The reactions of these biferrocene polymers with HAuCl<sub>4</sub> in dichloromethane–methanol provided the formation of Au<sup>0</sup>NP-containing nanostructures **7a** and **8a** that were stabilized by the green mixed-valent triazolylbiferrocenium polymer **7<sup>+</sup>Cl<sup>-</sup>** or **8<sup>+</sup>Cl<sup>-</sup>** (Scheme 2) according to the stoichiometry of eq 1:



IR spectroscopy of **7a** and **8a** shows the presence of both Fe<sup>II</sup> (ferrocene C–H bending, 813 cm<sup>-1</sup>) and Fe<sup>III</sup> (ferricenium C–

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**Scheme 2. Formation of Biferrocenium Chloride Polymer-Encapsulated AuNPs upon Reaction of 7, 8, or 9 with HAuCl<sub>4</sub>**


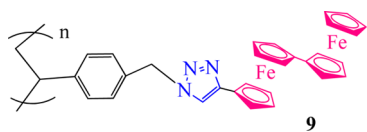
H bending, 834  $\text{cm}^{-1}$ ), near-infrared spectroscopy shows the presence of the intervalent charge-transfer band at  $\lambda_{\text{max}} = 1558$  nm, characteristic of class-II mixed valency,<sup>9</sup> and CV shows the same waves as the precursor polymers 7 and 8 (SI).

Incubation for 1 week progressively led to the formation of polymer nanosnakes 7b and 8b (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  $\pm$  1.5 nm, a length of 210  $\pm$  15 nm, and encapsulated 11 spherical AuNPs of 13.5  $\pm$  1.5 nm size observed by transmission electron microscopy (TEM) with inter-AuNP distances of 5.2  $\pm$  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.<sup>10</sup>

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 HAuCl<sub>4</sub>. 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.

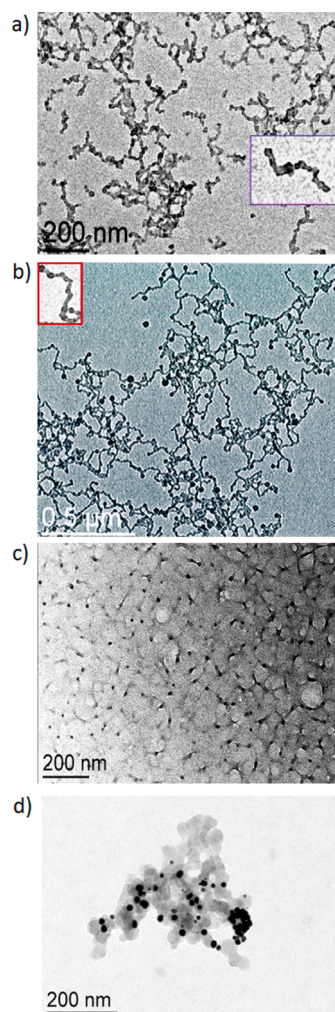
The polymer framework was modified otherwise by designing another monosubstituted polymer 9 containing biferrocenyl units in the side chain. The CuAAC “click” reaction with ethynylbiferrocene 5 and a polystyrene core with an azido terminus catalyzed by [Cu<sup>I</sup>tren(benzyl)<sub>6</sub>], 10,<sup>11</sup> provided the triazolylbiferrocene polymer 9 (Figure 1).

Upon treatment of 9 (containing approximately 30 biferrocene units; see SI, pp S48, S53, and S56) with HAuCl<sub>4</sub> 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  $\pm$  10 nm, a thickness of 8.5  $\pm$  2 nm and contained 14 AuNPs of 14.5  $\pm$  1.5 nm size with inter-AuNP distances of 13.5  $\pm$  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 NaBH<sub>4</sub> 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).<sup>4b</sup>

Reactions of these polymers with HAuCl<sub>4</sub> 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(triazolylbiferrocenium) in the main chain led to a well-organized non-nanosnake network 13b (TEM, Figure 2c). It can be concluded that the nanomaterial containing biferrocenium



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  $\text{HAuCl}_4$  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  $\text{HAuCl}_4$ . 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 ( $^1\text{H}$ ) and ( $^{13}\text{C}$ ) 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

The authors declare no competing financial interest.

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