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Dendronized triazolyl-containing ferrocenyl polymers as stabilizers of gold nanoparticles for recyclable two-phase reduction of 4-nitrophenol

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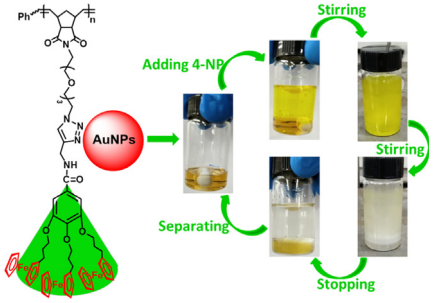
GRAPHICAL ABSTRACT



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ABSTRACT

A series of small-sized (about 2.0 nm) gold nanoparticles (AuNPs) with apparent lattice fringes are synthesized by $NaBH_4$ reduction of $HAuCl_4$ in the presence of stabilizing linear or dendronized 1,2,3-triazolyl-containing ferrocenyl polymers. These AuNPs show high catalytic activity for biphasic 4-nitrophenol (4-NP) reduction to 4-aminophenol (4-AP) by $NaBH_4$. The lower generation **G1** dendronized polymers (DPs) is a more efficient stabilizer for AuNP catalytic activity in the reduction of 4-NP than linear **G0** polymers or bulky **G2** DPs. The **G1** DP-stabilized AuNPs are robust and easily recyclable, and the catalyst is recovered and reused at least twenty times with progressive smooth AuNP size increase along with some decrease of catalytic activity.

1. Introduction

Due to their unique chemical and physical properties, gold nanoparticles (AuNPs) [1] have been the subject of intense investigation based on their significant applications in catalysis [1–10], optics [11–13] and biomedicine [14–18]. AuNPs are generated in a variety of different shapes based on both "top-down" and "bottom-up" approaches, such as nanospheres, nanorods, nanocages, multibranched and tadpole-like nanoparticles [19,20]. The use of the "top-down" approach is limited because of difficulties in controlling the size and shape of particles as well as obtaining a narrow particle size distribution [19,20]. On the contrary, the "bottom-up" approaches are inspired by the principles of molecular recognition in term of chemical reduction of Au salts,

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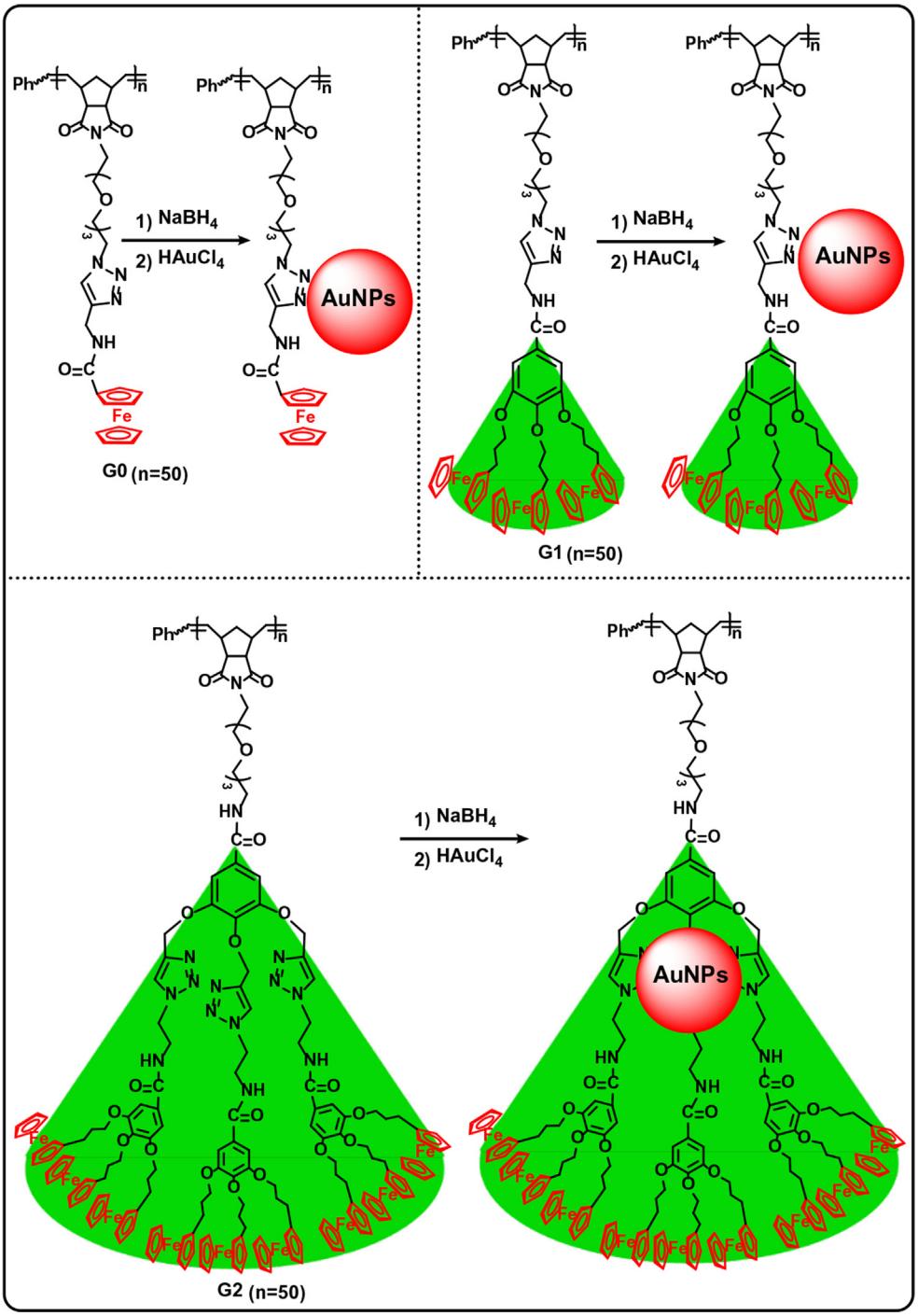
electrochemical pathways and decomposition of organometallic compounds, in which the formation of AuNPs stems from individual molecular components. The chemical reduction method is simple concerning the control of sizes and shapes of AuNPs [19–21]. Therefore, it is important to choose suitable stabilizers, such as trisodium citrate dihydrate, sulfur ligands, phosphorus ligands, nitrogen-based ligands, oxygen-based ligands, surfactant, linear polymers and dendrimers [22–29]. Among these stabilizers, dendrimers with a core-shell structure show significant advantages for the stabilization of small-sized AuNPs in their functional interior [30,31]. For example, Jiang and coworkers have reported amphiphilic dendrimer polyethylenimine (PEI) used as AuNPs stabilizer with an very long lifetime in the catalytic reduction of 4-nitrophenol (4-NP).[23] Murugan et al. reported that dendrimer grafted recoverable core-shell Fe_3O_4-polymer magnetic nanocomposites were used to stabilize AuNPs for enhancing the catalytic degradation of Rhodamine B [32]. Crooks used poly(amido)amine (PAMAM) dendrimers to prepare 1–2 nm dendrimer-encapsulated AuNPs with very narrow size distributions [33], and other researchers also took advantage of PAMAM and other dendrimers to stabilize gold nanoparticles [34] and evaluate the catalytic activity of AuNPs in the reduction of 4-NP [35–38]. Although these dendrimers act as multi-ligand stabilizers and size controlling templates to fabricate stable and active AuNPs, the syn-



Scheme 1. Preparation of AuNPs using **G0**, **G1** and **G2** dendronized polymers as stabilizers.