

## Gold Nanoparticles with Externally Controlled, Reversible Shifts of Local Surface Plasmon Resonance Bands

Mustafa S. Yavuz,<sup>†,§</sup> Gary C. Jensen,<sup>†</sup> David P. Penaloza,<sup>†</sup> Thomas A. P. Seery,<sup>†,‡</sup> Samuel A. Pendergraph,<sup>†</sup> James F. Rusling,<sup>†,§</sup> and Gregory A. Sotzing<sup>\*,†,‡</sup>

<sup>†</sup>Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269, <sup>‡</sup>Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, and <sup>§</sup>Department of Cell Biology, University of Connecticut Health Center, Farmington, Connecticut 06032. <sup>§</sup>Present address: NanoMedicine and Advanced Technologies Research Center, Gazi University, Ankara, Turkey

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We have achieved reversible tunability of local surface plasmon resonance in conjugated polymer functionalized gold nanoparticles. This property was facilitated by the preparation of 3,4-ethylenedioxythiophene (EDOT) containing polynorbornene brushes on gold nanoparticles via surface-initiated ring-opening metathesis polymerization. Reversible tuning of the surface plasmon band was achieved by electrochemically switching the EDOT polymer between its reduced and oxidized states.

### Introduction

In recent years, metal nanoparticles have been widely exploited for use in catalysis,<sup>1</sup> biological labeling,<sup>2</sup> photonics,<sup>3</sup> optoelectronics,<sup>4</sup> information storage,<sup>5</sup> photothermal cancer therapy,<sup>6</sup> and surface-enhanced Raman scattering<sup>7</sup> due to their optical and electronic properties. Gold nanoparticles (AuNPs) have unique plasmonic properties due to the interaction of light with freely mobile electrons in the AuNPs which give rise to collective oscillations, commonly known as localized surface plasmon

resonance (LSPRs).<sup>8</sup> The location and intensity of the LSPR bands of AuNPs mainly depend on the size and shape of the particle and the dielectric constant of the surroundings.<sup>9</sup> By carefully controlling these parameters, one could tune the LSPR band from wavelengths in the near-infrared region to visible wavelengths.<sup>10</sup> Tuning of the LSPR band is often irreversible and may not be easily tuned by an external physical input.

There has been significant interest in preparing polymer brushes on AuNPs.<sup>11</sup> Polymer brushes can be formed either by adsorption of end-group-functionalized polymers or initiation and propagation of monomers from surface-bounded initiating groups. Adsorption is the traditional approach depending on the reaction between the end-group and the surface upon diffusion to the interface.<sup>12</sup> Though this method is appropriate for many polymer systems where low polydispersity is desired, the method has a limited control of grafting density and is subject to steric effects in the binding of high molecular weight polymers due to the high barrier energy required to stretch the surface-bound polymers with diffusion of other polymer chains.<sup>13</sup>

Growing polymers from the surface is an attractive method for the formation of high molecular weight polymer brushes with controlled grafting density. Our interest in coated nanoparticles

\*Corresponding author. E-mail: sotzing@mail.ims.uconn.edu.

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includes applications such as high sensitivity labels in immunosensors.<sup>14</sup> Numerous publications have demonstrated the versatility of polymerizations initiated from the surfaces of ferrite, silica, and carbon black using radical, anionic, and cationic techniques.<sup>15</sup> Surface-initiated ring-opening metathesis polymerization (SI-ROMP) is an efficient strategy to grow polymer brushes from surfaces due to the control of molecular weight, molecular structure, and the bulk characteristics of the polymers.<sup>16</sup> The catalyst used in the polymerization offers many advantages including low polydispersity, mild reaction conditions, functional group tolerance, and high yields.<sup>17</sup>

Herein, we report the use of SI-ROMP for the preparation of 3,4-ethylenedioxythiophene (EDOT)<sup>18</sup> containing polynorbornene brushes and their solid-state oxidative conversion (SOC)<sup>19</sup> to conjugated polymer networks.<sup>20</sup> Furthermore, we show that the LSPR band of AuNPs can be controlled and modulated reversibly by electrochemically switching this conjugated polymer between its reduced and oxidized states.

## Experimental Procedures

**Materials.** Acetonitrile (ACN), sodium borohydride, dodecanethiol, tetrahydrofuran (THF), ethylvinyl ether, ethanol, tetraoctylammonium chloride, *N,N'*-dimethylformamide (DMF), *n*-pentane, petroleum ether, toluene, chloroform (CHCl<sub>3</sub>), and methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) were purchased from Acros Organics. CH<sub>2</sub>Cl<sub>2</sub> and ACN were distilled over calcium hydride (CaH<sub>2</sub>) under a nitrogen atmosphere prior to use. *N*-Bromosuccinimide (NBS), 3-methylthiophene, bromine (Br<sub>2</sub>), deuterated chloroform (CDCl<sub>3</sub>), chloroauric acid (HAuCl<sub>4</sub>), Grubbs's generation I alkylidene catalyst, tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>), *n*-butyllithium (*n*-BuLi), and tetraoctylammonium bromide were purchased from Aldrich Chemical Co. NBS was recrystallized from distilled water and vacuum-dried for 24 h, while the other chemicals were used as received. 3-Bromomethyl-2,5-dibromothiophene was synthesized according to the literature methods.<sup>21</sup> 1-Mercapto-10-(*exo*-5-norbornen-2-methyloxy)-decane, **2**, was synthesized by using a modified literature procedure.<sup>22</sup> In the literature procedure, the synthesis of **2** required four steps. Our modified procedure is three steps, which was excluding the last step of the literature procedure. In the third step, **2** was obtained using two times more addition of potassium thioacetate and stirring the reaction for 2 days under the same conditions.

**Instrumentation.** A CHI-400 potentiostat (CH Instruments) was used for all electrochemical experiments. <sup>1</sup>H NMR spectra were recorded on a Bruker 400 FT-NMR spectrometer. The

<sup>1</sup>H chemical shift is reported in ppm downfield from a tetramethylsilane (TMS) reference. Optical properties of the polymer solution were measured by a Perkin-Elmer Lambda 900 UV–vis–NIR spectrophotometer. Indium-doped tin oxide (ITO)-coated glass (dimensions 7 mm × 50 mm × 0.7 mm, *R<sub>s</sub>* = 15–25 Ω, unpolished float glass) was purchased from Delta Technologies. Thermal analysis was performed using TA Instruments Hi-Res TGA 2950 for thermal gravimetric analysis (TGA). Transmission electron microscopy (TEM) images of poly3-AuNPs were obtained using a Philips EM300 transmission electron microscope.

Atomic force microscopy (AFM) characterization of the AuNPs before and after polymer growth was performed with a Digital Instruments Nanoscope IV, in Tapping mode. Silicon AFM probes from Veeco Probes (model MPP-11100, symmetric tip, frequency 300 kHz, spring constant 40 N/m) were used. Dilute filtered samples were cast on freshly cleaved mica surface and dried with a stream of nitrogen immediately before scanning.

**Synthesis of *endo*- and *exo*-3-(((Bicyclo[2.2.1]hept-5-en-2-yl)methoxy)methyl)-2,5-dibromothiophene.** 129 mg of NaH (1.5 equiv) and 15 mL of anhydrous DMF were added to a 100 mL vacuum-dried and nitrogen purged round-bottom flask. 0.65 mL of 5-norbornene-2-methanol (1.5 equiv) was mixed, and the solution was stirred for 1 h at room temperature (RT). The resulting solution was cooled to 0 °C for 10 min. 1.2 g of 3-bromomethyl-2,5-dibromothiophene (3.58 mmol) in 7 mL of anhydrous DMF was added dropwise. After the addition, the reaction solution was heated to 100 °C for 15 h, then poured into 150 mL of 1 M NaOH solution, and extracted thrice with 100 mL of dichloromethane. After drying with sodium sulfate and filtration, the solvent was evaporated in a rotary evaporator. 0.60 g (44.3%) of colorless liquid was obtained via column chromatography using 5:1 petroleum ether to CHCl<sub>3</sub> as the eluent (*R<sub>f</sub>*: 0.25). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.01 and 7.00 (s, 1H, CH); 6.16–6.12 (dd, 1H, CH); 6.10–6.08 and 5.93–5.88 (dd, 1H, CH), 4.40–4.3 (dd, 2H, CH<sub>2</sub>); 3.55–3.51 and 3.23–3.19 (dd, 1H, CH<sub>2</sub>); 3.43–3.36 and 3.09–3.04 (d and t, 1H, CH<sub>2</sub>); 2.95 (s, 1H, CH<sub>2</sub>); 2.82 (s, 1H, CH<sub>2</sub>); 2.43–2.36 and 1.79–1.7 (q, 1H, CH); 1.88–1.82 and 1.47–1.43 (dd, 1H, CH); 1.37–1.25 (m, 2H, CH<sub>2</sub>); 1.17–1.12 and 0.54–0.49 (d and q, 1H, CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 139.75, 139.64, 137.32, 136.72, 136.54, 132.34, 130.85, 130.83, 111.25, 11.16, 109.76, 109.68, 75.24, 74.28, 66.79, 66.68, 49.43, 45.03, 43.95, 43.73, 42.21, 41.57, 38.86, 38.75, 29.75, 29.12. FTIR: 3057 cm<sup>−1</sup> (aromatic C–H stretching); 2967 and 2864 cm<sup>−1</sup> (aliphatic C–H stretching); 1098 cm<sup>−1</sup> (aliphatic C–O stretching).

**Synthesis of *endo*- and *exo*-5-(4-(((Bicyclo[2.2.1]hept-5-en-2-yl)methoxy)methyl)-5-(2,3-dihydrothieno[3,4-*b*][1,4]-dioxin-7-yl)thiophen-2-yl)-2,3-dihydrothieno[3,4-*b*][1,4]-dioxine (**3**).** To a round-bottom flask, 500 mg of EDOT (2.1 equiv) dissolved in 10 mL of THF under nitrogen was cooled to −78 °C via a dry ice/acetone bath. *n*-BuLi (1.4 mL, 2.2 equiv) was then added dropwise via a syringe. After 45 min, the reaction was warmed to 0 °C using an ice bath, and 903 mg of MgBr<sub>2</sub>·Et<sub>2</sub>O (2.2 equiv) was added in one portion. After 45 min, 605 mg of 3-(((bicyclo[2.2.1]hept-5-en-2-yl)methoxy)methyl)-2,5-dibromothiophene (1.6 mmol) in 15 mL of THF was added, followed by the addition of 87 mg (10 mol %) of NiCl<sub>2</sub>·dppp. The reaction was warmed slowly to room temperature, during which the solution changed color from dull yellow to red. After 2 h the mixture turned to a desirable black-brown as reported in prior studies and was further stirred for 1 day.<sup>18</sup> THF was rotary evaporated, and the crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. After washing with water, the organic layer was saved and the water phase was extracted twice with 50 mL of CH<sub>2</sub>Cl<sub>2</sub>. All organic layers were collected and dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration, dichloromethane was then evaporated. The crude product was purified by column chromatography using 2:1 petroleum ether to CHCl<sub>3</sub> to yield 183 mg (22.8%) of **3** (pure brown solid) (*R<sub>f</sub>*: 0.37). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.24 and 7.23 (s, 1H, CH), 6.37 (s, 1H, CH), 6.21 (s, 1H, CH), 6.10–6.08 and 5.91–5.90

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(dd, 2H, CH<sub>2</sub>), 4.55–4.45 (dd, 2H, CH<sub>2</sub>), 4.33–4.32(m, 2H, CH<sub>2</sub>), 4.29–4.28 (m, 2H, CH<sub>2</sub>), 4.24 (s, 4H, 2CH<sub>2</sub>), 3.53–3.44 and 3.19–3.18 (dd, 1H, CH<sub>2</sub>), 3.38–3.33 and 3.06–3.04 (t, 1H, CH<sub>2</sub>), 2.95 and 2.79 and 2.77 (s, 2H, CH<sub>2</sub>), 2.38–2.35 (m, 1H, CH), 1.87–1.83 and 1.42–1.40 (dd, 1H, CH), 1.29–1.13 (dd, 2H, CH<sub>2</sub>), 1.14–1.09 and 0.50–0.45 (m, 1H, CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 141.84, 141.51, 138.22, 137.64, 137.12, 136.79, 136.67, 136.63, 133.98, 132.56, 128.17, 124.59, 112.14, 109.78, 99.49, 97.00, 74.89, 73.97, 67.97, 67.11, 64.98, 64.89, 64.59, 64.50, 49.42, 44.03, 43.79, 42.22, 41.55, 38.87, 29.79, 29.21. FTIR: 3109 cm<sup>-1</sup> (aromatic C–H stretching); 2931 and 2867 cm<sup>-1</sup> (aliphatic C–H stretching); 1071 cm<sup>-1</sup> (aliphatic C–O stretching).

**Synthesis of Functionalized AuNPs.** AuNPs were synthesized in a similar procedure to that published by Brust and co-workers.<sup>23</sup> An aqueous solution of gold salt (HAuCl<sub>4</sub>) (60 mL, 30 mM) was added to 160 mL of toluene solution, which contained a surfactant, tetraoctylammonium bromide (50 mM). After stirring this mixture for 1 h, the surface-functionalizing reagents, 323 mg of 1-dodecanethiol (1.6 mmol) and 53 mg of 1-mercapto-10-(*exo*-5-norbornen-2-methyloxy)decane (0.178 mmol) in 20 mL toluene, were added. 0.40 M of NaBH<sub>4</sub> in 50 mL of water was added dropwise to this mixture. After complete addition, the solution was stirred for 6 h. The organic layer was separated, ~90% of toluene was evaporated in a vacuum aspirator, and then the nanoparticles were precipitated in 400 mL of ethanol. The precipitate was filtered on a Teflon filter. This precipitate was redissolved and precipitated in ethanol again. After filtration, 450 mg of a dark colored product was obtained for the 2 nm AuNPs (<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.15 (1H, CH); 5.95 (1H, CH); 2.71 (2H, CH<sub>2</sub>); 1.70 (2H, CH<sub>2</sub>); 1.29 (18H, CH<sub>2</sub>); 0.91 (3H, CH<sub>3</sub>). TGA: *T*<sub>decomp</sub> = 187 °C; 29.77% remaining after 800 °C; spectrum available in the Supporting Information). To produce 7 nm sized AuNP, a 6:1 mol equiv of HAuCl<sub>4</sub> to thiols was implemented under the same conditions as the aforementioned conditions (<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.15 (1H, CH); 5.96 (1H, CH); 2.66 (2H, CH<sub>2</sub>); 1.67 (2H, CH<sub>2</sub>); 1.30 (18H, CH<sub>2</sub>); 0.93 (3H, CH<sub>3</sub>). TGA: *T*<sub>decomp</sub> = 183 °C; 88.72% remaining after 800 °C; spectrum available in the Supporting Information). 100 mg of **2** modified-AuNPs was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> in a glovebox. One equivalent of Grubbs' catalyst (**1**), **1**, was added to the solution (1 equiv was calculated with respect to the number of moles of norbornene on the AuNPs, calculated by using the NMR and TGA spectra). After 1 h stirring, 20 equiv of **3** in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added. The reaction solution was stirred for 2 h and then quenched with excess ethyl vinyl ether. The CH<sub>2</sub>Cl<sub>2</sub> solution was poured into 400 mL of pentane solution to precipitate the poly(**3**)-AuNPs. The precipitate was filtered and then recrystallized in a CH<sub>2</sub>Cl<sub>2</sub>/MeOH solvent mixture to obtain 40 mg of product.

**Characterization of Functionalized AuNPs.** All electrochemical experiments were performed using a three-electrode cell configuration in 0.1 M TBAPF<sub>6</sub>/ACN. The reference electrode was a nonaqueous Ag/Ag<sup>+</sup> electrode consisting of a silver wire immersed in a glass capillary body fitted with a Vycor tip and filled with 0.1 M silver nitrate and 0.1 M TBAPF<sub>6</sub>/ACN solution. The Ag/Ag<sup>+</sup> reference electrode was calibrated to be 0.412 V vs the normal hydrogen electrode (NHE) using 10 mM ferrocene/ACN. A 1 cm<sup>2</sup> platinum flag was used as a counter electrode in all electrochemical measurements. A 1 wt % solution of poly(**3**)-AuNPs in CH<sub>2</sub>Cl<sub>2</sub> was prepared. A thin film of poly(**3**)-AuNPs was coated on a platinum electrode (2 mm diameter) by dipping the electrode in the poly(**3**)-AuNPs/CH<sub>2</sub>Cl<sub>2</sub> solution followed by drying in air for 10 min. The electrochemical cross-linking of poly(**3**)-AuNPs was then carried out at a scan rate of 50 mV/s in 0.1 M TBAPF<sub>6</sub>/ACN (10 mL) solution by cycling two subsequent times between –600 and 800 mV. After polymerization, the

polymer-coated Pt working electrode was washed with ACN. The cyclic voltammogram of the polymer was obtained in 0.1 M TBAPF<sub>6</sub>/ACN.

Samples for TEM analysis were prepared by solution casting. Poly(**3**)-AuNPs was dissolved in THF. A 5 μL sample was placed on a carbon grid supported with carbon film (Figure S3 in Supporting Information). UV–vis analysis was taken of the sample by spin-coating a 1 wt % solution of poly(**3**)-AuNPs in CH<sub>2</sub>Cl<sub>2</sub> onto an ITO glass slide (control spectrum of the conjugated polymer without AuNPs is found in the Supporting Information). After electrochemical conversion, the sample was washed with ACN to remove residual electrolyte and then dried under a stream of nitrogen before taking UV–vis analysis.<sup>24</sup>

## Results and Discussion

A modification of the Brust method was used for preparing AuNPs by reducing a gold salt in a thiol solution.<sup>1,23</sup> The dilution of **2** with dodecanethiol was used to minimize surface cross-linking of norbornene groups and propagating polymer during the SI-ROMP process as shown in Scheme 1.

The norbornene molecule has distinct olefinic protons, which are at 6.15, 6.05, and 5.95 ppm in the <sup>1</sup>H NMR spectrum of the thiol-modified AuNPs as shown in Figure 1A,B. This confirms that the norbornene thiols are attached to the AuNPs after the reduction process. The number of moles of norbornene units per gram of thiol-functionalized AuNPs was calculated by using the <sup>1</sup>H NMR spectrum and TGA analysis of the AuNPs<sup>25</sup> (see Supporting Information). After addition of 1 equiv of ruthenium catalyst (Grubbs' generation (I)), **1**, with respect to the norbornene group, ring-opening metathesis polymerization (ROMP) is observed by a decrease in integration intensity of the distinct olefinic protons of norbornene and generation of a new olefin peak at 5.25 ppm, as shown in Figure 1C. The completion of ROMP is achieved in 30 min as shown by the loss of the olefinic peaks at 6.15, 6.05, and 5.95 ppm and formation of the new peak at 5.25 ppm, as shown in Figure 1D.

After addition of 20 equiv of **3** to this solution, the polymerization of **3** ensued and is evidenced by the appearance of a new broad peak between 5.4 and 5.1 ppm in the <sup>1</sup>H NMR spectrum, as shown in Figure 1E. This new peak is characteristic of polynorbornene homopolymer prepared via solution polymerization.<sup>16</sup> During the polymerization process, the intensity of the broad peak between 5.4 and 5.1 ppm increases while the intensities of the peaks at 6.15, 6.05, and 5.95 ppm decrease. After 2 h the polymerization is complete as indicated by the disappearance of norbornene olefinic peaks. The growing polymer chains are terminated by the addition of excess ethyl vinyl ether.<sup>26</sup> The growth of the norbornene chains off of the AuNPs creates a nonconductive brush, soluble precursor system with pendant conjugated moieties.

Poly(**3**)-AuNPs are then drop-cast onto platinum and electrochemically converted to the corresponding conjugated polymer AuNPs, poly(**4**)-AuNPs, via a solid-state oxidative conversion, as shown in Figure 2A. It should be noted that poly(**3**)-AuNPs are insoluble in the electrolyte as evidenced by the UV–vis spectrum of the electrolyte solution. The onset of oxidation of poly(**3**)-AuNPs was at 0.33 V vs Ag/Ag<sup>+</sup> standard. At this potential, the linear brushes cross-link to form poly(**4**)-AuNP conjugated polymer cross-linked network where conjugated moieties are

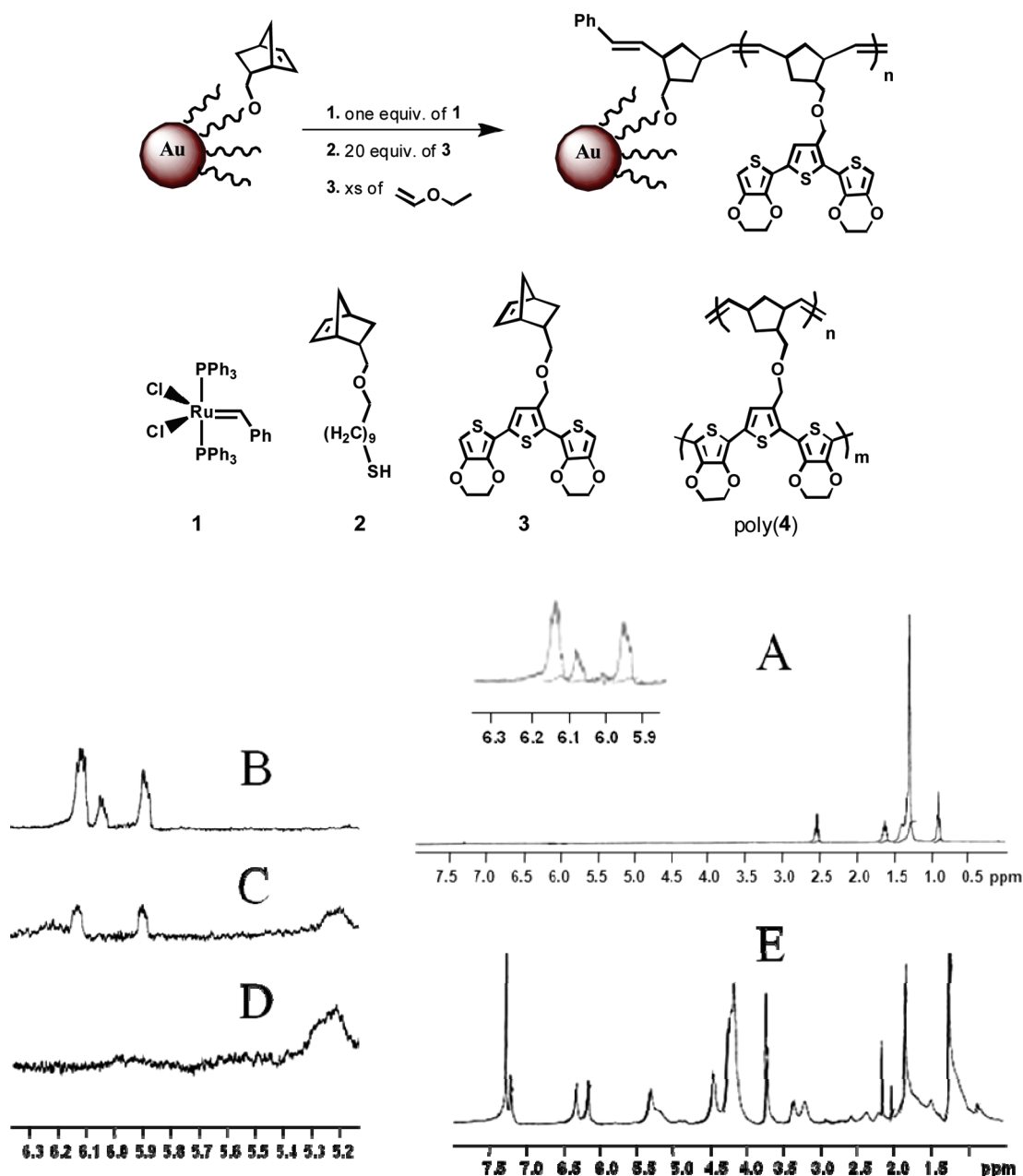
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**Scheme 1. Structures of Grubbs' Catalyst (1), Initiating Molecule (2), the Monomer (3), the Cross-Linked Conjugated Polymer (Poly(4)), and the Schematic Diagram of Surface-Initiated Ring-Opening Metathesis Polymerization (SI-ROMP)**



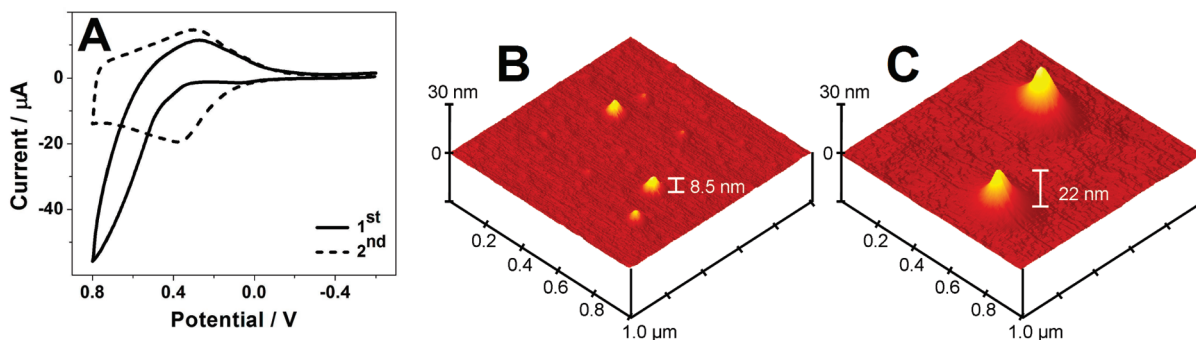
**Figure 1.**  $^1\text{H}$  NMR spectra of (A) AuNPs functionalized with a mixture of 1-dodecanethiol and 2 ( $\delta$  8 to 0 ppm), (B–D) AuNPs functionalized with a mixture of 1-dodecanethiol, 2 ( $\delta$  6.4 to 5.1 ppm), with the initial addition of 1 (B), during polymerization of 3 (C), and the completion of the polymerization of 3 (D), showing the disappearance of the bicyclic olefin peak ( $\delta$  6.4 to 5.1 ppm). (E) Poly(3)-AuNP system after 3 has been grafted off of 2-modified AuNPs ( $\delta$  8 to 0 ppm).

connected within one brush and adjacent brushes from other AuNPs. In the second scan, the disappearance of the high potential oxidation process with an onset voltage of 0.33 V is indicative of this conversion. The disappearance of the peak is due to the lack of available conjugated moieties that can undergo electrochemical conversion. The poly(4)-AuNPs show reversible electrochemistry, with two distinguishable peaks associated with oxidation and reduction at 0.38 and 0.29 V, respectively.

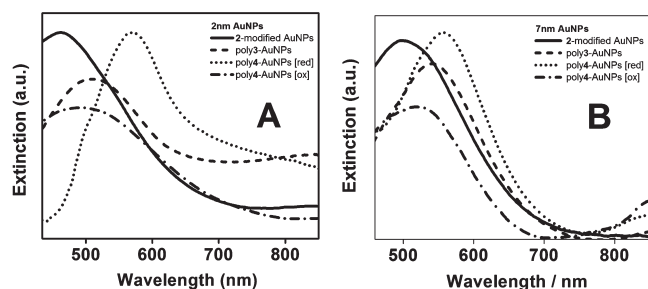
Characterization of the AuNPs before and after brush formation by AFM clearly showed an increase in the height of the particles. Analysis of the AuNPs before brush formation showed an average height of  $7.0 \pm 0.8$  nm at 95% confidence ( $n=34$ ) from TEM. After brush formation the AuNPs showed an increase in

height with an average size of  $21 \pm 3$  nm at 95% confidence ( $n=36$ ) from TEM. The change in height of the AuNPs as seen in Figure 2B, and Figure 2C is consistent with the growth of a polymer layer  $\sim 7$  nm in thickness around the AuNPs.

Figure 3A shows the optical extinction of the 2 nm AuNPs prior to and after precursor polymer growth. For recording the optical extinction spectra, a reference spectrum was taken of the ITO/polymer area allowing the extraction of the surface plasmon band of AuNPs from the ITO/polymer-functionalized AuNPs area. The reference state was taken by drop-casting a film of the precursor polymer from a 1 wt % film of poly(3), which was formed by reacting 3 with Grubbs generation I catalyst without particles onto an ITO slide. Normalization was performed in a



**Figure 2.** (A) Cyclic voltammetry of poly(3)-AuNPs showing the first and second scan 50 mV/s in 0.1 M TBAPF<sub>6</sub>/ACN. (B) Tapping mode atomic force microscopy (AFM) image of 2-modified AuNPs, prior to grafting a norbornene brush. (C) Tapping mode AFM image of poly(3)-AuNP after grafting norbornene brush.



**Figure 3.** Visible spectra in 0.1 M TBAPF<sub>6</sub>/ACN of films of (A) [2 nm AuNPs] 2-modified AuNPs (line); poly(3)-AuNPs (dash); reduced state of poly(4)-AuNPs (dot); oxidized state of poly(4)-AuNPs (dash-dot). (B) [7 nm AuNPs] 2-modified AuNPs (line); poly(3)-AuNPs (dash); reduced state of poly(4)-AuNPs (dot); oxidized state of poly(4)-AuNPs (dash-dot).

similar manner to prior literature.<sup>12c</sup> A red shift (from 452 to 514 nm) was observed as a result of an increase in dielectric constant of surroundings once polymer growth via surface-initiated ring-opening metathesis polymerization of **3** had taken place. The polymerizable units of precursor polymer on the same gold nanoparticles were then electrochemically cross-linked by applying a potential of 400 mV. After conversion of precursor polymer to conjugated polymer (reduced form), another red shift of the SP band is observed from 514 to 573 nm. The red shift can again be attributed to a modification of the refractive index of AuNPs' dielectric surrounding medium. More interestingly, when the cross-linked conjugated polymer is switched from the reduced state to the oxidized state, the LSPR band is blue-shifted (480 nm), a value below that of the SP band observed for precursor polymer growth AuNP prior to cross-linking. Accompanying the blue shift is a decrease in peak intensity of the LSPR band for the oxidized form of poly(4)-AuNPs in comparison with the reduced form of poly(4)-AuNPs. Electrochemically switching poly(4)-AuNPs between -400 and +600 mV is a reversible and stable process. No change in respective peak intensities was observed for electrochemically switching between each of the two states upon 100 steps.

In order to generalize the plasmon shifting due to conjugated polymer brushes on the surface of AuNPs, 7 nm AuNPs (larger

ones) were prepared in the same procedure except using a 6:1 ratio of HAuCl<sub>4</sub> to thiol mixture. As in 2 nm AuNPs, the same trend of the LSPR band shifting was observed in these larger AuNPs. As shown in Figure 3B, a red shift (from 497 to 541 nm) is observed after growth of precursor polymer due to an increase in the dielectric constant of the surroundings. Another red shift of the SP band (from 541 to 562 nm) is observed after electrochemically conversion of precursor polymer to poly(4)-AuNP (reduced state). Furthermore, the LSPR band is blue-shifted from 562 to 524 nm after oxidation of poly(4)-AuNPs. As observed in the 2 nm AuNPs, the 7 nm AuNPs functionalized with conjugated polymer brushes are also reversible with respect to electrochemical switching.

## Conclusion

In conclusion, we have demonstrated that polymer brushes containing polymerizable aromatic units can be efficiently produced on AuNPs via surface-initiated ROMP to synthesize nanoparticles with electrochemically reversibly tuned LSPR bands. The polymer growth process was monitored using <sup>1</sup>H NMR. The observed increase in the AuNPs height as observed by AFM is consistent with the growth of a polymer layer on the surface. After formation of precursor polymer brushes, the polymerizable EDOT moieties were electrochemically converted to conjugated polymers via an oxidative solid-state conversion process. More importantly, the plasmon bands of the resulting conducting polymer-functionalized AuNPs were reversibly tuned via electrochemical reduction and oxidation. The use of surface-initiated ROMP to obtain different brush lengths of conjugated polymer using AuNPs of different diameters and their respective electrochemically reversible plasmon band shifting effects is currently underway.

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**Supporting Information Available:** <sup>1</sup>H NMR spectra of the AuNPs, TEM image, and UV-vis spectrum of pure poly(3). This material is available free of charge via the Internet at <http://pubs.acs.org>.