

# ELECTRONIC AND OPTICAL PROPERTIES OF ELECTRODEPOSITED OLIGOTHIOPHENE-LINKED GOLD NANOPARTICLE FILMS

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One of the most innovative directions for current materials research is directed towards technologies based on nanoparticles (NP). NP based materials are of interest because of their unique optical, electronic, and mechanical properties. Specifically, gold NPs have attracted much interest due to their ease of synthesis, stability and potentially important role in microelectronic devices.<sup>1</sup> A focus of the work to date in this area has been on the assembly of these Au NPs into three dimensional structures using alkyl dithiols, dicyanides or phosphines. The predominant mechanism for the electronic conductivity of these Au NP assemblies is electron tunneling<sup>2</sup> and is dependent on two factors: the individual particle size and the inter-particle distance. There appears, however, to be little agreement on whether or not the chemical nature of the molecular linker affects the conductivity and optical properties of the NP arrangement.<sup>3</sup> Recently, Torma *et al.*<sup>4</sup> and Wessels *et al.*<sup>5</sup> synthesized several different Au NP assemblies linked by partially conjugated linkers and demonstrated substantially lower activation energies for inter-particle electron transfer (ie. higher conductivities) relative to nonconjugated linkers and strong absorbance in the near-IR comparable to that observed for gold films. It is therefore desirable to link Au NPs using fully conjugated linkers to further elucidate how the chemical structure of the linker affects the properties of the material.

To generate Au NPs linked by fully conjugated linkers, individual Au NPs were first synthesized with the conjugated phosphines 5-diphenylphosphino-2,2':5',2''-terthiophene ( $d_{\text{core}} = 1.7 \pm 0.3$  nm) and 5-diphenylphosphino-3',4'-ethylenedioxy-2,2':5',2''-terthiophene ( $d_{\text{core}} = 1.8 \pm 0.4$  nm) as capping groups (Figure 1). Electrochemical oxidation of these particles results in the deposition of thin films consisting of intact nanoparticles linked by oligothiophene moieties evident in the TEM images of the films (Figure 2).<sup>6</sup>

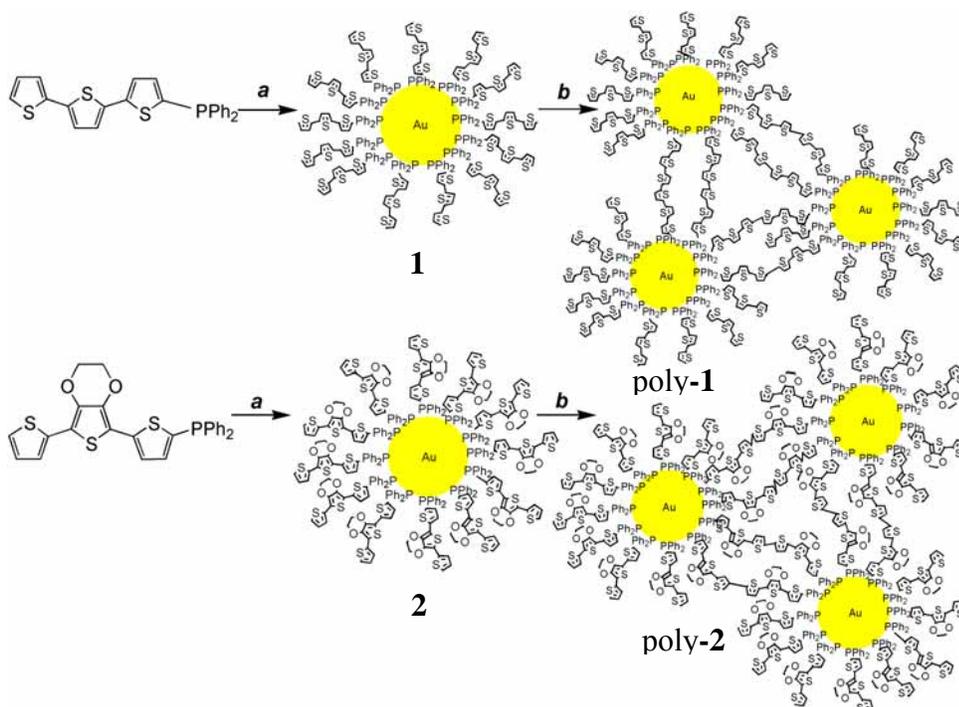
Some electronic and optical properties of poly-**1** and -**2** are also examined. Conductivity at room temperature of both unlinked and linked Au NPs are measured and the latter shown to have substantially higher conductivities than unlinked particles or Au NPs linked by saturated alkyl chain linkers. This increase in conductivity suggests that the main mechanism of electrical conductivity involves propagation through the  $\pi$ -conjugated bridging molecules.<sup>6</sup> Optical properties are equally interesting, there is an absorption at 380 nm corresponding to the  $\pi$ - $\pi^*$  transition for the terthiophene moiety of **1** that red-shifts to 435 nm upon cross-linking due to increased conjugation upon formation of sexithiophene (Figure 3). There is also an absorption in the near-IR corresponding to coupled surface plasmon resonance in poly-**1**. Effects of varying the dielectric environment on the optical properties will be discussed

Au NPs linked by  $\pi$ -conjugated bridges also presents *in situ* control of inter-particle interactions and conductivity via doping of the polymer. Electro-optical measurements probing the emergence of polaron levels in the UV-Vis spectrum upon electrochemical doping is explored.

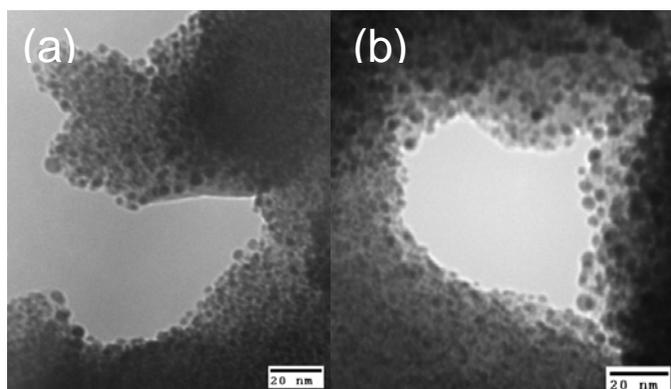
## References:

- [1] Simon, U.; Schön, G.; Schmid, G. *Anew. Chem., Int. Ed. Engl.* **1993**, 32, 250.  
 [2] Wuelfing, W.P.; Murray, R.W. *J. Phys. Chem. B* **2002**, 106, 3139.  
 [3] Sih, B.C.; Wolf, M.O. *Chem. Comm.* **2005**, DOI:10.1039/B501448D. (in press)  
 [4] Torma, V.; Vidoni, O.; Simon, U.; Schmid, G. *Eur. J. Inorg. Chem.* **2003**, 1121.  
 [5] J. M. Wessels, H.-G. Nothofer, W. E. Ford, F. von Wrochem, F. Scholz, T. Vossmeier, A. Schroedter, H. Weller, and A. Yasuda, *J. Am. Chem. Soc.*, 2004, **126**, 3349.  
 [6] B.C. Sih, A. Teichert, and M.O. Wolf, *Chem. Mater.*, 2004, **16**, 2712.

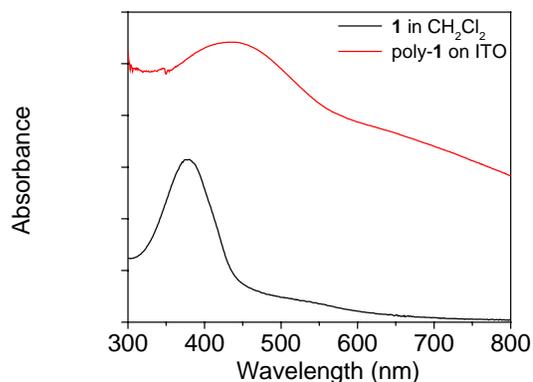
### Figures:



**Figure 1.** Preparation of oligothiophene-linked Au nanoparticles.  $\text{HAuCl}_4$ , Toluene,  $\text{H}_2\text{O}$ ,  $[\text{N}(\text{C}_8\text{H}_{17})_4]\text{Br}$  followed by addition of 15 equiv of  $\text{NaBH}_4$  at room temperature. <sup>b</sup>Electrodeposition in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $(n\text{-Bu})_4\text{NPF}_6$  on a Pt, ITO or Au working electrode.



**Figure 2.** TEM images of (a) poly-1 and (b) poly-2.



**Figure 3.** UV-Vis absorption spectra of **1** and poly-1.