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Electropolymerization of an N-Heterocyclic Carbene−Gold(I) Complex

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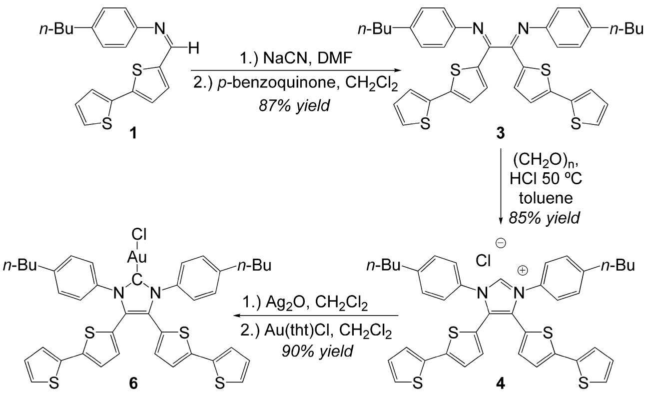
In contrast to the large number of useful polymeric materials that contain tethered N-heterocyclic carbenes (NHCs),[1] there are relatively few examples of polymers in which the NHCs are integral components of the main chain.[2] Several of these polymeric NHCs exhibit sensitivity to air and moisture, severely limiting their utility.[3] Furthermore, in all of these examples, the carbenes are essential for maintaining the polymer structure and generally not available for ligation or further reactivity.

We envisioned that electrochemical polymerization of an appropriately substituted thiophene-based monomer would constitute a new and promising approach to a polymer that contains an NHC orthogonally positioned with respect to its main chain. Arrangements of this type are of considerable interest for their ability to attach readily accessible entities with catalytic or biological properties or enable the addition of electronically tunable features to these systems. Furthermore, such an approach should be general and readily extended to incorporate a wide variety of NHC−metal complexes into polymeric materials. In view of the rapidly expanding interest in both the catalytic[4] and the medicinal applications of gold,[5] the efforts described herein focused on the polymerization of an NHC−AuCl complex.

Scheme 1. Synthesis of Gold(I) Carbene Complex **6**



As summarized in Scheme 1, monomer **6** was synthesized using a five-step procedure in an overall yield of ∼60%. Bithiophene monoimine **1**, which was prepared by condensing bithiophene carboxaldehyde with 4-*n*-butylaniline (92% yield), was dimerized to the corresponding ene-diamine **2** (structure not shown) via a NaCN-catalyzed aldimine coupling reaction.[6] Subsequent oxidation of **2** with *p*-benzoquinone afforded the desired diimine **3**, which, when treated with paraformaldehyde and anhydrous HCl, resulted in **4**. Treatment of the latter with Ag_2O afforded AgCl complex **5** (structure not shown). Finally, transmetalation of **5** with Au(tht)Cl (tht = tetrahydrothiophene) afforded the desired AuCl complex **6** (diagnostic ^{13}C NMR signal: $\delta = 172$ ppm in CD_2Cl_2).[7] Further confirmation of this structural assignment was obtained via X-ray diffraction (XRD) analysis (Figure 1, left). Although the key bond lengths and angles were similar to those of known NHC−Au complexes,[7] the packing diagram revealed a one-dimensional series of Au···Au contacts [3.2262(4) Å] between neighboring units of **6** that were arranged in a head-to-head fashion (Figure 1, right).

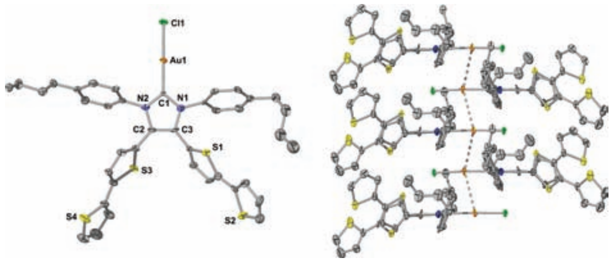
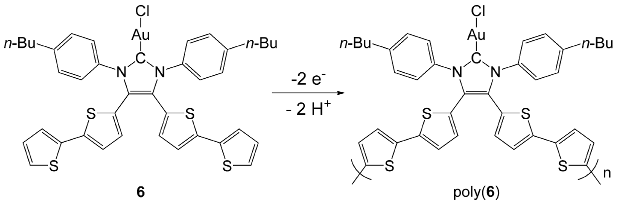


Figure 1. (left) POV-Ray view of **6** showing 50% probability thermal ellipsoids and selected atom labels. (right) Packing diagram for **6** showing Au···Au contacts. Hydrogen atoms have been omitted for clarity.

Scheme 2. Electrochemical Polymerization of Bithiophene-Substituted Gold(I) Carbene Monomer **6**



Electropolymerization of a 1 mM solution of **6** (in CH_2Cl_2) onto a platinum disk or an indium tin oxide glass slide afforded poly(**6**), as illustrated in Scheme 2.[8] The reaction was performed in a drybox using a three-electrode cell containing a silver wire quasi-reference electrode and $[(n\text{-Bu})_4N^+][PF_6^-]$ as the supporting electrolyte.[8] As shown in the top panel of Figure 2, the polymerization proceeded cleanly and in the anticipated fashion within a window of −0.2 to 1.5 V.[9] The polymer film oxidation wave grew with subsequent scans at 1.1 V and continued to increase for over 20 cycles, indicating good conductivity through the film. The shift to higher peak potentials with additional scans is typical and may originate from heterogeneous transfer kinetics and/or polymer growth on the electrode.[8] Similar to other thiophene-based polymerizations, the reduction peak (0.9 V) shifted cathodically with increasing number of scans.[10] Subsequent oxidation or reduction of the deposited film (in monomer-free solutions) resulted in no decrease in peak height, reflecting the high stability of the polymer.[11] Examination of the scan-rate dependence (Figure 2, bottom) revealed that the peak current for the electrodeposited film of poly(**6**) in a solution of $CH_2Cl_2/[(n\text{-Bu})_4N^+][PF_6^-]$ increased with scan rate, as expected on the basis of the Cottrell equation, and was in accord with related examples in the literature.[10] Scan rates above 100 mV/s resulted in distortion of the electrochemical profiles.

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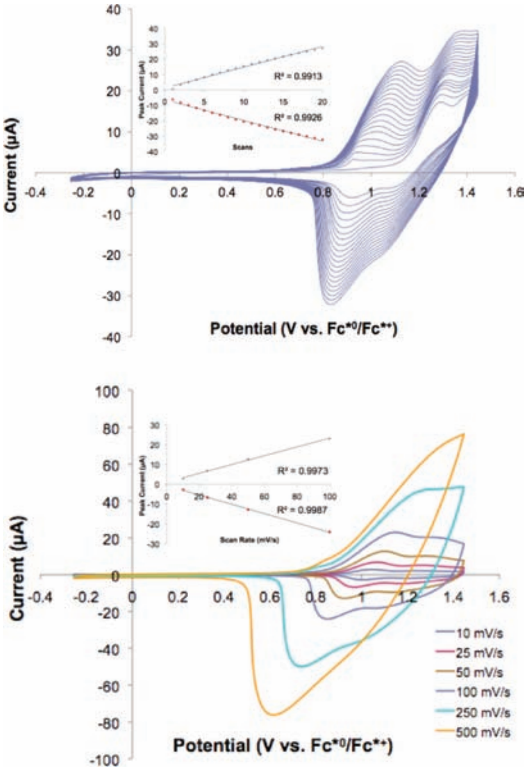

Figure 2. (top) Electropolymerization of **6**. Inset: plot of linear current increase vs number of scans. (bottom) Poly(**6**) scan-rate dependence. Inset: plot of linear current increase vs scan rate.

Films of poly(**6**) were also examined by X-ray photoelectron spectroscopy (XPS). The N 1s, S 2p, and Au 4f signals were observed at 401.5, 165, and 87 eV, respectively. The integrated N/Au and S/Au ratios (2.08 and 4.17, respectively) were within experimental error[12] of the values anticipated for the structure of poly(**6**) shown in Scheme 2. The S 2p signal featured a shoulder that was assigned to sulfur atoms in slightly different chemical environments. Because the monomer contains distinct thiophene units, such splitting was anticipated. A small amount of metallic gold deposition may be present in the analyzed samples, since the Au 4f signals revealed small shoulders at lower binding energies.

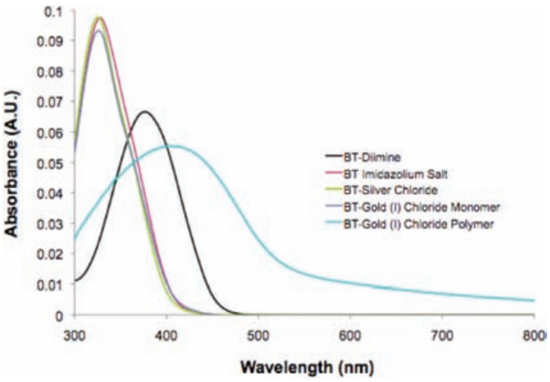

Figure 3. UV−vis spectra of monomers **3**−**6** and poly(**6**) in CH_2Cl_2. The concentration of **3**−**6** was 2.0×10^{-6} M.

Finally, the photophysical properties of poly(**6**) were explored and compared with those of compounds **3**−**6**. As shown in Figure 3, λ_{max} for **3** was 376 nm and attributed to the $\pi-\pi^*$ transitions of the diimine moiety. Upon cyclization to the imidazolium chloride **4**, λ_{max} hypsochromically shifted to 326 nm, an observation that is consistent with an increase of charge on the complex. Upon polymerization of **6**, however, λ_{max} shifted bathochromically to 406 nm and the absorption signature broadened, as expected for a polymeric system. On the basis of these results, we conclude that the spectroscopic character of **3**−**6** is dominated by ligand $\pi-\pi^*$ transitions. The electrochemical, XPS, and UV−vis spectroscopic studies collectively support the structural assignment of poly(**6**).

In summary, the first example of a polymer containing an NHC orthogonally connected to its main chain has been synthesized. Because of this structural arrangement, the carbene moiety in this material is poised to ligate transition metals or facilitate other carbene-based reactivities. The methodology presented may be general and readily extended to access a variety of materials containing NHC-based complexes connected directly to the main chains of polymers.

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Supporting Information Available: Additional experimental, NMR, electrochemical, XPS, UV−vis, and X-ray crystallographic data and a CIF file for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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