Carbodithioate-Terminated Oligo(phenyleneethynylene)s: Synthesis and Surface Functionalization of Gold Nanoparticles

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ABSTRACT



Carbodithioate-terminated bis(phenylene)ethynylenes and oligo(phenyleneethynylene)s have been synthesized from TMSE-protected 4-iododithiobenzoic acid ester (1) and 4-ethynyldithiobenzoic acid ester (3) via Pd-catalyzed cross-coupling reactions. TEM and spectroscopic studies demonstrate that the reaction of 4-(phenylethynyl)dithiobenzoate with alkylamine-protected gold nanoparticles (AuNPs) produces the corresponding organocarbodithioate-functionalized AuNPs.

Oligo(phenyleneethynylene)s (OPEs) have functioned as a structural mainstay in the field of molecular electronics.^{1–8}

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10.1021/ol070789j CCC: \$37.00 © 2007 American Chemical Society Published on Web 06/29/2007 These OPE-based molecular units have featured commonly a terminal thiol functional group, which provides the point of attachment to macroscopic metal surfaces^{1–8} or nanoscopic metal particles.^{9,10}

Aliphatic dithiocarboxylic acid derivatives have been shown recently to form well-packed and highly ordered selfassembled monolayers (SAMs) on Au surfaces.¹¹ Dithiobenzoic acid-modified CdSe quantum dots (QDs) have been obtained similarly via a ligand exchange protocol; these QD functionalization reactions are milder than those established previously for analogous thiol ligands.^{12,13} The characteristic

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instability of organic carbodithioic acid and carbodithioate moieties, however, has thus far limited their broad application as metal and semiconductor surface-functionalization reagents. For example, introducing the carbodithioic acid functionality through a Grignard reaction with CS_2 ,^{11,12,14} or oxidizing a benzylic carbon in the presence of sulfur and a strong base such as sodium methoxide,^{13,15} limits the range of functional groups that can be tolerated. Furthermore, because the carbodithioic acid group readily decomposes thermally,^{11,14} additional constraints are placed on reaction conditions; modification schemes, however, that rely on reacting secondary amines with CS₂ on a Au surface to produce structurally similar organodithiocarbamate anchoring ligands provide one approach to circumvent these issues.¹⁶ Here we show that the combination of Sonogashira cross-coupling¹⁷ and the (trimethylsilyl)ethyl (TMSE) protecting group enables the straightforward elaboration of a wide range of carbodithioate-terminated OPE compounds that make possible facile Au surface modification.

TMSE is a well-known protecting group for carboxylic acid and thiol;¹⁸ 4-iododithiobenzoic acid 2-(trimethylsilyl)ethyl ester (1), synthesized by oxidation of 1-benzenesulfonylmethyl-4-iodobenzene with elemental sulfur^{13,15} and subsequent reaction with (2-bromoethyl)trimethylsilane (Scheme 1), is stable under ambient conditions, and provides a key precursor for Sonogashira cross-coupling reactions.



Table 1 chronicles a range of Pd-catalyzed cross-coupling reactions of **1** with trimethylsilylacetylene. These studies and related experiments suggest that $Pd(PPh_3)_4$:*i*-Pr₂NH:DMF provides a suitable, general catalyst:base:solvent system; note that the carbodithioic acid TMSE ester was compatible with all the Sonogashira coupling reaction conditions screened for 4-[(trimethylsilyl)ethynyl]dithiobenzoic acid 2-(trimethylsilyl)ethyl ester (**2**) synthesis.

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 Table 1.
 Compound 2 Yield as a Function of Sonogashira

 Cross-Coupling Reaction Conditions

$I \longrightarrow S = I \\ I \longrightarrow S = TMS \\ SETMS = 20 \text{ h, } 60 \text{ °C} $ TMS $I \longrightarrow S = S \\ SETMS = 20 \text{ h, } 60 \text{ °C} $ TMS $I \longrightarrow S = S \\ SETMS = 20 \text{ h, } 60 \text{ °C} $			
		solvent/base	yield,
entry	catalyst	(20:1)	%
1	Pd(PPh ₃) ₄	DMF/i-Pr ₂ NH	83
2	$Pd(PPh_3)_4$	DMF/Et ₃ N	60
3	$Pd(PPh_3)_4$	DMF/i-Pr2NEt	48
4	$Pd(PPh_3)_4$	THF/i-Pr ₂ NH	77
5	$Pd(PPh_3)_2Cl_2$	DMF/i-Pr ₂ NH	45
6	$Pd_2(dba)_3,40\ mol\ \%\ P(o\text{-tol})_3$	DMF/ <i>i</i> -Pr ₂ NH	16

Reaction of **2** with 2 equiv of TBAF in THF deprotected simultaneously the carbodithioate TMSE and ethyne TMS groups; in situ reprotection with TMSE gives **3** (Scheme 2).



Compound **3** serves as a key synthon for the preparation of carbodithioate-terminated OPEs (Tables 2 and 3).

Tables 2 and 3 describe Sonogashira reaction products obtained from 1 and 3. Carbodithioate-terminated bis-(phenylene)ethynylenes were synthesized from (i) the reac-

 Table 2.
 Carbodithioate-Functionalized OPEs Derived from

 Pd-Catalyzed Cross-Coupling of 1 with Arylacetylene
 Compounds



^a 2.4 equiv of 1 based on diethynylbenzene. ^b In THF:*i*-PrNH₂ (20:1).

 Table 3.
 Carbodithioate-Functionalized

 Bis(phenylene)ethynylenes
 Derived from Pd-Catalyzed

 Cross-Coupling of 3 with Iodoarenes



tion of substituted arylacetylene derivatives featuring electronreleasing groups at the 4 position with **1** (Table 2) and (ii) the reaction of iodobenzenes bearing electron-withdrawing *para* substituents with **3** (Table 3). Note that these routes provide both monocarbodithioate- and α, ω -bis(carbodithioate)-functionalized OPEs (Tables 2 and 3).

Studies that have interrogated the molecular electronic properties of thiol-terminated OPEs motivated the synthesis of the Table 2 and 3 target structures. For example, α, ω dithiol OPEs have served as the classic molecular Au-to-Au bridge in pioneering break junction experiments;²⁻⁴ compounds 8, 9, and 12 define initial α, ω -bis(carbodithioate) analogues of these structures. An additional stimulus to synthesize 9 derives from reports indicating that nitrosubstituted OPEs having terminal thiol groups can function as molecular-scale switches and negative differential resistance (NDR) memory elements.⁴⁻⁸ Furthermore, underscoring a broader motivation for fabricating the OPEs listed in Tables 2 and 3 stems from conducting-probe AFM studies indicating that a 1,1'-bis(dithiocarboxylate)-4,4'-biphenyl electrode-molecule-electrode junction provides enhanced conductance with respect to an analogous 1,1'-bis(dithiolate)-4,4'-biphenyl junction;¹⁹ importantly, theory supports experiment, and implicates the disparity between thiol and carbodithioate electronic structure as the genesis of this effect.²⁰

Alkylamine-protected Au nanoparticles (AuNPs) facilitate subsequent surface modification under mild conditions (Figure 1A).²¹ Figure 1B shows a TEM image of AuNPs functionalized with 4-(phenylethynyl)dithiobenzoate that were derived from a ligand exchange reaction involving dodecylamine-protected AuNPs (**C12NH₂-Au**)²¹ and deprotected **4** (Supporting Information). After purification and drying under vacuum, **4**-functionalized AuNPs (**4-Au**) remain redispersible in organic solvents such as CHCl₃, even after months of dry storage; CHCl₃ solutions of **4-Au** evince no precipitate formation over a time frame of several months.

For comparison, a similar ligand exchange reaction involving dodecanethiol was carried out with $C12NH_2$ -Au. The



Figure 1. (A) Preparative scheme for 4-Au. (B) TEM images of 4-Au.

mean core sizes of both types of functionalized AuNPs were nearly identical (**4-Au**: 2.2 ± 0.4 nm; **C12S-Au**: 2.3 ± 0.4 nm) (Supporting Information). The TEM image of **4-Au** shows semiordered islands, a morphology often observed for arenethiol-modified AuNPs,^{22,23} and core-core spacings between neighboring particles of ~1.4 nm (Figure 1B).



Figure 2. (A) Electronic absorption spectra of 4-Au (-), 4 (\cdots), and C12S-Au (- -) in CHCl₃. (B) FT-IR spectra of 4-Au and 4.

Figure 2A shows the electronic absorption spectrum of **4-Au** in CHCl₃; following ligand exchange, **4**'s $\pi - \pi^*$

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transition centered at 345 nm broadens and blue shifts to 340 nm while its $n-\pi^*$ transition (501 nm) is obscured by the AuNP surface plasmon (SP) band (500–520 nm). FT-IR spectral analysis of **4-Au** and **4** (Figure 2B) confirms the ligand exchange reaction. While these spectra are very similar over the 3100–3000 (C–H stretching), 1600–1400 (aromatic C=C stretching), and 2220–2200 (ethyne stretching) cm⁻¹ energy regimes, note that **4**'s ν (CSS)²⁴ mode at 1039 cm⁻¹ disappears upon binding to the Au surface (Supporting Information). The **4-Au** FT-IR spectrum shows a ν_s (CSS) band centered at 898 cm⁻¹; a weak oscillator strength ν_{as} -(CSS) band likely contributes to the manifold of transitions evident at ~1020 cm⁻¹. These **4-Au** ν_s and ν_{as} CSS modes occur at frequencies similar to those reported for dithiobenzoate metal complexes^{25,26}(Supporting Information).

In summary, we have synthesized TMSE-protected 4-iododithiobenzoic acid ester (1) and 4-ethynyldithiobenzoic acid ester (3), and have utilized these species to prepare carbodithioate-terminated bis(phenylene)ethynylenes and OPEs. We have demonstrated via TEM and spectroscopic studies that reaction of 4-(phenylethynyl)dithiobenzoate with alkylamine-protected AuNPs produces the corresponding organocarbodithioate-functionalized AuNPs. (i) The prominent role played by thiol-terminated OPEs in molecular electronics,^{1–8} (ii) studies that indicate that carbodithioate enables augmented electronic coupling to Au relative to that provided by thiol,^{19,20} and (iii) the fact that the chemistry reported herein makes straightforward the synthesis of carbodithioateterminated oligo(phenyleneethynylene) compounds and subsequent Au surface functionalization all suggest the potential impact for monocarbodithioate- and α, ω -bis(carbodithioate)functionalized OPEs in fundamental nanoscience.

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Supporting Information Available: Synthetic procedures, characterization data, ligand exchange protocols, TEM images, FT-IR spectra, and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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