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

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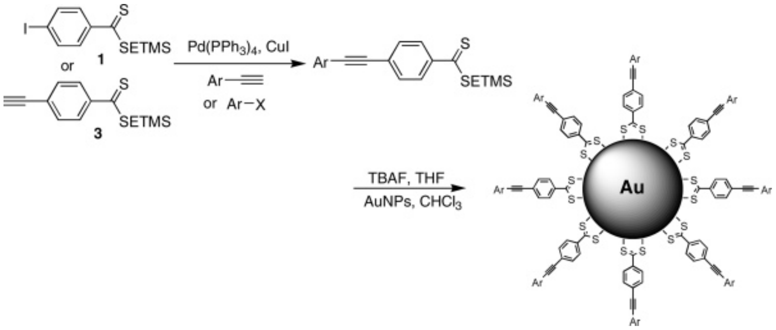
ABSTRACT



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] 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 self-assembled 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 CS$_2$ 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-coupling[17] 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.

Scheme 1. Synthesis of 4-Iododithiobenzoic Acid 2-(Trimethylsilyl)ethyl Ester (**1**)

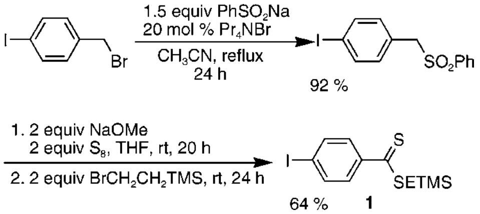
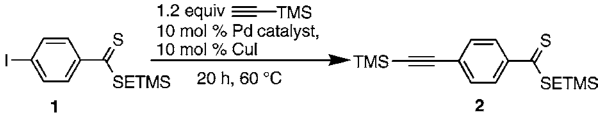


Table 1 chronicles a range of Pd-catalyzed cross-coupling reactions of **1** with trimethylsilylacetylene. These studies and related experiments suggest that Pd(PPh$_3$)$_4$:*i*-Pr$_2$NH:DMF provides a suitable, general catalyst:base:solvent system; note that the carbodithioic acid TMSE ester was compatible with all the Sonogashira coupling reaction conditions screened for 4-[(trimethylsilyl)ethynyl]dithiobenzoic acid 2-(trimethylsilyl)ethyl ester (**2**) synthesis.

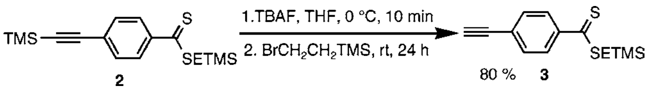
Table 1. Compound **2** Yield as a Function of Sonogashira Cross-Coupling Reaction Conditions



entry	catalyst	solvent/base (20:1)	yield, %
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*-Pr$_2$NEt	48
4	Pd(PPh$_3$)$_4$	THF/*i*-Pr$_2$NH	77
5	Pd(PPh$_3$)$_2$Cl$_2$	DMF/*i*-Pr$_2$NH	45
6	Pd$_2$(dba)$_3$, 40 mol % P(*o*-tol)$_3$	DMF/*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).

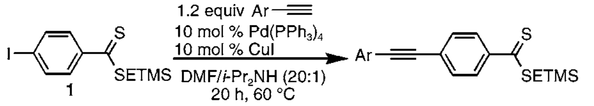
Scheme 2. Synthesis of 4-Ethynyldithiobenzoic Acid 2-(Trimethylsilyl)ethyl Ester (**3**)

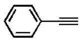
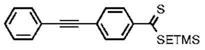
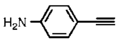
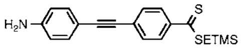
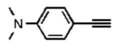
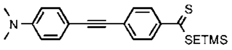
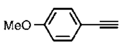
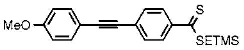
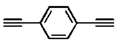
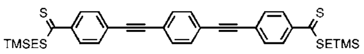
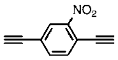
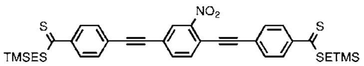


Compound **3** serves as a key synthon for the preparation of carbodithioate-terminated OPEs (Tables 2 and 3).

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



entry	Ar—≡	product	yield, %
1		 **4**	81
2		 **5**	57
3		 **6**	69
4		 **7**	68
5^a		 **8**	83
6^a		 **9**	23^b

^{a} 2.4 equiv of **1** based on diethynylbenzene. ^{b} In THF:*i*-PrNH$_2$ (20:1).

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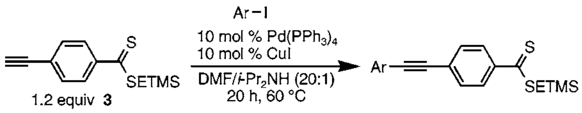
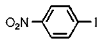
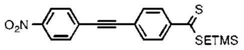
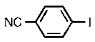
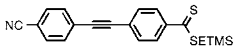
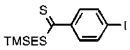
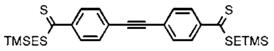
Table 3. Carbodithioate-Functionalized Bis(phenylene)ethynylenes Derived from Pd-Catalyzed Cross-Coupling of **3** with Iodoarenes



entry	Ar—I	product	yield, %
1		 **10**	66
2		 **11**	57
3		 **12**	60

tion of substituted arylacetylene derivatives featuring electron-releasing 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 nitro-substituted 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 (**C12NH$_2$-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 CHCl$_3$, even after months of dry storage; CHCl$_3$ solutions of **4-Au** evince no precipitate formation over a time frame of several months.

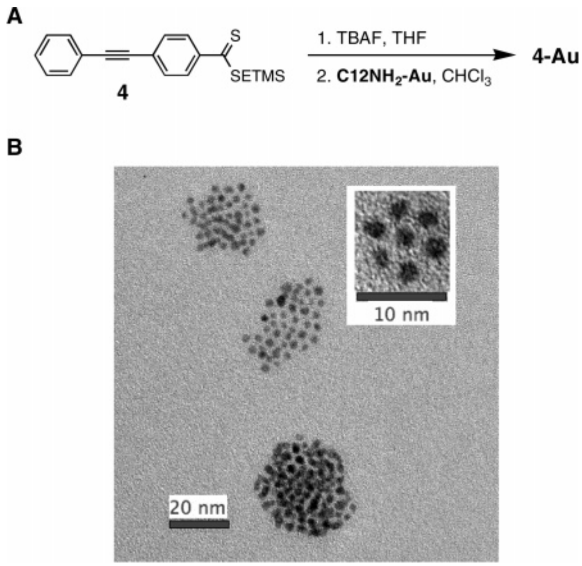


Figure 1. (A) Preparative scheme for **4-Au**. (B) TEM images of **4-Au**.

For comparison, a similar ligand exchange reaction involving dodecanethiol was carried out with **C12NH$_2$-Au**. The 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).

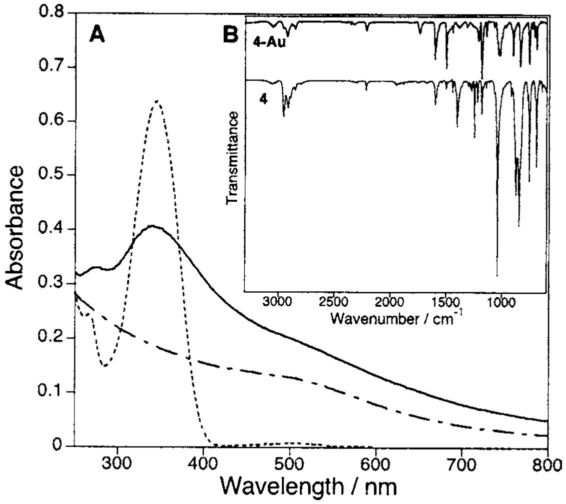


Figure 2. (A) Electronic absorption spectra of **4-Au** (—), **4** (···), and **C12S-Au** (− - −) in CHCl$_3$. (B) FT-IR spectra of **4-Au** and **4**.

Figure 2A shows the electronic absorption spectrum of **4-Au** in CHCl$_3$; 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−π* 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 carbodithioate-terminated 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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