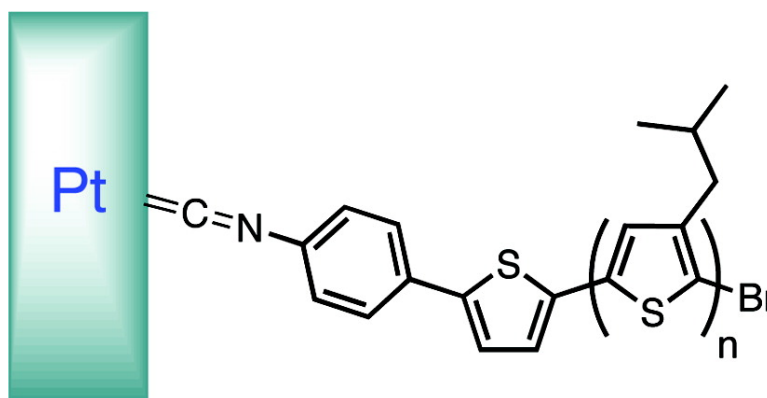


## Oligothiophene Isocyanides for Platinum-Based Molecular Electronic Applications

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## Oligothiophene Isocyanides for Platinum-Based Molecular Electronic Applications

Dennis Bong,<sup>†</sup> Iris Tam, and Ronald Breslow\*

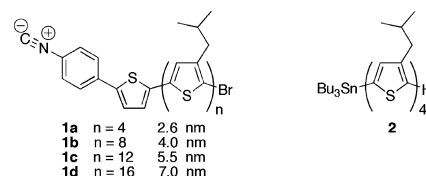
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Oligo- and polythiophenes are well-known semiconducting organic molecules and are of great interest as potential molecular wire candidates.<sup>1,2</sup> We report herein the synthesis of oligothiophenes end-functionalized with isocyanides and characterization of their chemisorption to platinum surfaces. While much work has described the coupling of low band-gap organic molecules to gold surfaces via gold–sulfur bonds,<sup>3,4</sup> specific chemisorption of molecules of this type to other metal surfaces has been less well-explored.<sup>2,3,5</sup> Gold is a convenient electrode material with regard to patterning and chemisorptive attachment of organic thiols, but it has significant disadvantages in grain mobility and susceptibility to surface etching by thiols;<sup>6</sup> it is therefore useful to investigate conjugated molecule–metal interfaces with more refractory metals such as platinum. This study details the first synthesis of isocyanide-functionalized oligothiophenes and characterization of their assembly on both platinum surfaces and nanoparticle form.

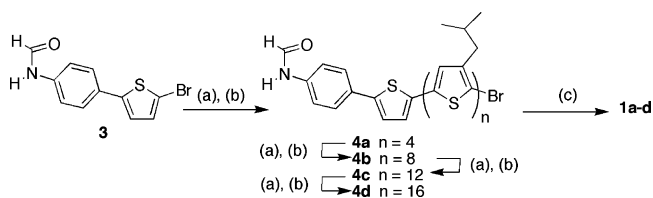
Different device applications may require molecular coupling to metal in both bulk and nanoparticulate form;<sup>7</sup> further, they will have different length requirements for the molecular bridge between metal source and drain electrodes. Thus, we have prepared a family of oligothiophene monoisocyanides in which the members differ only by the number of thiophene units, to investigate the dependence of platinum surface self-assembly on oligothiophene length. Regularly alkylated oligothiophenes **1a–d**, with calculated end-to-end lengths of 2.6, 4.0, 5.5, and 7.0 nm, respectively (Figure 1), were readily synthesized by cycles of thiophene terminal bromination and Stille couplings<sup>8</sup> with stannane **2** as a quaterthiophene building block through intermediates **3** and **4** (Scheme 1). Isobutyl functionality in one  $\beta$ -position of each thiophene ring of **2** was installed<sup>9</sup> to impart organic solvent solubility by inhibiting effective stacking of the flat ring systems. Isocyanide functionality was introduced in the final step of oligothiophene synthesis by dehydration of a terminal phenyl formamide.<sup>10</sup>

Interestingly, this series displays only a moderate red shift as the length of the conjugated system increases, as judged by ultraviolet and fluorescence spectroscopy (Table 1). While the UV maxima exhibit a small but steady shift to the red with increasing molecule length, the red-shifting trend in emission appears to plateau after **1c**; furthermore, the sizable and relatively constant Stokes shift of  $\sim 130$  nm is larger than that observed for thiophene systems of similar length but different alkylation pattern.<sup>11</sup> This is likely due to the sensitivity of conjugation length in the ground state to steric environment. The  $\beta$ -branching alkylation pattern may cause the oligothiophene backbone to twist, breaking conjugation and leading to larger ground-state electronic energy separations (smaller  $\lambda_{\text{max}}$ ) than would be expected for conjugated systems of these lengths. Emission spectra, however, are in line with literature values, indicating a conjugatively stabilized system that stretches over 3.5–5 nm.



**Figure 1.** Structure of oligothiophene isocyanides **1a–d** and respective end-to-end length. The structure of quaterthiophene stannane building block **2** is shown on the right.

### Scheme 1<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a) Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene reflux **2**; (b) NBS, CHCl<sub>3</sub>; (c) triflic anhydride, DIEA, CH<sub>2</sub>Cl<sub>2</sub>.

**Table 1.** Absorption and Emission Maxima, First Oxidation Potentials of **1a–d** in Solution and as a SAM on a Platinum Electrode, and Film Thickness on a Platinum Surface<sup>a</sup>

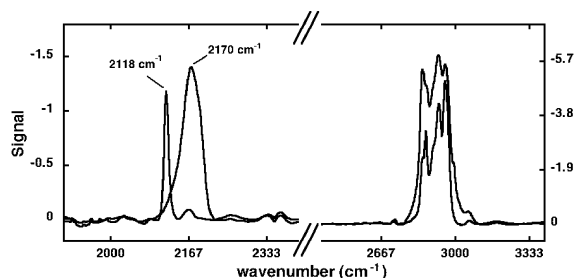
	UV (nm) $\lambda_{\text{max}}$	Fl (nm) $\lambda_{\text{max}}$	$E_{\text{pa}}$ (mV) (soln)	$E_{\text{pa}}$ (mV) (SAM)	film thickness (nm)
<b>1a</b>	409	542	450	410	1.8
<b>1b</b>	419	551	420	430	3.0
<b>1c</b>	423	555	410	440	4.1
<b>1d</b>	430	555	400	450	5.3

<sup>a</sup> Absorption and emission maxima were acquired in CH<sub>2</sub>Cl<sub>2</sub>. Cyclic voltammetry was measured at a scan rate of 100 mV s<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> using a Ag/AgCl standard electrode and Pt disk working electrode. For details, see Supporting Information.

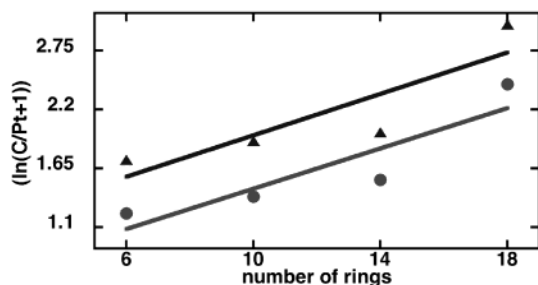
The ground-state similarity of this series of compounds is further reflected in CV studies of the isocyanides, both in solution and in the form of a self-assembled monolayer (SAM) on a Pt working electrode. The first oxidation potentials in solution (which are comparable to those previously reported for oligothiophenes<sup>12</sup>) display a slight decrease (become more easily oxidized) as the molecules become longer, but in the SAM they appear to be more difficult to oxidize as molecule size increases. Despite this, the absolute differences are small, possibly because ground state twisting of the backbone renders these differently sized molecules electronically similar. The critical observation, however, is that the oligothiophene isocyanides not only bind to platinum but also can be electrochemically charged,<sup>13</sup> as would be required in a device format.

Infrared spectroscopic examination of **1a–d** confirmed the installation of the isocyanide functional group by the presence of a characteristic CN stretch at 2118 cm<sup>-1</sup>. Unequivocal evidence for platinum binding is provided by a CN band shift to higher wavenumbers (2170 cm<sup>-1</sup>) upon treatment of isocyanide with

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**Figure 2.** Representative overlaid transmission infrared spectrum of **1b** on  $\text{CaF}_2$  before treatment with platinum nanoparticles ( $2118\text{ cm}^{-1}$ ) and after platinum nanoparticles ( $2170\text{ cm}^{-1}$ ). The isocyanide region is shown on the left, and the unperturbed thiophene region is shown on the right.



**Figure 3.** Plot of logarithm of the ratio of XPS signal intensity of carbon to Pt4d electrons (●) and Pt4f electrons (▲) against the number of rings in **1a–d**. Lines shown are the respective linear regression fits of each data set. Each data point is the average of three measurements in different areas of the surface; error bars are not visible at this scale.

organic solvent soluble platinum nanoparticles,<sup>14</sup> indicating the formation of an isocyanide–platinum bond (Figure 2). Isocyanide functionality also proved to be essential for effective coverage of platinum surfaces from X-ray photoelectron spectroscopy (XPS) analysis of oligothiophenes **1a–d** deposited on evaporated Pt films, suggesting chemisorption through isocyanide–platinum coupling rather than nonspecific modes of surface deposition.

XPS further revealed a positive correlation between molecular size and film thickness<sup>15</sup> (Table 1, Figure 3); the longer the oligothiophene, the larger the ratio between the carbon (molecule) signal and the substrate (Pt) signal. The relationship between film thickness and calculated molecular length indicates that these oligothiophenes deposit on platinum with a tilt angle of  $\sim 41^\circ$  from the surface normal (assuming a constant angle for all molecules). This significant tilt differs from the reported near normal orientation of unalkylated thiophene thiols on gold.<sup>16</sup>

Without alkylation, 2-D assembly is dominated by  $\pi$ -stacking, which forces the backbone in an upright configuration for maximal surface burial. Both the IR and XPS results support a Pt surface binding model in which the substituted oligothiophenes are surface-bound by an isocyanide–Pt bond, and the molecular backbone projects away from the surface rather than adhering to it, rendering this class of molecule suitable for many electronic device configurations. Understanding molecular orientation on the metal surface is key to designing molecule-bridged junctions, and these experiments taken together detail the first description of the ability and manner in which these soluble oligothiophenes, of a range of lengths, chemisorb onto platinum surfaces. This new context for the well-studied conducting thiophene backbone lays the foundation for future study of oligothiophenes as single molecular wires and semiconducting organic monolayers with platinum-based devices.

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**Supporting Information Available:** Experimental details for the synthesis of **1a–d**; Pt film evaporation, XPS of Pt films, nanoparticle IR, and solution and SAM CV experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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