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Cruciform π -Systems for Molecular Electronics Applications

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This study details a modular and general synthesis of a new class of molecules (1) consisting of two perpendicularly disposed π -systems. Once formed, these rigid compounds assemble into ordered monolayer films that orient their bis-oxazole subunits upright from the surface. This orientation is useful in molecular electronics test structures that require a path of conjugation perpendicular to the metallic electrode surface.¹⁻³ Molecules typically used in these devices are linear aromatics that terminate in surface-active endgroups.^{4,5} The molecules shown in Figure 1 have orthogonal terphenyl and bis-phenyloxazole arms. The crowding in the central ring forces the external phenyl substituents out of the ring plane, thereby preventing the prone conformation in self-assembled monolayer (SAM⁶) films.

The 6,5-ring junction between the phenyl and benzoxazole rings is utilized in these studies because polymers with this linkage have been shown to be flat and conjugated.⁷ Also, these polymers have been shown to be of high tensile strength,⁷ resistant to oxidation,⁸ and conductive.^{7–9} The typical reaction conditions used to make phenyl oxazoles are harsh¹⁰ and do not allow the formation of oligomers with sensitive groups such as acetate-protected thiols. Shown in Scheme 1 is a new synthesis of a variety of substituted bis-phenyloxazoles that affords these unusually shaped molecules through an unprecedented¹¹ double Staudinger cyclization¹² of bisazide **3**. The unpurified reaction mixtures do not show any significant byproducts and can be easily purified by a simple filtration if polymer-bound triphenylphosphine is used.¹³

The azides are remarkably stable and easily introduced into this crowded ring structure through a Michael addition/elimination on the bis-bromoquinone 2. Sodium dithionite reduction of the bis-azidoquinone 3 to its hydroquinone form, followed by an in situ coupling with either carboxylic acids or the acid chlorides produces the Staudinger precursors 4a-f. For 4e and 4f, differential substitution of the hydroquinone was successful through sequential introduction of two different activated benzoic acids. Moreover, the monoaldehyde 1e can be cleanly oxidized through Lindgren conditions¹⁴ to yield the monocarboxylic acid 1g. Some of the bisoxazoles in Scheme 1 were synthesized to carry surface-active groups such as thioesters (1b, 1f),^{5b} carboxylic acids (1g),¹⁵ and nitriles (1d).¹⁶

To test for monolayer formation and structure, **1b** and **1f** were deposited, by the method of Tour et al.,^{5b} onto films of gold. Likewise, **1g** was chemisorbed onto a native aluminum oxide layer. For **1f**, monitoring the binding energy of the S_{2p} core electron at ca. 162 eV shows the characteristic transition and peakshape for a thiolate bound to gold.¹⁷ For monolayers of alkane thiols, XPS has given close estimates as to the thickness of the organic layer by using a two-layer model.¹⁸ By this method, monolayers of **1f** were estimated to be 2.19 ± 0.05 nm thick. In an upright configuration on gold, as shown in Figure 2a, molecular models predict the distance between the terminal carbon, and the attached gold atom is 2.26 nm, implying that the molecule has a ca. 15° tilt angle.¹⁹



Figure 1. (a) Cruciform π -systems: terphenyl (red) and bis-phenyloxazoles (black); (b) CPK molecular model showing the out-of-plane twist of the phenyl side chains blocking the prone position (carbon, gray; nitrogen, blue; oxygen, red; sulfur, yellow).



^{*a*} Reagents and conditions: (a) NaN₃; (b) *i*, Na₂S₂O₄, H₂O, *ii*, see the Supporting Information; (c) Ph₃P•polystyrene.

The XPS-derived film thickness is in good agreement with the 1.9 \pm 0.1 nm determined from ellipsometry from a monolayer of **1f** on gold.

Shown in Figure 2b are the IR spectra for **1f** in a monolayer and in bulk. Similar spectra were acquired for monolayers of **1b** on gold films. Loss of the 1693 cm⁻¹ carbonyl stretch in the monolayer indicates that the thioacetate is cleaved.^{5b} The oxazole vO-C=N stretch²⁰ (at ca. 1613 cm⁻¹), whose transition dipole is parallel to the axis of conjugation, has a higher relative intensity in the monolayer—in agreement with the XPS and ellipsometry data that the bis-oxazole is upright from the substrate.

On going from the bulk to the SAM, the 1495 cm⁻¹ (ν C=C aromatic stretch^{10d}) increases and the 1470 cm⁻¹ (δ CH₂ scissoring) decreases in relative intensity. This change is an indication that the aliphatic side chains are anisotropic as in Figure 2a. Advancing and receding water contact angle measurements of monolayers of **1f** were found to be 86° and 76° ± 2°, respectively, similar to what would be expected from a surface that is presenting a methylester.²¹



Figure 2. (a) Molecular model of **1f** on a Au (111) surface. (b) Infrared spectrum (KBr) of bulk **1f** (blue trace) and PEM-IRRAS spectrum from a monolayer of **1f** (red trace).

In aggregate, the results presented above indicate that monolayers of **1f** form with high coverage, orienting the bis-phenyloxazole upright from the surface. Although the results are not as clear for **1b** and **1g**, the XPS data indicate that the molecules are also oriented roughly upright in monolayers. A direct comparison with compounds that lacked the phenyl side chains was not possible due to their insolubility.

In summary, this study has put forth a new, modular method to produce highly functionalized cross-shaped molecules. One arm serves as the conjugated portion while the other provides structure to thin films. In monolayer films the molecules orient upright from the surface. This provides a means to conjugate a diversity of functionality to a metallic underlayer and to test the electrical properties of these films.³ Moreover, more complex functionalization of the phenyl side chains is a promising route to molecularscale patterning of conductive substrates.

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Supporting Information Available: Experimental details for the synthesis and characterization of (1-4); XPS (1b, 1f, and 1g) and IR (1b and 1f) for monolayer films (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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