

Chemical Reactions with Upright Monolayers of Cruciform π -Systems

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The study below details the synthesis and self-assembly of new cruciform π -systems and their in situ chemical reactions in monolayer films. Analysis of the packing in the crystal structure of one of these unusually shaped molecules reveals that the terphenyl arm, which is twisted out of conjugation, makes edge-to-face contact with neighboring molecules aligning the conjugated bisoxazole arms in rows. In self-assembled monolayers on metal surfaces, these cruciform π -systems present reactive groups at the film/air interface. Films that present aldehyde functionality react with aromatic anilines to give surface-bound imines. Dimers that are >4.5 nm in length and contain a conjugated imine linkage can be made in situ on gold substrates through this strategy.

Introduction

It would be generally useful for molecular electronics if in situ methods could be developed to grow sizable and diverse conjugated structures from aromatic monolayers. Compared with the relatively well-developed chemistry on the surface of nonconjugated, aliphatic SAMs (self-assembled monolayers),¹ there are only a few reactions with the simplest of building blocks that have been tested for the homologation of aromatic molecules on metal surfaces.² The monolayers explored here are formed from cruciform π -systems that have a terphenyl arm that is crossed with a conjugated bisoxazole arm (Figure 1a).³ This crossed architecture is crucial in forcing the conjugated segment to be upright in SAM's.⁴ Detailed below is a study in the synthesis and assembly of new cross-shaped molecules. The crystal structure of a derivative shows that the molecules stack through edge-to-face contacts between the terphenyl arms, aligning the rows of the

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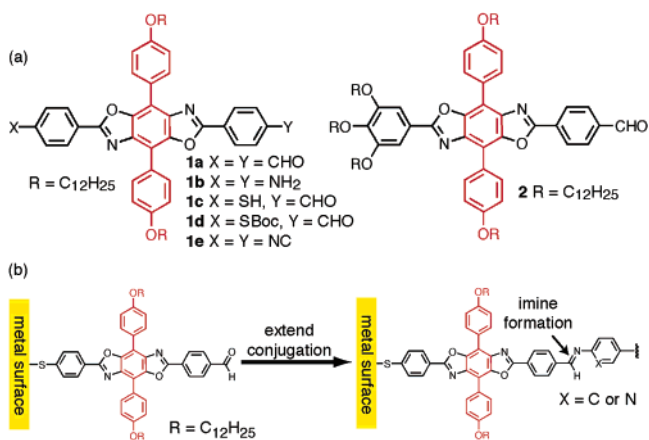


Figure 1. (a) Molecules synthesized for solution and monolayer studies of imine condensations. (b) Condensation reactions on monolayers of cruciform π -systems to extend π -conjugation.

bisoxazole arms. In monolayer films attached through thiols or isonitriles to metals, the bisoxazole arm orients upright. The path of conjugation can be extended through imine bond formation⁵ between any number of anilines and monolayers that present aldehydes at their termini. Using this approach, sizable and conjugated nanostructures can be grown in situ from relatively simple pieces.

Results and Discussion

Synthesis. The synthesis used for **1a–e** employs a method^{3,6} based on a double Staudinger⁷ cyclization, illustrated in Scheme 1, where an aryl azide is converted to a nitrogen-based ylide using polystyrene-bound⁸ triphenyl phosphine. This reaction is exceptionally mild and

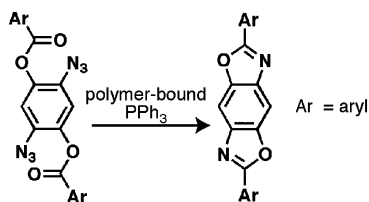
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Scheme 1. General Staudinger-Cyclization Route to the Synthesis of Bisoxazoles



provides a means for the creation of a diverse library of cruciform π -systems. Previous methods used to produce phenyl oxazoles generally employ harsh reaction conditions⁹ for the dehydration of a carboxylic acid and an *ortho*-aminophenol. These conditions are incompatible with many surface-active groups or their precursors, such as thioacetates. Additionally, this reaction allows for the facile synthesis of differentially terminated bisoxazoles.

To study the imine condensation in solution, two symmetrical bisoxazoles, aldehyde **1a** and amine **1b**, were synthesized. Three unsymmetrical bisoxazoles (**1c**, **1d**, and **2**) were also synthesized that carried both an aldehyde and either a surface-active thiol group or a solubilizing group.¹⁰ The thiol derivatives were protected with a *tert*-butyl carbamate group (Boc)¹¹ due to its increased stability relative to the more commonly used acetyl group. The Boc is cleanly removed using a trifluoroacetic acid/methylene chloride mixture to yield the free thiol.

Solid State Structure. To understand the packing of these unusually shaped molecules, attempts were made to crystallize derivatives of **1**. Unfortunately, crystals suitable for diffraction studies could not be obtained presumably due to the fluidlike side chains that prevent crystallization. To circumvent this problem, **3**, shown in Figure 2a, was synthesized¹² without the aliphatic side chains. This compound formed needlelike crystals from solvent interdiffusion of hexanes into a methylene chloride solution of **3**. The crystal structure in Figure 2b shows that the bisoxazole backbone is essentially planar and forms slipped rows 3.4 Å apart. The terphenyl rings are twisted 34° out of planarity with the backbone. The phenyls alternatively twist to allow for edge-to-face intermolecular contacts, similar to those observed in calamatic liquid crystals.¹³

Solution Imine Formation and Conjugation Studies. The imine condensation reaction is tolerant of a number of functionalities, such as amines, pyridines, and thiols, that are useful in molecular assembly on metal and metal oxide surfaces. All of the imines in Figure 3 and many others synthesized in the course of this study can be formed in essentially quantitative yield by warming the aldehydes (**1a**, **1d**, or **2**) with the corresponding anilines.¹⁰ The reactions do not require any catalysts or harsh reaction conditions that could degrade the monolayer. Unlike traditional metal-based coupling reactions, it is easy to create a large library of diverse structures due to the mildness of the reaction and the ubiquity of the aniline starting materials.

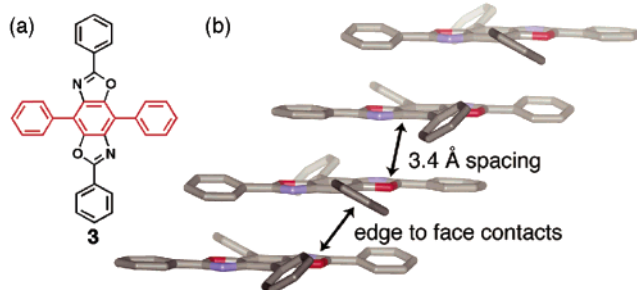


Figure 2. (a) Chemical structure of **3**. (b) Crystal structure of **3**: carbon, gray; nitrogen, blue; and oxygen, red. Hydrogen atoms have been removed to clarify the view.

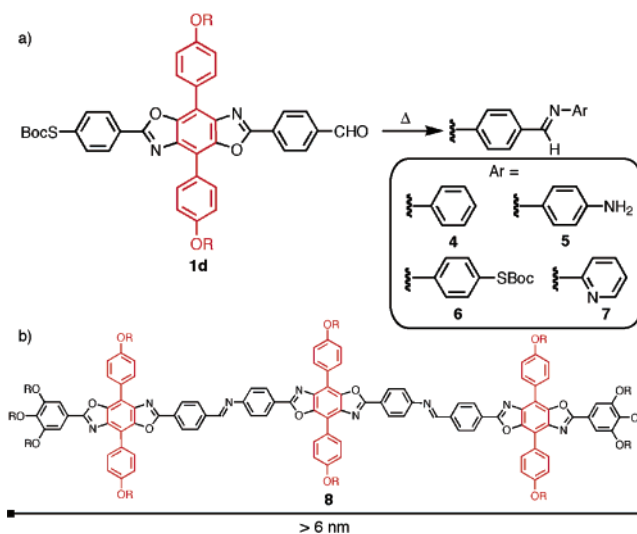


Figure 3. (a) Imine formation in solution without catalysts. (b) > 6 nm long trimer formed in solution by condensation of **1b** and **2**.

As shown in Figure 3b, the imine condensation reactions can be extended to long and conjugated nanostructures (>6 nm) by reacting the bifunctional diaminebisoxazole **1b** with the monoaldehyde **2**. The solution turns deep red upon heating these compounds in a 2:1 ratio. The ¹H NMR, unlike the ones for simple imines, was uninterpretable presumably due to aggregation. The UV-vis spectrum showed broadened and red-shifted absorbances also indicative of aggregates. MALDI mass spectrometry showed an intense peak at 3657.4 amu, further confirming the trimeric structure. There was no evidence in the mass spectrum for either dimer formation or higher oligomerization. Given the similar size and shape, the trimer may aggregate into structures similar to those of self-assembled oligophenylenevinyls terminated in trialkoxyl side chains.¹⁴

Simpler models were sought to assess how the length of conjugation affects the electronic structure of the oligomers due to the extensive aggregation of **8**. The UV-vis spectra from aldehyde **1d**, mono-imine **4**, and bis-imine **9** are overlaid in Figure 4b. The spectra clearly show a red-shift and an increase in the molar extinction coefficient as the length of the molecule increases. These data imply there is significant delocalization in these imines, making them suitable molecular wires. Previous studies of simple imines derived from aniline and benzaldehyde using crystal structure determination¹⁵ and UV-vis analysis¹⁶

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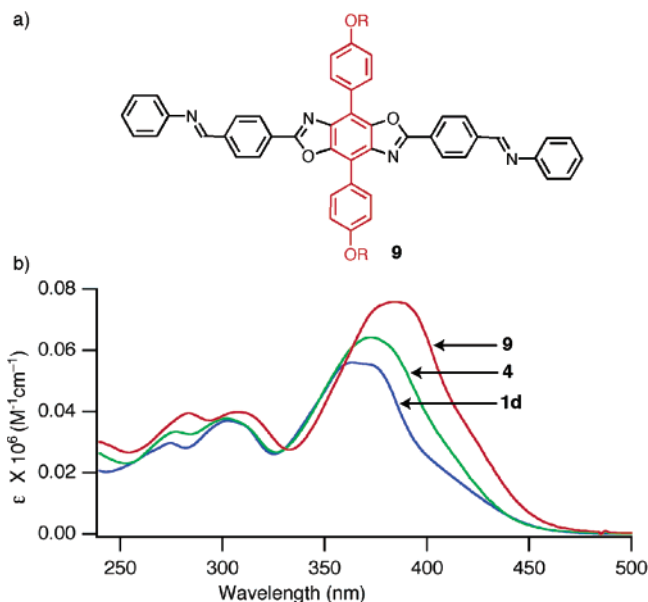


Figure 4. (a) Bis-imine from the condensation of **1a** with aniline. (b) UV-vis spectra of **9**, **4**, and **1d**.

indicate a 45° torsional angle for the Ar–N single bond. Either the push–pull electronic structure¹⁷ of the bis-benzoxazole or the long path of delocalization force these imines closer to planarity.

Self-Assembled Monolayers. In the initial communication on these molecules, we showed that SAMs of the methyl ester derivative of **1** were upright using photoelastic modulated infrared reflection absorption spectroscopy (PEM-IRRAS), X-ray photoelectron spectroscopy (XPS), water contact-angle measurements, and ellipsometry.³ A tilt angle of ca. 15° was estimated using the XPS film thickness. Here, we extend these studies to include isonitriles (**1e**) and new monothiol derivatives that are terminated in aldehydes (**1c**) to study the imine condensations discussed above. SAMs of diisonitrile **1e** and thiol **1c** were formed by immersing freshly evaporated gold films on silicon substrates in 0.1 mM THF solutions for 24–48 h, rinsed, and dried under a stream of nitrogen.

The SAM of diisonitrile **1e** on gold shows evidence of an upright surface conformation. The bulk (KBr) spectrum, displayed in red in Figure 5a, shows one peak from both of the $\nu\text{C}=\text{N}$ s at 2126 cm^{-1} . This is consistent with the C_2 -symmetry of the molecule. However, the presence of the metal surface in the SAM breaks this symmetry, resulting in the differentiation of the $\nu\text{C}=\text{N}$ s into two separate peaks. The unbound $\nu\text{C}=\text{N}$ slightly shifts to 2119 cm^{-1} , while the bound $\nu\text{C}=\text{N}$ shifts to a much higher frequency of 2182 cm^{-1} . The degree of shifting observed in the isonitrile stretches in the comparison between the bulk spectrum and the SAM is consistent with aryl diisonitriles on gold.¹⁸ Isonitrile monolayers can be useful for the creation of 3-D structures by the controlled formation of multilayers that use metal atoms as chelating agents between each layer.¹⁹

We have previously shown that the ester derivative of **1** forms high-coverage monolayers with the bis-phenyl-oxazole oriented upright from the surface.³ The SAM of

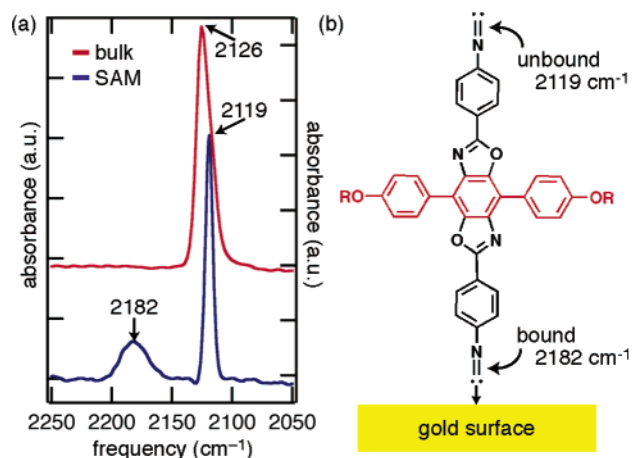


Figure 5. (a) PEM-IRRAS of the bulk isonitrile **1e** (red) and the SAM (blue). The red spectrum was displaced vertically. (b) Schematic of **1e** bound to a gold surface.

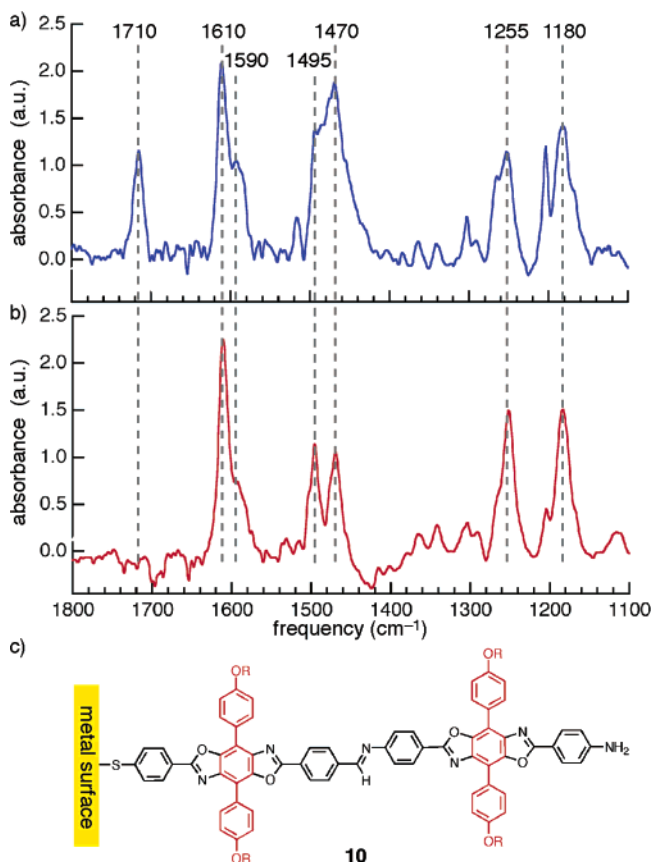


Figure 6. PEM-IRRAS of the (a) monolayer of **1c** on gold. (b) In situ reaction of **1b** with the monolayer of **1c**. (c) Schematic of the reaction product from Figure 6b.

aldehyde **1c** also forms upright monolayers on gold, placing the reactive carbonyl at the top of the film. The ellipsometry and XPS²⁰ show film thicknesses that are consistent with the length of the molecule (ca. 2.1 nm). The PEM-IRRAS shown in Figure 6a, exhibits the $\nu\text{C}=\text{O}$ stretch from the aldehyde at 1710 cm^{-1} , the $\nu\text{O}-\text{C}=\text{N}$ stretch from the oxazole at 1610 cm^{-1} , the $\nu\text{C}=\text{C}$ aromatic

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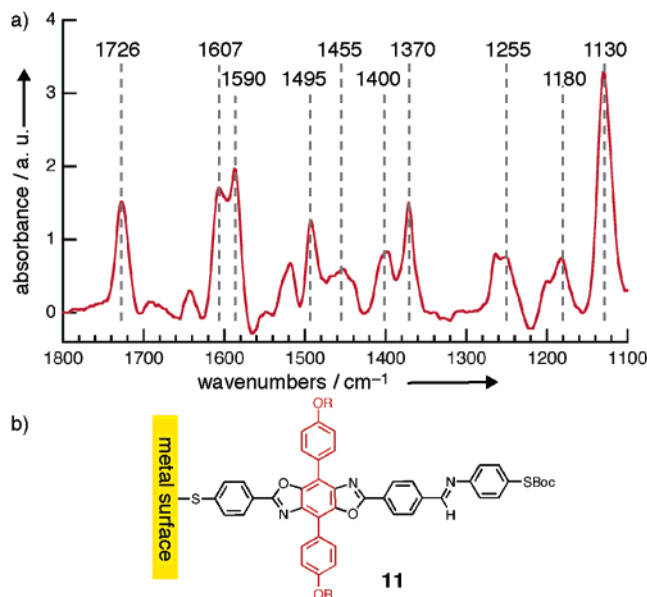


Figure 7. (a) PEM-IRRAS of the monolayer **11** formed from an in situ reaction of the monolayer of **1c** and 4-SBoc-aniline. (b) Schematic of SBoc-terminated monolayer formed in situ.

stretch at 1495 cm^{-1} , and the δCH_2 bending stretch at 1470 cm^{-1} .³

In Situ Imine Formation in Monolayers. The aldehyde-terminated monolayers of **1c** were warmed with solutions of the same type used in the solution studies.²¹ The most striking result is from the reaction of the diaminobisoxazole **1b** with the monolayer of **1c**. A schematic of the reaction product is shown in Figure 6c. The thickness of **10** measured with ellipsometry is in good agreement (4.2 nm) with the value predicted from models of ca. 4.1 nm.²² The PEM-IRRAS of dimer **10**, formed in situ, is displayed in Figure 6b. It lacks the aldehyde carbonyl but retains the other features diagnostic of the bisoxazole monolayers. The imine stretch cannot be distinguished from the oxazole stretch. However, the peak shape and the relative intensity for the transitions at 1590 cm^{-1} change considerably when converting the aldehyde to the imine.

A number of different functionalities can be placed at the termini of these molecules by changing the nature of the amines that reacted with the aldehyde monolayers. Reactions of 2-aminopyridine, 1,4-phenylenediamine, and 4-SBoc-aniline with the monolayer of **1c** were followed by infrared spectroscopy. There is loss of the carbonyl stretch at 1710 cm^{-1} in the IR spectrum, while the aromatic and oxazole stretches remain. The PEM-IRRAS spectrum of **11** in Figure 7a shows the characteristic peaks of the oxazole core seen in the PEM-IRRAS of dimer **9** and also two intense stretches that are characteristic of a Boc group at 1726 and 1130 cm^{-1} . In all of these imine-forming reactions on surfaces, the yield is high because none of the starting aldehyde could be detected.

Conclusion

Detailed above is a set of reactions that produce diverse families of conjugated nanostructures on metal surfaces. These reactions will find utility in molecular electronics

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because they are so facile, high yielding, and chemoselective in monolayer films. Given the large number of anilines that are available, this method can easily yield combinatorial libraries of programmed endgroups for electrical testing. A significant problem for simple aromatic molecules in general, and dithiols in particular is that their orientation in films is often parallel to the surface.²³ The cruciform π -system used in this study enforces an upright conformation of the molecules in the monolayers. Moreover, this strategy obviates the use of dithiols for molecular electronics that can complicate measurements through disulfide formation. Reactions of this type provide an untested route for the high-throughput formation and evaluation of a number of different endgroups either with SAM devices^{24,25} or scanning probe measurements.^{25,26} Moreover, this methodology holds promise for creating molecular-scale devices²⁷ by bridging closely spaced monolayers.

Experimental Section

Synthesis. The synthetic schemes used to synthesize **1–9** can be found in the Supporting Information along with the details of their syntheses and characterization of synthetic intermediates.

UV–Vis Spectroscopy. Spectra were recorded on an Agilent 8453 spectrometer. The quartz cells were cleaned with nitric acid, washed thoroughly with water and ethanol, and dried in an oven prior to use. Solutions of compounds **8**, **3**, and **1d** were $4.84\text{ }\mu\text{M}$ in CH_2Cl_2 .

Monolayer Preparation. Silicon wafers (Prime grade) were purchased from Silicon Sense. Gold was purchased from Aldrich. Chromium was purchased from R. D. Mathis Co. Metals were deposited on piranha-cleaned silicon pieces with an Edwards Auto 306 thermal evaporator. The gold films were prepared by depositing 10 nm of Cr followed by 100 nm of Au onto $1 \times 3\text{ cm}^2$ cleaned silicon substrates. After deposition, the samples were immediately submerged into a 0.1 mM solution of thiol **1c** or bis-isonitrile **1e** in THF. All solutions were prepared with inhibitor-free, anhydrous THF. For monolayer formation, the gold films were allowed to sit for 48 h in the solutions at room temperature. Monolayers of aldehyde **1c** were annealed by heating at $55\text{ }^\circ\text{C}$ in fresh THF for 1 h. The samples were rinsed with CH_2Cl_2 , ethanol, and dried with purified nitrogen. For imine **9** preparation, the monolayer of aldehyde **1c** was immediately immersed in a 0.6 mM solution of diamine **1b** in toluene and heated at $60\text{ }^\circ\text{C}$ for 48 h. The sample was then rinsed with CH_2Cl_2 , ethanol, and dried with purified nitrogen. For simple imines, such as –SBoc **10**, monolayers of **1c** were heated in 0.1 M solutions of the respective aniline in toluene at $60\text{ }^\circ\text{C}$ for 48 h and then

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rinsed as above. Heating above 60 °C resulted in degradation of the monolayer.

XPS. XPS measurements were recorded on a Perkin-Elmer PHI 5500 spectrometer equipped with a monochromatic Al K α X-ray source. The pass energy was set to 23.50 eV for high-resolution scans with a takeoff angle of 35°. The typical operating pressure was below 3×10^{-9} Torr. All binding energies were referenced to the Au_{4f7/2} position at 84.0 eV. All intensities were determined after subtraction of a linear background and calculated by numerical integration with Perkin-Elmer software.

PEM-IRRAS. PEM-IRRAS spectra were obtained on a Digilab FTS 7000 (Rudolph, MA) spectrometer equipped with a step scan interferometer, a liquid nitrogen-cooled narrow-band MCT detector, a global source, and a UDR-8 filter. The IR irradiation was phase modulated at a frequency of 400 Hz at an amplitude of 1.0 or 2.0 λ HeNe while stepping at 1 Hz. A gold grid polarizer was used to obtain p-polarized light, which was then modulated by a Hinds ZnSe PEM operating at 37 kHz and an amplitude of 0.5 λ before reflecting off the sample at an incident angle of ca. 80° from the surface normal. The spectra were recorded at 4 cm⁻¹ resolution and were the result of 4–8 scans.

Ellipsometry. A Rudolph Research AutoEL NIR III ellipsometer operating at an angle of incidence of 70° and a wavelength of 632.8 nm was used for ellipsometric measurements. The n_L of the organic layer was approximated at 1.45. The gold n and k were measured from a bare substrate for each evaporation run.

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Supporting Information Available: Details on the synthesis and characterization of **1–9** and the crystallographic information file (cif) for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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