

Chemically Transformed Monolayers on Acene Thin Films for Improved Metal/Organic Interfaces

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Anhydride terminated acene thin films were chemically transformed to thiol or carboxylic acid functionalities, groups heretofore incompatible with monolayer reactions. The molecular surface imparts large rate acceleration when imides are formed, while disfavored disulfides can be formed from the thiols. The modified surface imparts improved adhesion to top metal contacts in flexible/bendable applications.

The performance of organic semiconductors in optoelectronic and sensing applications improves dramatically when the top surface of the semiconductor is controllable.^{1,2} In sensing applications, the ability to covalently link receptors or add coupling reagents to the surface result in more reliable analyte binding and improved signal.³ In organic thin film transistors (OTFTs) and organic light emitting diodes (OLEDs), controlling the interface of the semiconductor with a metal top contact eliminates injection barriers,⁴ reduces metalation damage,⁵ and improves adhesion.⁶ For *inorganic materials*, interfaces are often improved via self-assembled monolayers (SAMs),⁷ but SAMs on *organic semiconductors* (Fig. 1b,c) are generally incompatible with the functional groups necessary for device improvements. For example, SAMs on acenes require molecules with an activated double bond, higher vapor pressures, and faster reaction rates,⁸ thereby excluding many desirable termini such as thiols and carboxylic acids. As such, scientists must resort to weakly physisorbed adlayers to address issues such as adhesion,⁶ rather than a more robust method. Small molecules and polymers have been examined.^{6,9}

Since the chemical repertoire which can be directly generated on an organic semiconductor surface is limited, a workaround is needed. The solution is to treat the SAM

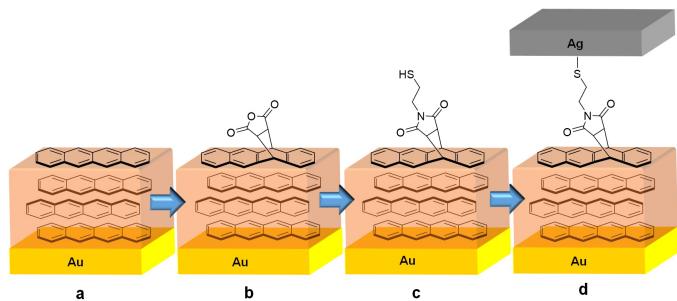


Fig. 1 Functionalization of a tetracene film (a) via previously established Diels-Alder chemistry to form the precursor anhydride films (b). Transformation of SAMs provides further derivatization, in this case generating an imide (c), which allows for coordination of a thermally deposited metal film (d).

functional groups as a launching point rather than a final state, whereby the SAM is reacted to a more useful terminus (Fig. 1c). This approach is often referred to as a chemically transformed monolayer,¹⁰ and it has proved useful for generating highly varied SAMs on a range of materials such as inorganic,¹⁰ polymeric,¹¹ and graphitic surfaces.¹² This work demonstrates similar transformations to organic semiconductors by reacting an anhydride terminated SAM to generate a range of groups, including previously inaccessible thiols and carboxylic acids. Importantly, we demonstrate that SAMs can be reacted despite many of the challenges associated with molecular surfaces, including recessed reaction sites, and the propensity to amplify side reactions in the solid phase.^{13–15} Furthermore, transformation of SAMs on organic semiconductors have the potential to impact numerous applications such as chemical sensing,¹⁶ biofunctionalization,¹⁷ multifunctional polymer coatings,¹⁸ and metallization,⁴ and as such we demonstrate, as proof of concept, its ability to improve the adhesion of metal top contacts to the organic semiconductor (Fig. 1d).

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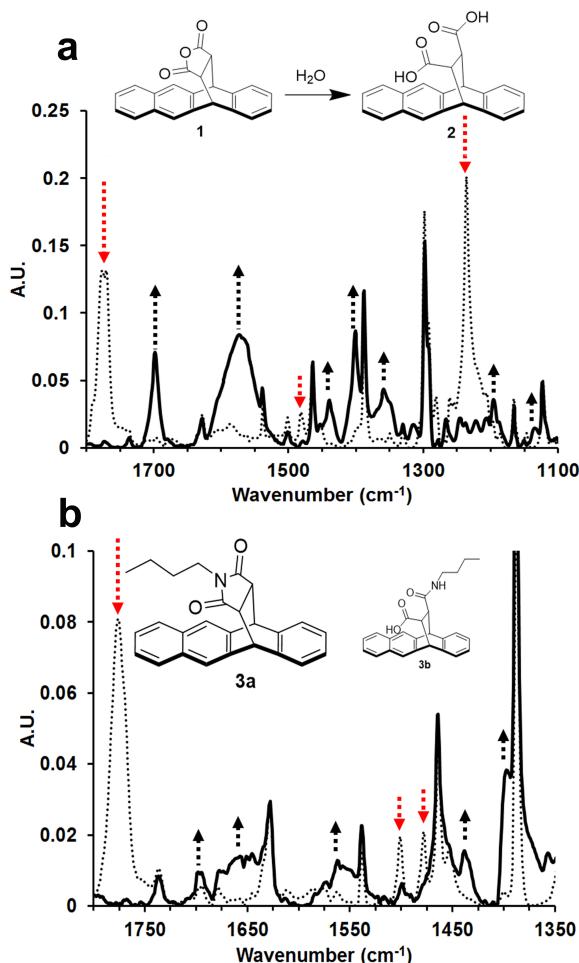


Fig. 2 PM-IRRAS spectra of the reaction of the anhydride functionalized tetracene thin-films (dotted line) with water (a, solid line) and *n*-butylamine (b, solid line) on the surface. Red arrows indicate the consumption of diagnostic stretches of **1** while black arrows indicate the production of (a) **2** or (b) **3a** (major product) and **3b** (minor).

Our chemical transformations utilize an anhydride terminated SAM on tetracene (Fig. 1b) as the starting point.¹⁹ Monolayer transformations were induced by exposing the anhydride to vapors of water (70 °C), *n*-butylamine (40 °C), or cysteamine (40 °C). The anhydride moiety is an ideal starting point for these purposes as it has an exceptional range of reactions, allowing for a wide variety of functional groups to be generated at the surface.²⁰ Our initial reaction was the hydrolysis of the anhydride species to the diacid **2** (Fig. 2a), a simple reaction chosen for its lack of side products. The reaction was determined successful by comparing surface IR spectra to IR of solution-generated reference compounds (Fig. S1), allowing for identification of newly formed stretches. Surface data was acquired via polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), an effective tool for thin-film characterization due to its surface selectivity and high sensitivity.¹⁹ Matching IR stretches for the diacid **2** appeared at 1698, 1561, 1441, 1359, 1195, and 1135 cm⁻¹ (Fig. 2a), and the entire anhydride stretch (1770 cm⁻¹) is consumed in 48 h. In terms of reaction effectiveness, no other species are

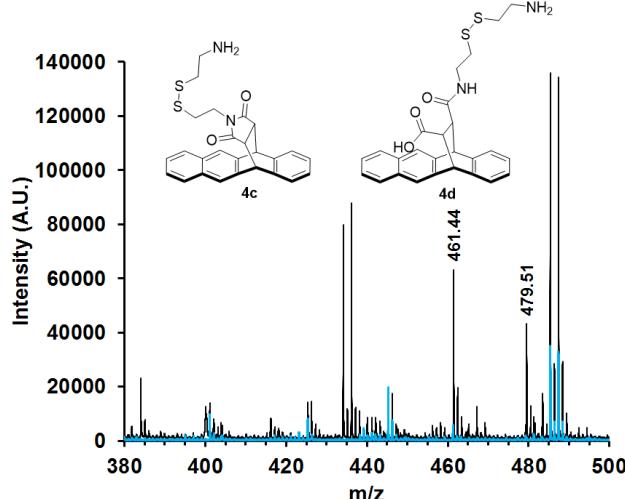


Fig. 3 MALDI-TOF spectra of a cysteamine reacted thin film (black) compared to CHCA matrix only (blue). [M+H]⁺ ions of **4c** and **4d** are highlighted.

detectable; outside of hydrogen bonding within **2** (Fig. S2), transformations are efficient.

Additional examples are provided in the form of reactions with primary amines. Two different molecules were utilized, specifically *n*-butylamine and cysteamine; the first served to confirm likely adduct identity, while the second installed the desired thiol via an alkyl linker. Both reactions were successful in their own right (Fig. 2b, S3) and in combination, the two are extremely useful in demonstrating the difference that arise when reactions occur at molecular surfaces.

Mechanistically, for both the reactions, the acid amide (e.g. **3b**) is formed before the imide (**3a**). Generally this species is isolatable as an intermediate and is stable for wide temperature ranges; uncatalyzed cyclization to the imide requires temperatures exceeding 180 °C.^{21,22} However, with a molecular solid, the rules governing reactivity (molecular orientation, vibration, crystal structure, reaction cavity size) are rather orthogonal to those for solution phase synthesis.¹³⁻¹⁵ Accordingly, cyclization to form the imide is extremely rapid for the transformed monolayer. For the reaction with *n*-butylamine, even when the reaction temperature is reduced to 30 °C, the anhydride is fully converted almost exclusively to the imide in less than 30 min. Attempts to isolate the acid amide on the surface were unsuccessful. Similarly, the major product for the cysteamine reaction is the imide **4a** (Fig. S3-6) and conversion is complete in less than an hour. Such acceleration is not seen either in the conversion of solid acid amides²³ nor co-crystals of amines and anhydrides.²⁴ We believe the most likely explanation for such acceleration is unusually effective expulsion of water at the interface.²⁵

In molecular solids, it is also possible for molecular packing to facilitate side reactions which cannot occur in solution.²⁶ Accordingly we examined the cysteamine reaction for unexpected products with matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. Indeed, under certain reaction conditions, a significant amount of disulfide can be formed (Fig. 3). The reaction to form **4c** and **4d** appears to initiate from the

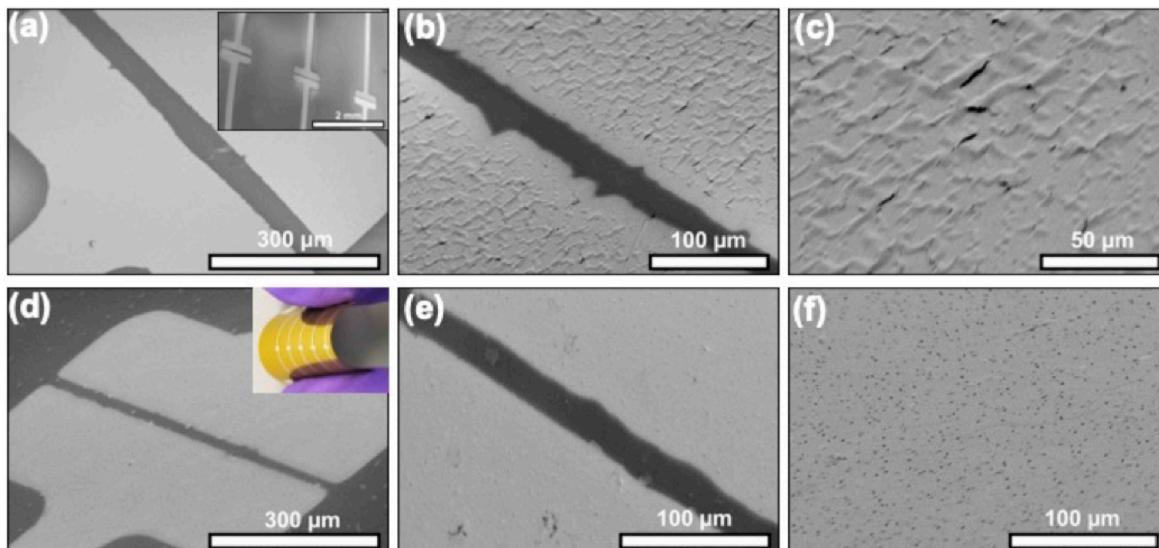


Fig. 4 Analysis of silver electrodes thermally deposited onto tetracene samples (pristine on top, reacted on the bottom), which have been repeatedly bent. (a) SEM image of a single silver electrode (80 nm) deposited on unreacted tetracene (100 nm) before bending; Inset is low magnification SEM of the electrodes array. (b) SEM image of this same sample after repeated bending (50 times). (c) Higher magnification image of the same electrode. (d) SEM image of a single silver electrode (80 nm) deposited on tetracene (150 nm) which had been reacted with both maleic anhydride and then cysteamine. Inset is a photo of the bending process. (e) SEM image of the electrode on the same cysteamine reacted sample after bending 100 times. (f) Higher magnification SEM image of the same electrode on the cysteamine reacted surface after bending 100 times. All the SEM were taken at 1.75 kV acceleration voltage with the samples tilted 70°.

reaction of the free thiol (**4a**, ESI), which is then converted on the surface to disulfide. We theorize this as the rate at which cystamine (the disulfide) reacts with the surface differs from that of the cysteamine reaction.

At this point, the linker provided by the cysteamine bears a thiol functional group capable of improving the interfaces of organic semiconductors with other materials.⁷ As a proof of principle demonstration, we tested the ability of the chemically transformed monolayers to improve the adhesion to a top metal contact. Specifically, simple bending tests²⁷ were performed on PET/gold (100 nm)/tetracene (150 nm)/silver (80 nm) samples where the reacted sample had undergone secondary reaction with cysteamine, while the unreacted sample received no treatment. These films were bent to a radius of 2.5 mm up to 100 times. As can be seen in Fig 4, the untreated samples show significant delamination of the silver after the bending cycles when imaged by scanning electron microscope (SEM, Fig. 4a-c). Rippled areas where the silver is free from the tetracene surface appear in as few as 10 bending cycles, while the tearing and flaking shown in Fig 4c become prominent in 50 cycles. In contrast, samples that have been reacted display no obvious damage after 100 bending cycles. The only features visible in the SEM images is a small amount of texturing which stems for the slight change in topography which occurs during reaction. These features are present before bending and have been detailed extensively elsewhere.^{28,29} Additional magnifications before bending, and additional areas/samples after bending can be found in the SI (Fig S7-10). These results demonstrate a direct way to address adhesion and a methodology capable of addressing other interfacial flaws within organic devices.

In summary, anhydride terminated tetracene thin films are an effective pretreatment for further transformations of the

SAMs. We have demonstrated their conversion to groups including carboxylic acids and thiols, groups that are normally incompatible with established SAM chemistry. Moreover, the uniqueness of reactions at molecular surface was displayed via rapid acceleration of dehydration during imide formation and the occasional observation of disfavored side products during cysteamine reactions. Bending tests performed on contacts deposited on top of the reacted films demonstrate improved adhesion in surfaces bearing metal coordination moieties compared to unreacted films. Overall, this chemistry has shown the ability to control the surface properties of organic semiconductors and is a methodology easily extended to other optoelectronic applications.

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Conflicts of interest

The authors declare no conflict of interest.

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