

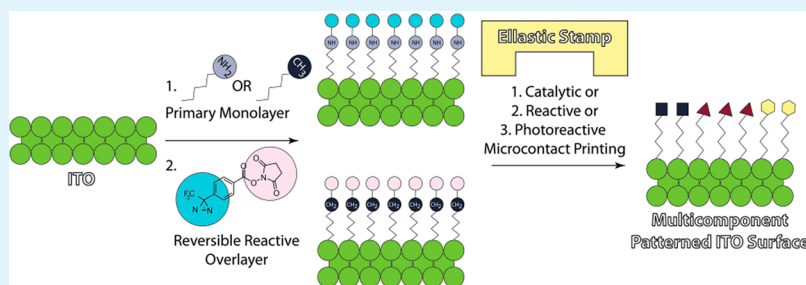
# Multicomponent Patterning of Indium Tin Oxide

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## S Supporting Information



**ABSTRACT:** We report a versatile functionalization and patterning technique that permits multicomponent pattern-specific modification of indium tin oxide (ITO) with organic species. The method relies on a bilayered molecular system that simultaneously protects ITO from degradation and provides uniform chemical functionality suitable for further elaboration. Pattern-specific modification is achieved via specific reaction between functionality on an elastomeric stamp and functionality of cognate reactivity at the surface of a bilayered molecular substrate. We demonstrate that a single molecular system in a combination with different printing approaches can be used to immobilize multiple organic functionalities with exquisite spatial control on a single ITO surface. Our study provides the first general approach that permits patterning and functionalization of ITO with different molecules using a single set of printing conditions and materials.

**KEYWORDS:** indium tin oxide, functional self-assembled monolayers, soft lithography, catalytic microcontact printing, reactive microcontact printing

Low electrical resistance, outstanding conductive properties, and optical transparency make indium tin oxide (ITO) an important substrate in materials science, chemistry, physics, and chemical engineering. ITO has found use as an electrode or a substrate in photovoltaic, optical, and electroluminescent devices;<sup>1–3</sup> sensors;<sup>4,5</sup> and DNA chips.<sup>6</sup> ITO is an especially important substrate for organic semiconducting materials (e.g., organic-light emitting diodes (OLEDs)) and organic photovoltaics (OPV), because of a tunable work function and high conductivity.<sup>7–10</sup> The current generation of organic semiconductors relies primarily on direct coating of ITO with conducting polymers and/or small molecules. Several studies have indicated that well-ordered and stable self-assembled monolayers (SAMs) both improve charge transfer efficiency between the polymer and ITO and enhance the structuring and nanomorphology of the applied polymer.<sup>11–13</sup> Such SAMs can be formed on ITO using organosilanes, carboxylic acids, phosphonic acids and alkanethiols.<sup>14</sup> Each of these functionalities form relatively stable ordered films on ITO, with long-chain alkylsilanes forming the most stable and robust monolayers.<sup>15,16</sup>

Simple alkyl monolayers, however, are of only limited utility. The modification of work functions requires the introduction of a wide range of functionalities of varying polarity and polarizability, while the robust immobilization of biomolecules requires chemical “handles” that can be selectively accessed

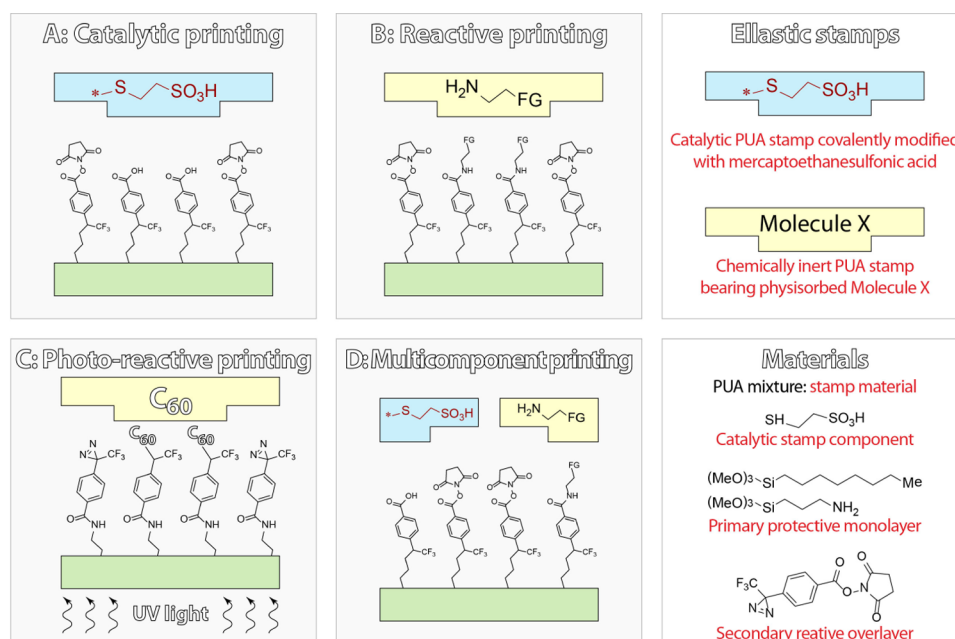
under mild conditions.<sup>17,18</sup> Surprisingly, few immobilization strategies exist for the modification of ITO surfaces with diverse functionality, and no simple method exists for patterning ITO with functional monolayers. Techniques such as microcontact printing ( $\mu$ CP) and dip pen lithography, which rely on diffusive ink transfer from a polymeric stamp or AFM tip, have not been routinely successful for patterning ITO. Such diffusion-based methods require long reaction times and high reaction temperatures due to the high kinetic barrier to Si–O–In/Sn bond formation.<sup>19</sup> An alternative to direct patterned SAM formation is afforded by the initial formation of a reactive SAM followed by catalytic or reactive  $\mu$ CP to introduce new functionality through chemical reaction in regions of substrate-stamp conformal contact.<sup>20</sup>

We have previously reported a bilayered patterning strategy that permits patterning of inorganic materials with durable, robust monolayers using catalytic microcontact printing. In this approach, the formation of a stable primary monolayer on an inorganic support provides a surface that can be modified with a functionalized elastomeric stamp in a second step to decorate the surface with a variety of organic and biological molecules.

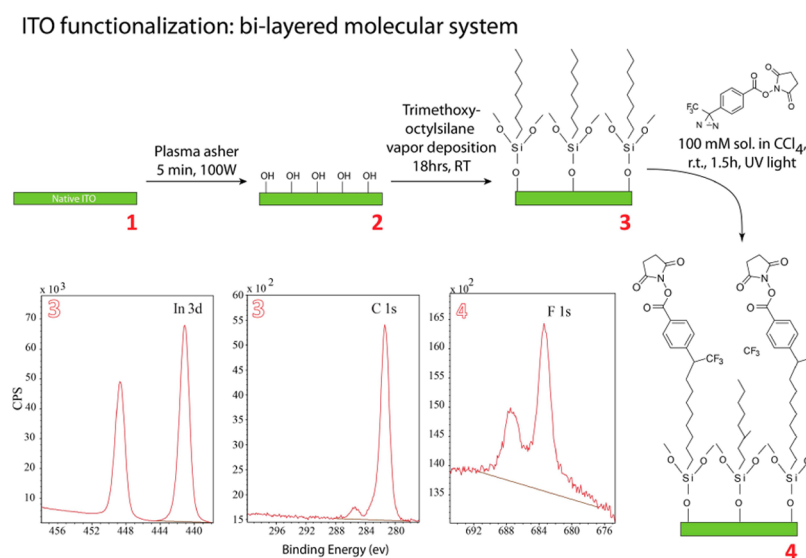
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**Figure 1.** Schematic description of the molecular systems and printing techniques used to functionalize and pattern ITO. (a) Catalytic inkless  $\mu$ CP with a sulfonic acid stamp produces patterns of activated and free carboxylic acid. (b) Reactive transfer  $\mu$ CP with an amine-modified stamp produces patterns with two distinct functionalities. (c) Photoreactive transfer  $\mu$ CP allows site-specific immobilization of C60. (d) Combining catalytic and reactive  $\mu$ CP techniques facilitates the formation of three distinct functionalities on a single substrate.



**Figure 2.** Functionalization scheme for the preparation of a bilayered molecular system on ITO and corresponding XPS spectra.

This approach is especially suitable for ITO, providing a simple and convenient method to passivate, functionalize, and pattern ITO with diverse molecules, overlaying a variety of organic and biological functional groups on a robust alkyl substratum.

Here we report a patterning strategy for ITO substrates through both catalytic and reactive  $\mu$ CP techniques, passivated with simple alkyl SAMs, using a variety of organic molecules (Figure 1). The primary advantages of the approach are its ability to (1) form stable and functional monolayers on ITO; (2) pattern ITO with virtually any functionality with precise spatial control at the microscale; (3) accurately form multi-component patterns with organic and biological species on a single ITO substrate. We demonstrate the versatility of the

approach through reactive and catalytic  $\mu$ CP, as well as a novel photocatalytic  $\mu$ CP.

### ITO FUNCTIONALIZATION: FORMATION OF A BILAYERED MOLECULAR SYSTEM

To pattern orthogonally reactive SAMs on ITO, we required a functional monolayer that is both cognate to the reactive features on an elastomeric stamp and sufficiently stable to survive the patterning step. SAMs are typically formed on ITO using organosilanes, carboxylic acids, phosphonic acids or thiols. Neither carboxylic acids nor thiols bind strongly to ITO, and monolayers of these species are labile.<sup>21</sup> Silanes, on the other hand, bind strongly to ITO, forming homogeneous, oriented monolayers.<sup>16</sup> Alkylsilane monolayers have been successfully

Catalytic microcontact printing: sulfonic acid-catalyzed hydrolysis of *N*-hydroxysuccinimide ester in the place of conformal contact

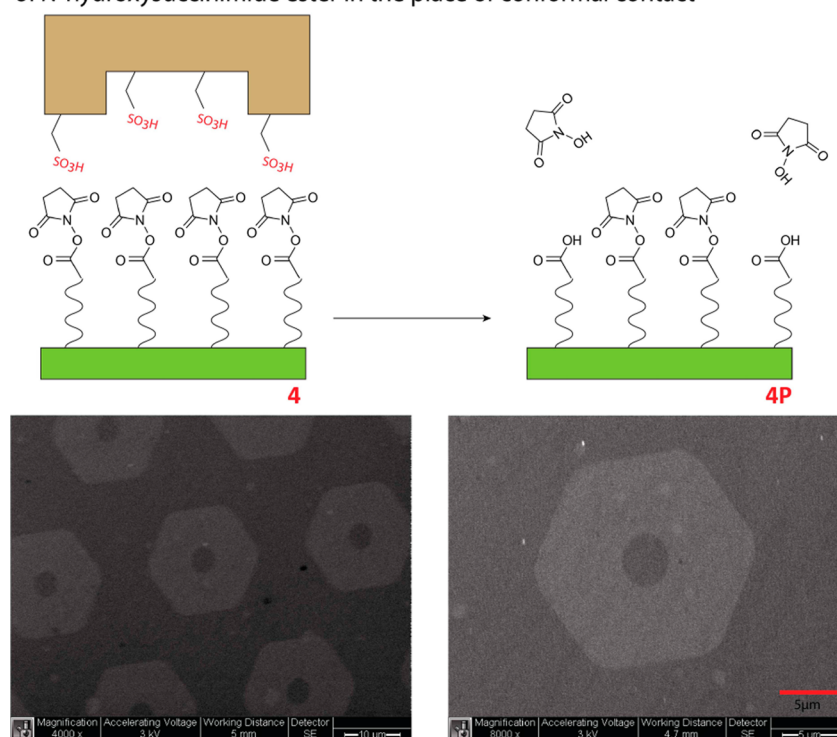


Figure 3. SEM images of patterned SAMs on ITO using a sulfonic acid modified PUA stamp.

Conformal contact- and solution-based surface reactions with azidoazide

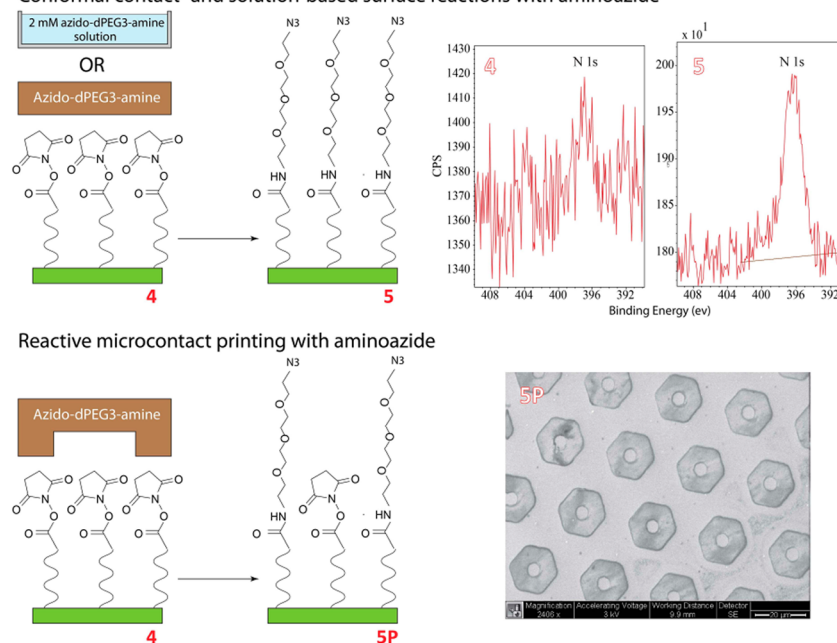
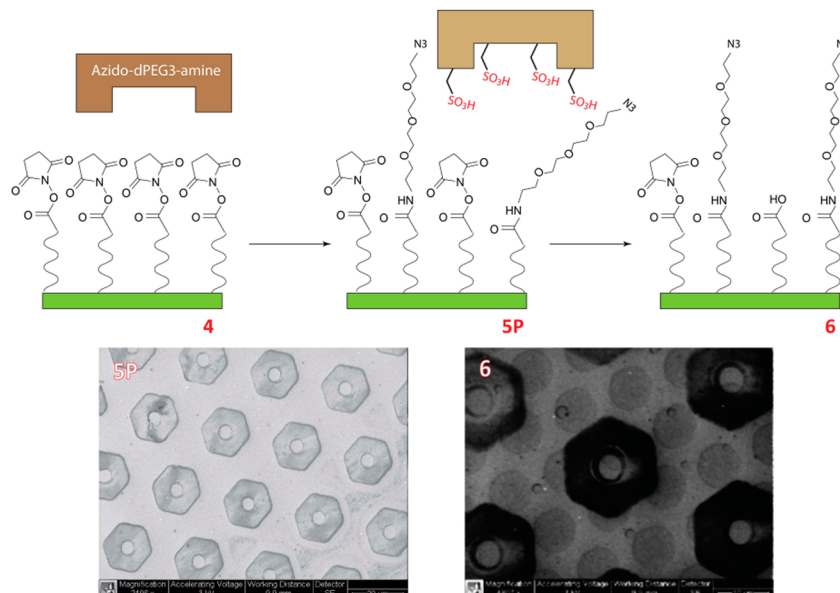


Figure 4. Modification of NHS-terminated ITO with an azido-dPEG<sub>3</sub>-amine in solution and by reactive  $\mu$ CP with corresponding XPS spectra and SEM images.

used as low-energy self-developing e-beam resists.<sup>15</sup> We exploited the stability and order imparted by silanes to create a primary monolayer on ITO.<sup>22</sup> The subsequent incorporation of a reactive overlayer provides a functional moiety cognate to the reactivity borne by the elastomeric stamp. The approach allows for facile, site-specific immobilization of multiple organic molecules.

The formation of a bilayered molecular system on ITO begins from a native ITO surface (1) (Figure 2). The surface was oxidized in a plasma asher, generating surface hydroxyl groups (2).<sup>23</sup> Exposure of the hydroxyl-terminated surface to trimethoxyoctylsilane for 18 h under high vacuum produced the corresponding alkyl-terminated surface (2). The C1s/In3d intensity ratio in the XPS spectrum is greater for surface 3 than

## Reactive microcontact printing with aminoazide followed by catalytic microcontact printing



**Figure 5.** Preparation protocol for multicomponent ITO with reactive and catalytic  $\mu$ CP techniques.

2, consistent with the deposition of carbon at the surface during SAM formation. Goniometry analysis using water ( $\theta_{\text{adv}} = 95^\circ$ ,  $\theta_{\text{rec}} = 90^\circ$ ) suggests a homogeneous, well packed aliphatic SAM.<sup>14</sup> Following the formation of the primary silane monolayer, surface 3 was reacted with an NHS-diazirine-derived carbene, producing a reactive surface displaying N-hydroxysuccinimide (NHS) activated acids at the surface (4). XPS analysis revealed an F 1s signal, indicative of successful UV-catalyzed insertion of the diazirine-derived carbene to the methyl terminated SAM. Goniometry analysis, again using water ( $\theta_{\text{adv}} = 86^\circ$ ,  $\theta_{\text{rec}} = 72^\circ$ ), indicated an increase in the hydrophilicity of the surface due the presence of the NHS moiety. A contact angle hysteresis of  $14^\circ$  is presumably indicative of a loosely packed overlayer.

Surface 4 exposes reactive head groups patternable by both catalytic and reactive microcontact printing. In contrast to traditional  $\mu$ CP, both catalytic and reactive printings rely on modification of a preformed, functional monolayer (Figure 1), facilitating patterning of substrates normally incompatible with fast SAM formation.

### ■ CATALYTIC $\mu$ CP ON ITO

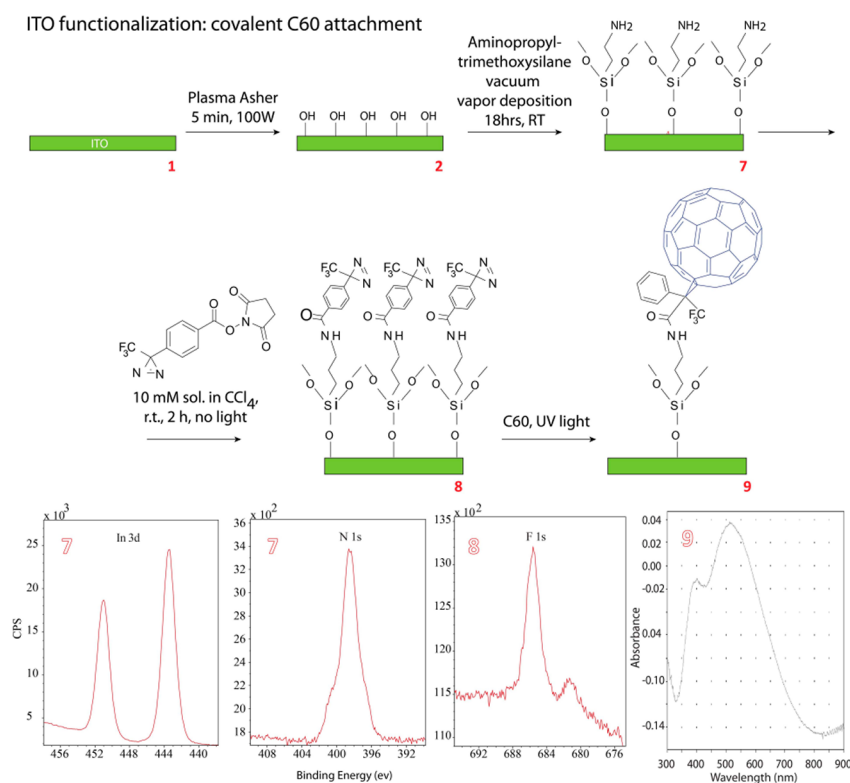
Our patterning approach utilizes an elastomeric stamp bearing covalently bound sulfonic acids to achieve catalytic pattern-specific hydrolysis of NHS-functionalized SAMs (Figure 3).<sup>22,24</sup> Patterned SAMs on ITO were formed by bringing a freshly prepared NHS-terminated ITO surface (4) in to conformal contact with a sulfonic acid stamp bearing  $20 \mu\text{m}$  hexagons for 1 min at room temperature. Following removal of the stamp, the surface was rinsed with isopropanol, dried under argon and analyzed by scanning electron microscopy (SEM) (Figure 3). The acid-catalyzed reaction between stamp and surface 4P produced patterns containing both NHS-activated and free carboxylic acid groups; the size and shape of the replicated patterns were identical to those of the stamp, demonstrating high fidelity pattern transfer.

### ■ REACTIVE $\mu$ CP ON ITO

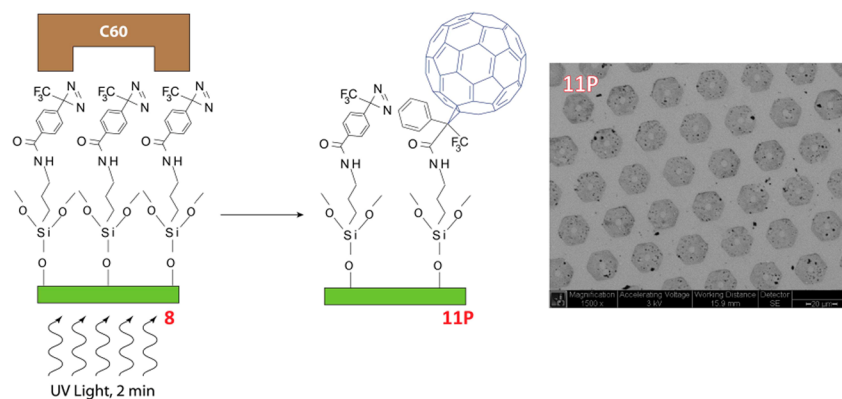
In contrast to catalytic printing, reactive microcontact printing relies on the diffusion of a reactive species adsorbed on a stamp to a surface bearing cognate reactive functionality (Figure 1). To demonstrate the suitability of NHS-terminated surfaces for reactive  $\mu$ CP, we employed azido-dPEG<sub>3</sub>-amine as a reactive ink. To verify the amine molecule was reactive toward surface 4, we initially exposed the NHS-terminated SAM to a 2 mM solution of azido-dPEG<sub>3</sub>-amine in anhydrous dichloromethane (DCM) for 1.5 h at room temperature (Figure 4a). XPS analysis revealed a significant increase in the N1s/In3d intensity ratio from surface 4 to 5, consistent with an increase in nitrogen at the surface as the result of reaction.

Patterned azido- and NHS-terminated SAMs on ITO were formed by bringing a freshly prepared NHS-terminated ITO surface (4) in conformal contact with an azide-inked PUA stamp bearing  $20 \mu\text{m}$  hexagons for 1 min at room temperature. Upon removal of the reactive stamp, surface 5P was immediately rinse with isopropanol, dried under argon and analyzed by SEM (Figure 4b). The reaction between the azide-inked stamp and surface 4 produced patterns containing both NHS-activated and azido functional groups. As was the case for catalytic patterning, the size and shape of the surface features were identical to those of the stamp, again demonstrating high fidelity pattern transfer.

To demonstrate the power and versatility of the approach, we achieved pattern-specific functionalization of ITO using three different organic moieties. NHS-terminated substrate 4 was successively treated with a reactive stamp bearing aminoazide ink, followed by a catalytic stamp bearing sulfonic acid moieties. The initial reactive printing step produced a pattern of azido-terminated molecules in the form of hexagonal rings (Figure 4), whereas the following catalytic step hydrolyzes unreacted NHS-groups to yield carboxylic acid-terminated areas. To facilitate analysis of the final surface, the catalytic stamp contained features different than those of the reactive stamp, producing a surface with two distinct sets of features. Figure 4 demonstrates that the initial reactive printing step



**Figure 6.** Functionalization scheme for the preparation of C60 modified ITO and corresponding XPS and UV/vis spectra.



**Figure 7.** SEM image of patterned SAMs on ITO using reactive  $\mu\text{CP}$  and C60 as the photoreactive ink.

produced uniform, clearly defined hexagonal rings across the entire substrate area. The subsequent catalytic printing step produced a second set of features; namely 8  $\mu\text{M}$  hexagons (Figure 5). This second set of features was replicated only in NHS-terminated areas without intrusion into azido-terminated space, consistent with the stability of the amide bond formed during the reactive  $\mu\text{CP}$  step.

### ■ PHOTOREACTIVE $\mu\text{CP}$ ON ITO

To further demonstrate the remarkable simplicity and versatility of the approach, we created a diazirine-terminated surface that facilitates photoreactive  $\mu\text{CP}$ . The formation of the required photoreactive bilayered molecular system on ITO begins with a native ITO surface (1) (Figure 6), which was oxidized in a plasma asher to generate reactive hydroxyl groups (2). Exposure of the hydroxyl-terminated surface to amino-propyltrimethoxysilanes for 18 h under argon produced the corresponding amino-terminated surface 7. XPS analysis

revealed the presence of a N1s peak, consistent with the generation of an amino-terminated substrate. Surface 7 was reacted with an NHS-diazirine-derived carbene. In contrast to the previous bilayered system, the NHS activated acid reacted at the amino-terminated surface, producing the photoreactive carbene precursor-terminated surface 8. XPS analysis revealed a F 1s signal, indicating successful reaction between the NHS activated acid and the amino-terminated substrate.

Surface 8 contains a photoreactive moiety capable of cyclopropanation reaction with olefins. To demonstrate the photoreactivity of the monolayer, we reacted it with Buckminsterfullerene (C60), which readily undergoes carbene insertion. C60 is of considerable interest in chemistry, physics and materials science due to its unusual structure and extended  $\pi$ -electron system.<sup>25</sup> C60 is an essential component of many OPV devices and the unique electronic properties of C60 can be used to modify the electronic and optical properties of ITO.<sup>25,26</sup>

Diazirine-terminated surface **8** was exposed to a solution of C60 in benzene for 1 h in the presence of UV light. UV-vis analysis suggested successful C60 modification, and the absorption spectra presented in Figure 6 agree with previously reported spectra for a C60-bearing SAM.<sup>27</sup>

To spatially resolve C60 on ITO, we used photoreactive microcontact printing. Employing C60 as the photoreactive ink, conformal contact of diazirine-modified surface **8** with a stamp bearing photoreactive molecules in the presence of UV light allows for a direct carbene insertion to the surface (Figure 6). The elastomeric stamp was "inked" in a 7 mM solution of C60 in benzene for 1 min, dried under argon and applied to surface **8**. The stamp was held in conformal contact with the surface for 2 min while UV light ( $\lambda = 254$  nm) was irradiated through the transparent glass/ITO surface. The surface was immediately rinsed with filtered isopropanol, dried with filtered argon, and analyzed by SEM. The UV-catalyzed reaction between stamp and surface **8** produced patterns containing C60. SEM analysis shows uniform and high fidelity pattern transfer (Figure 7). As a control, we performed the same stamping protocol in the absence of UV light. SEM analysis in this instance revealed no pattern transfer. As an additional control, we applied a patterned stamp lacking C60 to a freshly prepared carbene-terminated layer in the presence of UV light. The absence of C60 precluded pattern transfer, further demonstrating the selectivity of the C60 modified stamps in the photoreactive pattern protocol.

In conclusion, we have demonstrated a simple and reliable protocol for patterning multiple functional moieties on ITO. The technique begins with the formation of a stable, well-ordered primary monolayer. Construction of a secondary reactive overlayer using an NHS-diazirine-derived carbene provides a terminal functionality that can be further modified to incorporate a wide range of surface groups. The functional bilayered molecular system was subsequently patterned using three different printing approaches. In catalytic printing, a sulfonic acid bound PUA stamp was used to transfer chemically distinct patterns of NHS activated and free carboxylic acid groups. Following catalytic pattern transfer, reactive  $\mu$ CP was used to transfer patterns bearing azido functional groups. The resulting surface contained three chemically distinct groups (NHS activated acid, carboxylic acid, azide) site-specifically patterned on ITO. Finally, we demonstrated photoreactive microcontact printing of C60 in the presence of UV light. The ability to easily pattern multiple functional groups on ITO using a tunable bilayered molecular system enables myriad applications, including micro- and optoelectronics and sensing.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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