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## COMMUNICATION

### Site-selective metal-coordination-based patterning of silane monolayers†‡

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Herein, we report a method to pattern a derivatized nifedipine silane monolayer that aromatizes under UV irradiation. Using a functionalized SCS–Pd( $\pi$ ) pincer complex, we demonstrate that a strong metal-coordination complex between the aromatized nifedipine derivative and the pincer complex is formed. This methodology integrates SAM photolithography (top-down) and molecular recognition directed self-assembly (bottom-up) strategies to create simple and rapid synthesizable functional patterned surfaces.

Patterning functionalities on surfaces is essential for the development of many technologies such as electronics,<sup>1</sup> chemical sensor design,<sup>2</sup> optics,<sup>3</sup> microfluidics,<sup>4</sup> biotechnology<sup>5</sup> and bioanalytics.<sup>6</sup> Many surface patterning techniques have been developed including photolithography,<sup>7</sup> as well as electron and ion beam,<sup>8</sup> scanning probe,<sup>9</sup> and soft lithography.<sup>10</sup> The primary process of these patterning techniques is to chemically or physically modify properties of designated regions of the substrate of interest. Using light to modify surface properties is a very attractive approach largely due to its simplicity and compatibility with large-scale parallel processes. In recent years, photo-patternable self-assembled monolayers (SAMs) have attracted great interests.<sup>11–18</sup> The SAM approach has the advantage that it allows for the generation of well-defined active groups on the surface during the photopatterning process providing easy access to further functionalize substrates via an additive approach. Several strategies have been reported to photochemically generate well-defined active sites on SAMs including the use of (i) photo-induced degradation;<sup>12</sup> (ii) photo-initiated polymerization;<sup>13,14</sup> (iii) photo-deprotection of "caged" functional groups<sup>15,16</sup> and (iv) photoisomerization.<sup>17,18</sup>

Covalent bonds and/or physisorption are common to immobilize functional groups on photo-activated surfaces. Covalent bonds have the advantage of strength and specificity

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but usually involve synthetic efforts that can be difficult on surfaces, in particular when it comes to high yields. Physisorption processes are straightforward but lack specificity and kinetic stability. Supramolecular interactions such as metal-ligand coordination combine the advantages of covalent chemistry and physisorption, i.e. ease of formation while retaining strength and specificity.<sup>19-21</sup> Due to their dynamic nature, supramolecular interactions have unique properties such as self-checking and self-correction<sup>22</sup> making self-assembly a very attractive route for the fabrication of patterned functional surfaces.<sup>23,24</sup> We have introduced a surface functionalization strategy that uses coordination chemistry between pyridine and palladated pincer complexes thereby (i) providing for uniform film deposition, (ii) having a high degree of control of multilaver thickness. (iii) integrating a diverse set of polymer components, and (iv) affording stable, yet responsive multilayers that can be manipulated by chemical means.<sup>25,26</sup> In this study, we demonstrate a versatile methodology based on our metal-coordination surface functionalization strategy that integrates SAM photolithography (top-down) and molecular recognition directed self-assembly (bottom-up) strategies to create simple and rapidly synthesizable functional patterned surfaces.

Our strategy is based on the photo-reactivity of nifedipine, a derivative of 1,4-dihydropyridine, which is known as a generic drug for the treatment of high blood pressure. Studies showed that, upon exposure to UV irradiation, nifedipine undergoes rapid oxidization/aromatization to afford the corresponding pyridine through an intra-molecular charge transfer pathway.<sup>27,28</sup> After aromatization, the resulting pyridyl group is a versatile and efficient metal-binding ligand,<sup>29</sup> which is able to form stable coordination complexes with a variety of metal precursors including SCS–Pd<sup>II</sup> pincer complexes.<sup>30–32</sup> The high specificity and robustness of this metal complex reaction makes it very attractive as a smart "molecular glue" in microstructure fabrication on surfaces.<sup>33</sup>

The key to our strategy is the design and synthesis of the bi-functionalized silane 1 (Scheme 1) which contains a terminal nifedipine derivative as a photoactive group at one end and a triethoxy silane group for surface anchoring at the other end of the molecule. Photosensitive silane 1 is synthesized by a microwave-assisted one-pot Hantzsch reaction, followed by catalytic hydrosilylation to install the triethoxysilane anchor group (see ESI‡ for details).

We initially investigated the binding of an aromatized nifedipine derivative to SCS–Pd<sup>II</sup> pincer complexes. For these

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<sup>&</sup>lt;sup>‡</sup> Electronic supplementary information (ESI) available: Details of the preparation of the substrates and SAM, surface characterizations, the single crystal structure for aromatized **3**, and NMR studies of the photo-transformation reactions and the metal–ligand coordination processes. See DOI: 10.1039/c0cc05318j

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**Scheme 1** Schematic illustration of direct photo-patterning and site selective deposition of the fluorescence dye (coumarin) on the surface *via* SCS–Pd<sup>II</sup> pincer self-assembly as well as the structure of the model compound **3**.

studies, we prepared the model compound **3** and exposed it (in an ethanol solution) for 2 h to UV irradiation at 356 nm. The resulting aromatized **3** was characterized by NMR spectroscopy. Furthermore, the single crystal structure of aromatized **3** has been obtained and confirms the oxidation step (ESI<sup>‡</sup>). <sup>1</sup>H NMR spectroscopic binding studies proved that aromatized **3** formed a stable 1 : 1 complex with the Pd<sup>II</sup> pincer complex **4** (see ESI<sup>‡</sup> for details).<sup>30</sup> The equilibrium constant ( $K_{eq}$ ) for the self-assembly between the aromatized nifedipine **3** and an acetonitrile coordinated Pd<sup>II</sup> pincer complex (a hexyl group derivative of **4** was employed for solubility reasons) was determined by ITC using a single-site binding model. The  $K_{eq}$  was measured to be  $3.2 \times 10^3 \pm 10\%$  M<sup>-1</sup> in CHCl<sub>3</sub> (Fig. 1).

After demonstrating that aromatized nifedipine derivatives form strong coordination bonds with palladium pincer complexes, we investigated our surface patterning and functionalization



**Fig. 1** ITC binding isotherm for the model compound **3** and a hexyl-substituted pincer complex in CHCl<sub>3</sub> at 30 °C.

strategy. Due to its wide applications in many areas, Si wafers were chosen as substrates. For silane SAM formation, it is essential to obtain clean and fully hydroxylated silicon surfaces. Several surface cleaning processes were screened using an advancing water contact angle as the criterion. It was found that silica wafers sequentially treated with a RCA (HCl:H<sub>2</sub>O<sub>2</sub>) and piranha (H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>) gave the best results (see ESI<sup>t</sup> for details). The native silicon wafer had an advancing water contact angle of 20-25°. After the cleaning/ oxidizing treatment, the angle was reduced to  $<3^{\circ}$  suggesting that very hydrophilic surfaces with high hydroxyl group coverage were obtained. The pre-treated substrates were then immersed in a solution of 1 (10% v/v) in dry toluene at room temperature for one hour, rinsed with toluene and sonicated in toluene for three minutes. The wafers were then annealed overnight at 65 °C in  $\sim 80\%$  relative humidity. The value of the advancing water contact angle of the resulting substrate increased to  $>85^{\circ}$  demonstrating the presence of a silane 1 SAM on the silicon wafer. After blanket UV exposure at 356 nm for 15 minutes, the contact angles decreased slightly to 70-75°. The formation of the silane 1 SAM and the sequential photo activated aromatization were further confirmed by Fourier-transform infrared reflection absorption spectroscopy (FT-IRRAS) (Fig. 2a). The bands at  $3331 \text{ cm}^{-1}$ and 1647 cm<sup>-1</sup> are assigned to the N-H stretch of the dihydropyridine and the C=C stretches of the non-aromatic double band, respectively.<sup>34,35</sup> After UV exposure, the N-H stretch fully disappears. Furthermore, the non-aromatic C=C stretch either disappears completely too or at least diminishes significantly (there is a chance that the signal overlaps with other signals next to it). Both of these observations strongly suggest that the 1 SAM on the surface aromatized under UV irradiation.

For the fabrication of the patterned surfaces, the **1** SAM was irradiated with collimated UV light (356 nm) through a photomask for 10 minutes. The photo-patterned substrate was then immersed in a chloroform solution (5 mM) of dye functionalized acetonitrile–Pd<sup>II</sup> pincer (**2**) for 20 minutes. After thorough washing with fresh chloroform and drying by a stream of air, the resulting substrate was characterized by fluorescence microscopy and atomic force microscopy (AFM).

Fig. 2b–d shows the images of a square pattern (for other pattern, see ESI<sup>‡</sup>). A transparency with a 20  $\times$  20  $\mu$ m square



**Fig. 2** (a) FT-IRRAS spectra of **1** SAM before (black) and after (red) UV-vis (356 nm) exposure. 1320 scans were accumulated for each spectrum at a resolution of 4 cm<sup>-1</sup>. (b) Microscopy image, (c) fluorescence microscopy image and (d) contact-model AFM height image of a  $20 \times 20 \ \mu m$  square patterned surface.

pattern was used as photomask. Fig. 2b and c show that the photomask pattern was precisely registered on the Si substrate. The dye-functionalized Pd<sup>II</sup>–pincer complexes (**2**) were able to recognize and selectively bind to the UV-exposed area. No fluorescence was observed immediately adjacent to the squares. The AFM image in Fig. 2d confirmed that the pincer complexes specifically bind to the designated area on the patterned Si surface as evidenced by the height difference. The use of high-resolution photo masks, for instance chromium-based photomasks, as well as other illumination optics should allow for higher resolution images.

In summary, a triethoxysilane bearing photoactive derivatized nifedipine was designed and synthesized. A SAM of this photo-sensitive silane was prepared on a Si surface and photo-patterned through a photomask. We found that SCS Pd<sup>II</sup>–pincer complexes are able to recognize and selectively coordinate to the pyridyl group in the UV exposed areas. Considering that the pyridyl group is a very versatile ligand: (i) in its neutral form it has a strong affinity towards a wide variety of metals and the ability to form hydrogen bonds as the H-bond acceptor, and (ii) in its protonated form, it can electrostatically interact with other charged species, our method provides easy and rapid access to patterned pyridyl functionalities on surfaces and could be a very powerful tool for technology and device development.

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