

Photolithography

Photolithographic Encoding of Metal Complexes

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Abstract: A platform technology for the creation of spatially resolved surfaces encoded with a monolayer consisting of different metal complexes was developed. The concept entails the light-triggered activation of a self-assembled monolayer (SAM) of UV-labile anchors, that is, phenacylsulfides, and the subsequent cycloaddition of selected diene-functionalized metal complexes at defined areas on the surface. The synthesis and characterization of the metal complexes for the UV-light assisted anchoring on the surface and a detailed study of a short-chain oligomer model system in solution confirm the high efficiency of the photoreaction. The hybrid materials obtained by this concept can potentially be utilized for the design of highly valuable catalytic or (opto-)electronic devices.

The spatially defined immobilization of metal complexes through printing or lithographic methods provides patterned substrates partially coated with a thin layer of the compound.^[1] For applications in heterogeneous catalysis the minimization of the layer thickness without a loss in reactivity is critical to save precious material. Processes such as microcontact printing or sputtering have been developed to make advances towards this requirement while retaining the spatial control over the immobilization step.^[2] Ideally, the applied layer features a thickness of only one molecule, which is realized with disregard to spatial control in so-called self-assembled monolayers (SAMs), that is, homogenous single layers from thiols on noble metal substrates, carboxylic acids on indium tin oxide (ITO), or silanes on silicon substrates.^[3] Sawamura and co-workers have shown

the considerable catalytic activity of homogeneously monolayered metal complexes.^[4] Though examples for the direct immobilization of any metal complexes as a monolayer are scarce,^[5] the complexes are predominantly assembled stepwise.^[6] Similarly, the growth of supramolecular metallopolymers, molecular nanowires, or surface-attached metal-organic frameworks (SURMOFs) from the surface is realized.^[7] As already noted, however, these techniques most often lack spatial control in the immobilization step. For the efficient encoding of organic compounds on solid substrates, photolithographic techniques have been established with photo labile precursors immobilized as a homogenous SAM on the substrate. Employing a shadow mask, only the molecules in the irradiated area react with the in situ-provided organic compounds to give patterned functional materials with spatial and temporal control. Commonly employed UV labile groups include photoenol derivatives, phencyclones, or tetrazoles.^[8] We utilize the transient thioaldehydes formed from phenacylsulfides, which can either be trapped by nucleophiles,^[9] or act as dienophiles in subsequent cycloadditions.^[10] To the best of our knowledge, none of these techniques has to date been employed on metal-organic compounds enabling the spatially and temporally controlled immobilization of monolayered metal complexes. Transferring the knowledge of the photolithographic encoding from organic to metal-organic and inorganic compounds, we were able, for the first time, to generate spatially defined monolayer patterns composed of different metal complexes attached onto a single surface. The approach features mild and fast ligation conditions and can be employed for a variety of metal complexes. The versatile concept paves the way to tailor highly efficient and economic catalytic or electronic materials in a spatially defined environment.

In order to establish the novel metal complex encoding process, diene functionalized metal complexes were synthesized and tested in solution based model reactions prior to the surface encoding (Scheme 1). Versatile access for the synthesis of the metal-organic complexes was realized utilizing two well-established and commonly used ligand systems, that is, phosphines and 2,2'-bipyridines. Those ligands allow the complexation and fixation of numerous metal ions, for example, Pd^{II}, Pt^{II}, Ir^I, Ru^{II}, Rh^I, or Au^I and the corresponding complexes are widely used in industrial and pharmaceutical processes due to their well-established catalytic and photophysical properties. The introduction of a diene unit to the P/N-donor systems for the subsequent Diels-Alder reaction was conducted employing 2E,4E-hexadienol in a Steglich esterification with 4-(diphenylphosphino)benzoic acid providing ligand **L1**, or by Williamson etherification with 4-(4-bromobutyl)-4'-methyl-2,2'-bipyridine

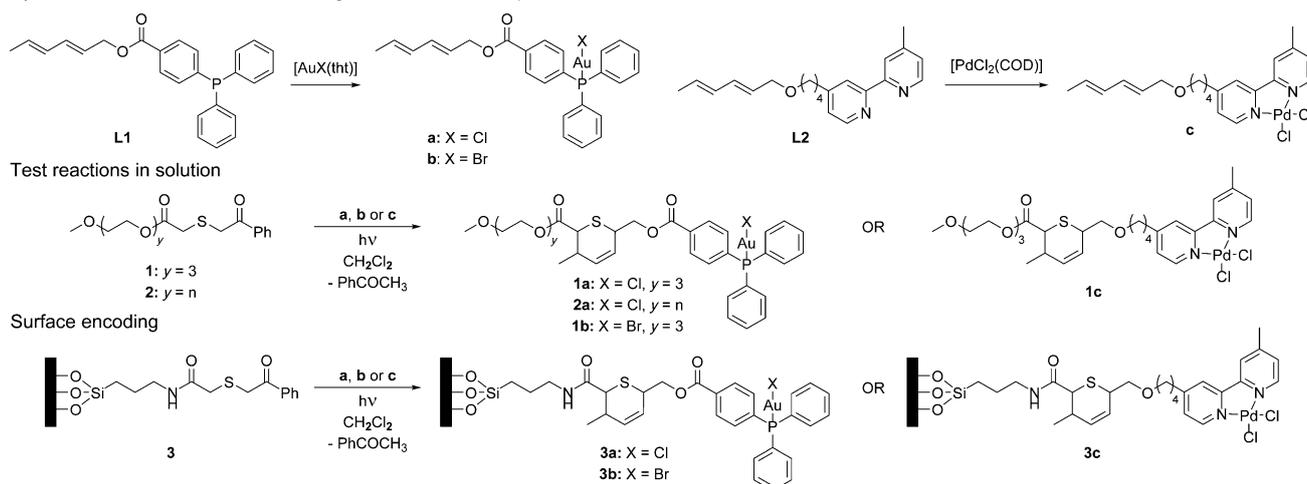
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Synthesis of the diene functionalized ligands and metal complexes



Scheme 1. Establishment of the photo-induced ligation of Au^I (**a**, **b**) and Pd^{II} (**c**) complexes including complex synthesis, test reactions, and surface encoding.

yielding ligand **L2**. The functionalized phosphine ligand **L1** was reacted with $[\text{AuCl}(\text{tht})]$ and $[\text{AuBr}(\text{tht})]$ (tht=tetrahydrothiophene) to afford the two gold complexes $[\text{L1AuCl}]$ (**a**) and $[\text{L1AuBr}]$ (**b**) in excellent yields. The bipyridine ligand **L2** was reacted with $[\text{PdCl}_2(\text{COD})]$ (COD=1,5-cyclooctadiene) to give $[\text{L2PdCl}_2]$ (**c**) in good yields. Sufficient photo stability of the gold complexes was verified by recording $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **a** and **b** before and after exposing the samples to UV light ($\lambda_{\text{max}}=355$ nm) for 4 h (Figure S8 in the Supporting Information). Next, we attached the metal complexes **a**, **b**, and **c** in a photo-induced Diels–Alder reaction to phenacylsulfide-derivatized triethylene glycol (TEG, **1**). The photoreactions were carried out in methylene chloride employing a 36 W compact fluorescent lamp with an emission maximum at $\lambda_{\text{max}}=355$ nm in a custom built photoreactor (Figure S1 in the Supporting Information). The corresponding metal complex-functionalized oligomers **1a**, **1b**, and **1c** were analyzed without further purification using electron spray ionization MS (ESI-MS) showing quantitative conversion (Figure 1).

The observed changes in the m/z ratios, as well as the characteristic isotopic patterns of the products, are in excellent agreement with the theoretically expected values. In the spectra of **1a** and **1b** a small amount of the oxidized cycloadduct is visible, however, because the addition of the metal complex was still successful, the side reaction will have no effects on the efficiency of the encoding process.

The diene-functionalized metal complex **a** was also reacted with phenacyl sulfide derivatized poly(ethylene glycol) monomethyl ether (PEG, **2**) to give **2a**. Due to the dispersity of the polymer, the ESI-MS spectra of **2** and **2a** (Figure S5 in the Supporting Information) exhibit a distribution that is shifted completely to higher masses upon the ligation reaction. According to these results, the applied method is not only suitable for surface encoding but also for the efficient metal complex functionalization of polymers featuring a UV-labile phenacylsulfide endgroup. As an outlook, the incorporation of a polymeric spacer between the surface and the metal complex could increase the complex accessibility, for example, in catalytic processes.

Next, we applied our method for the spatially resolved surface encoding. Figure 2 summarizes the synthetic strategies for the single and dual encoding process of the silicon substrates, which were homogeneously prefunctionalized with a SAM of phenacylsulfide silane (**3**).^[10] Prior to the irradiation the substrates were covered with the photomask and fixed into mask holders (Figure 3h). The photoreactions of **3** with **a**, **b**, or **c** were conducted under the same reaction conditions as used for the test reactions. Subsequently, the surfaces were washed thoroughly to remove any physisorbed residuals.

The patterned surfaces with the metal complexes immobilized on the irradiated area of the surface were analyzed by time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging the spatially resolved composition of the substrate surface with high sensitivity (Figure 3). The single encoded surfaces were analyzed both for the fragment of the metal counter ion, for example, Cl^- or Br^- , as well as for fragments

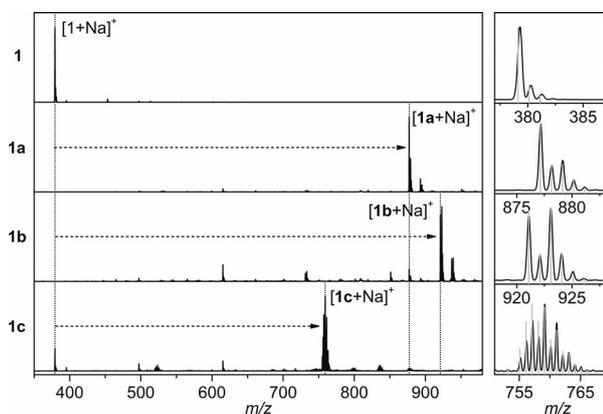


Figure 1. ESI-MS spectra of **1** and the Diels–Alder-adducts **1a**, **1b**, and **1c**. Main peaks are enlarged on the left.

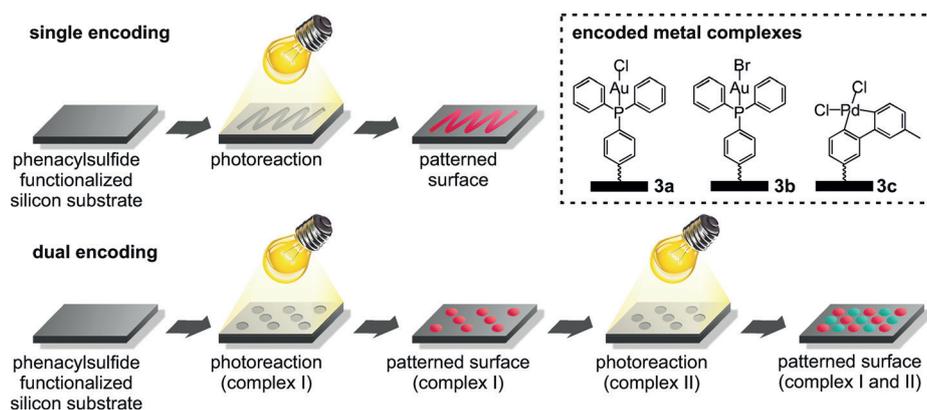


Figure 2. Preparation of single- (top) and dual-encoded (bottom) substrates.

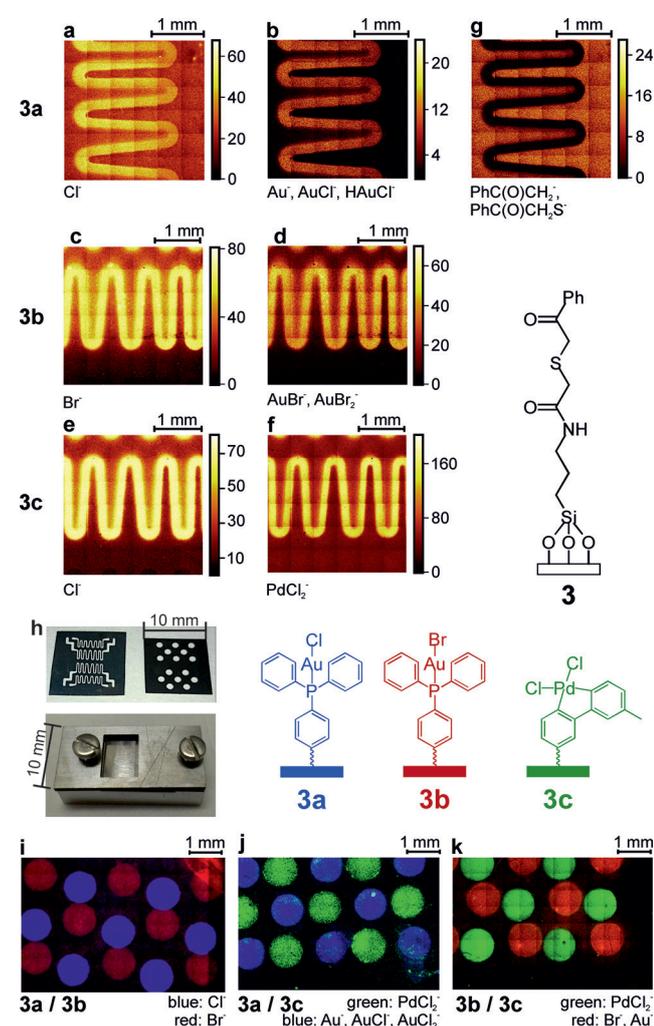


Figure 3. ToF-SIMS images of the single- (a–g) and dual-encoded (i–k) silicon surfaces (fragment ions specified below each image). Middle: Encoded metal complexes, the photomasks (h), and sample holder (h).

containing the metal ion itself (Figure 3a–f). The metal complexes are only immobilized on the irradiated area of the surface. Exemplarily, Figure 3g depicts the imaging of frag-

ments assigned to the phenacysulfide moiety on substrate 3a that are exclusively located on the nonirradiated area. These viable UV-activatable groups can be addressed in another photoreaction to obtain dual-functionalized substrates by two subsequent photoreactions. The ToF-SIMS images of the dual-encoded surfaces are depicted in Figure 3i–k. All combinations of the employed metal complexes (a, b, and c) were obtained, highlighting the versatility of our photolithographic concept.

In summary, a highly versatile and effective procedure for the preparation of patterned surfaces with a monolayer of multiple metal complexes was developed. Solution-based reactions evidence the targeted conjugation on a molecular scale. Arbitrary structures can be produced on the surface by simple variation of the employed photo-mask. At the same time, other metal centers can readily be integrated to create an entire library of encoded metal complexes. ToF-SIMS imaging enabled the spatially resolved analysis of the surface composition. Utilizing polymeric spacers with variable chain lengths could additionally increase the metal complex accessibility. As a perspective, the presented platform technology could, for example, be employed to design highly valuable flow-through cascade reactors where the catalytically active metal complexes need to be arranged in a spatially defined way.

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