Chemical Photolithography

Surface Modification with Orthogonal Photosensitive Silanes for Sequential Chemical Lithography and Site-Selective Particle Deposition**

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The site-selective adsorption of molecules and mesoscopic objects at predefined positions on solid surfaces is a key fabrication step and a major challenge in many applications, such as multifunctional biosensors and novel electronic, mechanical, and photonic devices. The adsorption process is strongly influenced by the functional groups on the surfaces, which can be introduced by different strategies for depositing molecular layers (e.g. self-assembled monolayers, SAMs). In order to direct the adsorption process to predefined regions of the substrate, chemical patterning of these surface layers with discrete micro- to nanometer features is required; this is a critical stage in device fabrication and usually involves iterative combinations of several patterning and surface activation steps.

For this purpose various patterning techniques have been developed, like photolithography and electron beam lithography,[1] microcontact printing,[2] micromachining, and several techniques based on scanning probe microscopy.[3] Light is a particularly convenient medium to introduce lateral patterns, as multiple methods for its generation, handling, and control are available that exploit different mechanisms of how light interacts with molecular surface layers.

In the following, a very brief overview of the fundamental photopatterning strategies is provided with some representative references:

1) Irradiation at very short wavelengths (< 250 nm, high-energy UV) in the presence of oxygen can lead to the chemical degradation of a whole molecular layer; this was shown for aryl- and alkylsilanes at 193 nm.[4]
2) For certain materials under similar irradiation conditions, but often longer wavelengths, specific photoconversion of only the anchor group might take place (rather than degradation of the whole layer). This method has been employed for the photooxidation of thiol monolayers on gold to sulfonates, which bind more weakly to the substrate and can displaced by a second thiol.[5]
3) Instead of photocleavage from the surface, the opposite process of light-induced attachment of a molecular layer onto the substrate was demonstrated with aldehydes and 1-alkenes onto hydrogenated silicon surfaces,[6a] and the photografting polymer layers onto benzophenone-modified silane layers.[6b]
4) Photopolymerization and cross-linking of physisorbed monomers can lead to permanent layer immobilization in the exposed areas due to substantially increased mechanical stability and reduced solubility of the polymerized species. This patterning technique was applied to polydiacetylene lipid layers with subsequent dissolution of the monomeric lipids in the nonirradiated regions.[7]
5) Finally, photoactivation of a surface layer can be achieved if the monolayer-forming molecules are functionalized with a photosensitive group. This is a particularly interesting approach, since a large variety of photosensitive and -reactive species are known that can be combined with many different functional groups.[8] The typical procedure for preparing monolayers with such photosensitive moieties usually involves two steps. First, the surface-active molecules with unprotected functional groups are deposited onto the substrate. These functional groups determine the properties of the newly formed surface, like reactivity, polarity, and charge. In the second step, the photosensitive moieties are introduced into the monolayer by reaction with the functional surface groups.[9] Restrictions of this method are the limited control over the protection step (the coexistence of free and protected functional groups depends on the surface

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reaction yield) and the limited choice over the layer composition, since mixing of incompatible functional groups in their free form is nontrivial.

A consequential improvement is based on the synthesis of surface-active molecules (like thiols and silanes) with the photosensitive moieties directly attached to the functional groups prior to monolayer preparation.[10] The surface layers are thus intrinsically protected, as we demonstrate here with novel triethoxysilanes bearing light-sensitive nitroveratryl and benzoin protecting groups on terminal amino, hydroxy, and carboxylic acid functionalities.

This advanced silane chemistry opens attractive possibilities for simplying the preparation of chemically patterned surfaces. A major advantage of this method lies in the highly defined, quantitative reactions of the protected surface functionalities (achieved during synthesis and purification prior to layer fabrication) and full control over the layer preparation process. Lateral patterning can be achieved easily by direct irradiation and deprotection of the silane layer through a mask, as performed in standard photolithography. Thus, no additional investment is required for its implementation in current industrial processes, and further processing steps (like developing and removing photoresists) can be minimized. In addition, mixed surface layers can be prepared in one step with different types of functional groups (which may be incompatible in their free form and cause reactions, segregation, or salt formation) and different protecting groups that can be independently addressed by their specific deprotection wavelengths (in line with the orthogonality concept, see Figure 1).[11] The surface density of the free functional groups can be tuned conveniently by irradiation time and intensity during the photolysis reaction, which cleaves the protecting group and restores the initial activity of the functional groups.[9b] Further chemical modification or specific adsorption of targets is possible at the deprotected functionalities in the irradiated regions. A schematic representation of the process is provided in Figure 1.

The principle of orthogonality is defined as the possibility to selectively remove one type of protecting group in the presence of others in any chronological sequence. It represents a mayor challenge but is also the primary virtue of protecting group chemistry. In the case of photosensitive protecting groups, individual addressing requires specific differences in sensitivity to selected wavelengths and intensities, as has been recently demonstrated by C. G. Bochet et al. for nitroveratryl and benzoin derivatives in solution.[11] Amongst the reported photoprotecting groups, 3,5-dimethoxybenzoin esters are known to be effectively cleaved by low-intensity irradiation at wavelengths below 300 nm,[12] while nitroveratryl (Nvoc) derivatives, being less reactive, are cleaved at much longer wavelengths (up to 420 nm).[13]

Based on our previous experience with the Nvoc-protected aminosilane **1**, and to transfer and extend the orthogonality concept from solution to solid surfaces (Scheme 1) we synthesized photoprotected triethoxysilanes with terminal amino- (**1**), hydroxy- (**2**), and carboxylic acid groups (**3**, **4**) with nitroveratryloxycarbonyl (NH-Nvoc for **1**/-NH_2; O-Nvoc **2**/-OH; and CO-Nvoc **3**/-COOH[14]) and 3,5-dimethoxybenzoin substituents (CO-Bzn for **4**/-COOH). The synthesis was achieved by first linking the protecting groups to the corresponding functional 1-alkenes by reported coupling procedures, followed by hydrosilylation to introduce the triethoxysilyl anchor group.[15] The triethoxysilyl anchor group was chosen since it favors the formation of a dense monolayer through the three alkoxy valences and at the same time it is less reactive than chlorosilanes), which facilitates handling of the compounds under laboratory conditions (no inert-gas atmosphere required). Furthermore, the silane anchor group is particularly attractive for the modification of a large variety of technologically relevant materials like silica (SiOH groups on glass, quartz, and oxidized Si wafers) and other oxide surfaces (e.g. ITO, TiO_2, Fe_3O_4, ZrO_2, and oxidized polymer surfaces).

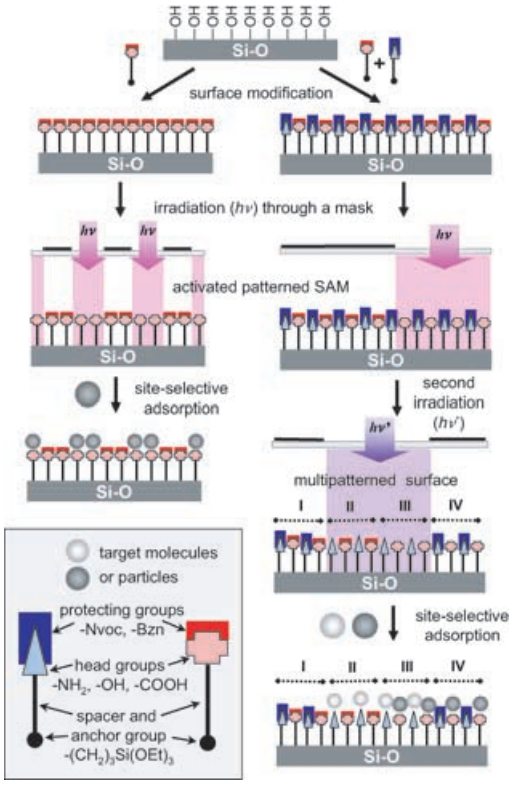
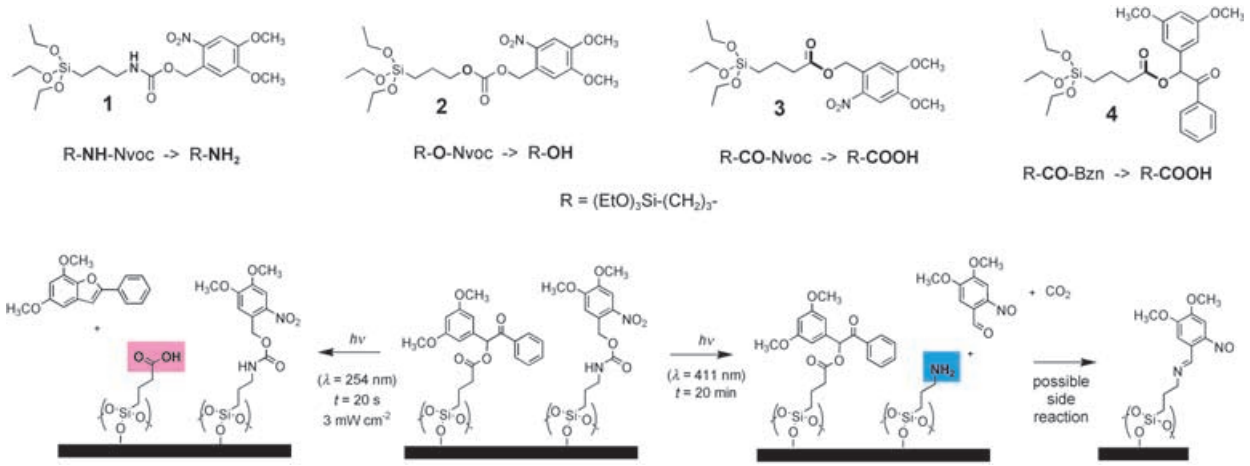


Figure 1. Surface modification and direct monolayer patterning with photosensitive silanes. Left: Formation of a homogenous monolayer by chemisorption of a photosensitive silane. Selected regions of the monolayer are activated by irradiation through a photomask to liberate functional groups. Right: Simultaneous coadsorption of two different silanes (with different functionalities and orthogonal protecting groups) leads to mixed monolayers. Each type of protecting group can be addressed individually in two deprotection steps by irradiation with their corresponding wavelength ($h\nu$ and $h\nu'$), leading to four chemically distinct surface types: I) nonirradiated, fully protected region, II) one in which only one functional group (A) is activated, III) one in which both functional groups are deprotected, and IV) one in which only the second group (B) is liberated. In the deprotected regions adsorption and chemical modification may be achieved for each individual functionality. Nvoc = nitroveratryl, Bzn = benzoin.

During the surface modification process two types of reactions take place simultaneously. First, the trialkoxysilyl groups hydrolyze to give the highly reactive silanol species,



Scheme 1. Chemical structures of the photoprotected triethoxysilanes synthesized and used in this study. Selective deprotection of the amino (blue, from NH-Nvoc **1**) and the carboxylic acid function (red, from CO-Bzn **4**) is shown for a mixed monolayer. A possible side reaction between the liberated amino group and the benzaldehyde fragment might lead to an imine.

which condense in a second step with each other and with free OH groups of the surface to form stable Si-O-Si bonds. In this reaction sequence oligomerization to 1D, 2D, and 3D structures competes with covalent binding to the surface and requires particular consideration. Extensive oligomerization may lead to larger 3D aggregates that would ultimately result in substantial surface roughness.[18b] The progression of these reactions and consequently the characteristics of the final surface layer critically depend on experimental variables such as type of solvent, temperature, and reaction time, as well as on the catalyst and the concentration of the organosilane. Post-silanization curing of the modified substrates at elevated temperature has been shown to improve the stability of the silane films by covalent cross-linking of free silanol groups.

The synthesized silanes were chemisorbed from solution onto quartz substrates and Si wafers at individually optimized prehydrolysis and surface reaction conditions in order to obtain homogeneous and smooth surface layers.[10a,15] The flat layer topography was confirmed by AFM measurements (average roughness of the silane layers was similar to that of the bare substrate, rms ca. 0.4 nm over several 10^4 nm^2). The layer thickness from ellipsometric measurements was in the range of 1–2 nm (±0.5 nm), and advancing water contact angles were around 65–70° (±2)° for the Nvoc surfaces (**1**, **2**, and **3**) and 56 (±2)° for the CO-Bzn **4** layer (bare silica surface ≈0°). After irradiation and deprotection the water contact angles dropped by 10–20° (±5)°, indicating the liberation of the more polar functional groups. The ellipsometric thickness was slightly reduced after irradiation by about 0.2–0.5 nm (within the error range).

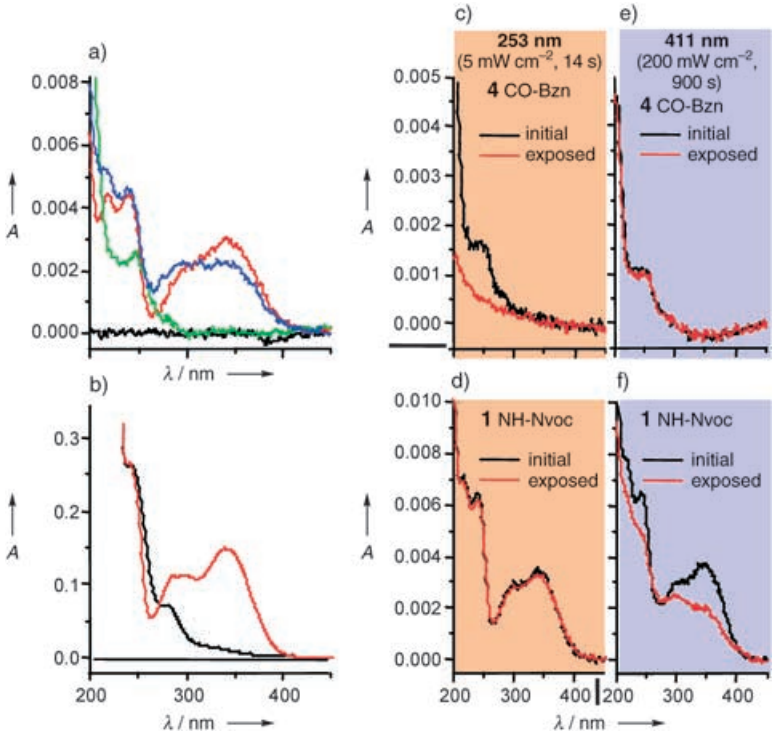


Figure 2. a) UV/Vis spectra of quartz substrates modified with the individual silanes **1** (Nvoc-protected; red), **4** (Bzn-protected; green), a binary mixture of both silanes (blue), and the bare substrate (black). b) UV/Vis spectra of the silanes **1** and **4** in THF; for **4** the absorption band tails far into the visible range. c, d) The absorption for the layer of CO-Bzn **4** decays upon irradiation at 253 nm (c), while that for the layer of NH-Nvoc **1** remains stable at this wavelength (d). During irradiation at 411 nm the layer of CO-Bzn **4** (e) remains stable, while NH-Nvoc **1** (f) is cleaved.

The presence of the photoprotecting groups in the surface layers was also confirmed by their characteristic chromophore absorption in the UV/Vis spectroscopic analysis of silanized quartz substrates. This is demonstrated in Figure 2a for substrates modified with silane **1** (characteristic absorption of the NH-Nvoc group, red curve), with **4** (CO-Bzn group, green curve), and with an equimolar mixture of both (blue curve). These spectroscopic profiles are identical for the corresponding silanes in solution (Figure 2b). The coexistence of both chromophores (Nvoc and Bzn) in the mixed layer corroborates that combinations of different functionalities and protecting groups can be obtained in a single chemisorption

step, as also shown for the NH-Nvoc silane and a quaternary ammonium silane.[10a]

A possible problem with the coadsorption of different silanes from a mixture in solution might result from a deviation of the relative ratio of silanes in the adsorbed state and the ratio in solution. Based on the relative UV absorption intensities of the individual components **1**, **4**, and the mixed layer (Figure 2a) and the assumption of random chromophore orientation in the disordered silane layers, one can infer an equimolar coadsorption. The different absorbance maxima of the Nvoc (λ_{max} above 300 nm, tailing beyond 400 nm) and Bzn (λ_{max} below 300 nm, tailing up to 380 nm) protecting groups explain the specific wavelength sensitivity of the deprotection process. In fact, irradiation at 254 nm (5 mW cm^{-2}) for 14 s results in almost quantitative cleavage of the Bzn group of **4** (see Figure 2c), while the NH-Nvoc layer **1** remains fully stable under identical conditions (Figure 2d).[16] The Nvoc group can be effectively photolyzed at its absorbance maximum around 365 nm, but also the Bzn derivative **4** fragments at this wavelength (for a more detailed kinetic analysis see Figure S1 in the Supporting Information). This instability of the Bzn group at 365 nm may be a consequence of the weak absorbance band up to 380 nm evident in the solution spectrum (Figure 2b). In contrast, irradiation at 411 nm leads to a strong decrease of the Nvoc chromophore in layer **1** (Figure 2f), while the CO-Bzn layer **4** remains stable (Figure 2e, see also Figure S1 in the Supporting Information). These results clearly illustrate the possibility of orthogonal deprotection at the substrate surface.

Closer analysis of the photolysis reactions reveals that the relative chromophore intensity in the Nvoc-protected amine **1** never drops below 40–50% even in the presence of a carbonyl scavenger.[17] In contrast, the Nvoc-protected alcohol **2** and carboxylic acid **3** can be cleaved almost quantitatively under identical conditions. This particular behavior might be explained by imine formation between the benzaldehyde fragment and the primary amino group at the surface as a side reaction after photolysis (Scheme 1); this is not possible for **2** and **3**. This result is indicative of a diffusion-controlled process at the substrate surface, in which the separation of the photofragments is slow (compared to the imine formation) due to the 2D confinement imposed by the solid surface.

When the substrates are irradiated through a mask, a pattern of activated and nonactivated areas with the shape of the mask is generated. The resulting chemical contrast between exposed and nonirradiated regions can be used to direct the assembly process of specific targets onto the activated areas (like colloidal particles[10a,18] and fluorescence dyes, see Figure S2 in the Supporting Information). Figure 3 shows the site-selective assembly structures from carboxylated poly(butylmethacrylate) (PBMA) colloids[18a] after photolytic patterning of the surface groups for substrates modified with **1** (a: NH-Nvoc/NH_2), **2** (b: O-Nvoc/-OH), **3** (c: CO-Nvoc/-COOH), and **4** (d: CO-Bzn/-COOH).[15] The contrast in the optical-microscope images (dark-field mode) results from differences in the density of adsorbed particles, which is higher in the brighter areas. On the free amino surface of the irradiated layer **1** a relatively high particle density of 3.5(±0.5) particles per μm^2 is found, while essentially no particles adsorbed onto the nonirradiated regions. This is similar to results obtained by direct functionalization with an aminopropylsilane.[10a] Strong electrostatic attraction between the partially protonated and positively charged amino groups at the substrate and the partially deprotonated and negatively charged carboxyl functions on the latex particles may drive the assembly process. The individual particles at the NH_2 surface are isolated due to a strong repulsion between the like-charged colloids, as seen at higher magnification in the SEM image (inset Figure 3a). On the hydroxy-modified surface of the irradiated layer **2** the

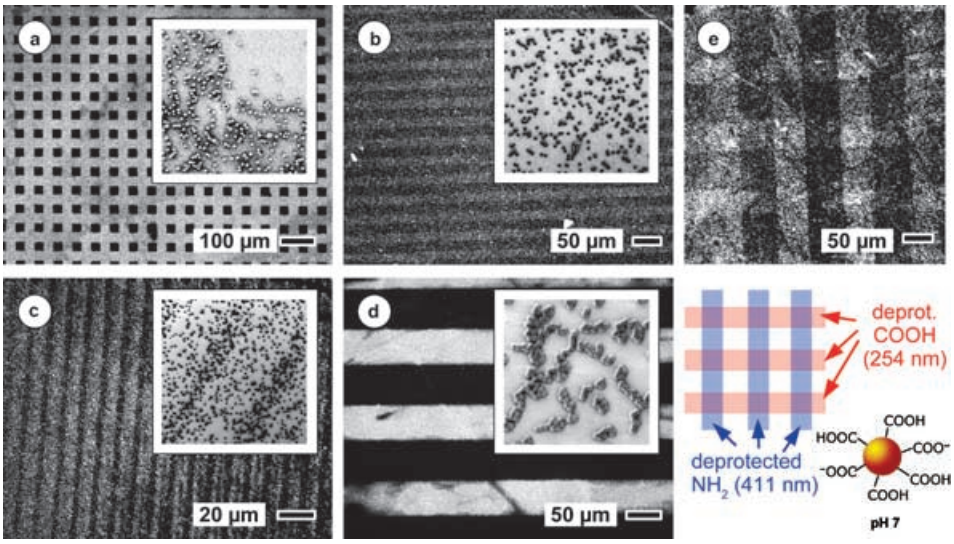


Figure 3. Optical-micrographic images (dark field) of assembly patterns from carboxylated PBMA particles (diameter 183 nm) adsorbed from aqueous suspension at pH 7 onto silane layers of a) **1** (NH-Nvoc/NH_2), b) **2** (O-Nvoc/-OH), c) **3** (CO-Nvoc/-COOH), and d) **4** (CO-Bzn/-COOH) irradiated through a mask. The insets show SEM images of individual particles at higher magnification (width ≈5 μm). Image (e) shows the colloid assembly pattern on a mixed layer of **1** and **4**, which has been irradiated at two different wavelengths (254 and 411 nm) a 90°-rotated line masks (according to the color scheme).

particle affinity is apparently weaker and a low density of individually dispersed colloids is observed (1.7 particles per μm^2) with unspecific adsorption in the nonirradiated areas (1.3 particles per μm^2). In this case the adsorption process might be driven primarily by polar and hydrogen-bonding interactions between the OH and COOH groups.

Surprisingly, on COO surfaces from exposed layers **3** and **4** a relatively strong colloid adsorption (4.1/1.4 particles per μm^2 for irradiated/nonirradiated **3**; 8.5/1.2 particles per μm^2 for **4**) and substantial particle clustering is found (seen at higher magnification in the SEM image, Figure 3d). This is in contrast to initial expectations, since the carboxy functions on the particles and at the substrate surface should show electrostatic repulsion. Indeed, no particle adsorption is achieved when pure water is used instead of buffer solution as the suspending medium; this indicates the important role of charge screening by the salt. Colloidal adsorption onto a mixed layer of **1** and **4** after successive irradiation through a striped mask, first at 254 nm (CO-Bzn deprotection) and secondly with the mask rotated by 90° at 411 nm (NH-Nvoc deprotection), leads to the checkered pattern shown in Figure 3e, in which the particle density depends on the activated functional groups and the irradiation dose (highest particle density in cross regions).

Other methods for particle assembly have been reported,[19] and one prominent example of orthogonal particle deposition is based on DNA-assisted specific recognition between DNA-modified spots on a substrate and DNA-labeled particles.[20] This method was demonstrated successfully for two different kinds of particles,[20b] but it requires specific DNA labeling of both the substrate and the particles. The advantage of the method presented here is the the fact that a simple silanization process introduces the mixed protected functionalities and patterning is achieved by means of standard photolithographic irradiation; the particles need not be specifically modified with complementary recognition elements (besides the functional surface groups introduced during particle synthesis).

In conclusion, the new photosensitive silanes presented here can be used for direct monolayer lithography and the introduction of functional surface groups, which is not possible directly by silanization (OH and COOH functions are incompatible with the triethoxysilane anchor group). Complex combinations of different functional and protecting groups can thus be achieved by simultaneous coadsorption of the corresponding silane mixtures and orthogonal activation, as demonstrated here for NH-Nvoc **1** and CO-Bzn **4**. Specific colloid assembly onto the photoactivated regions is possible and mediated by the free surface functionalities. Further experiments are currently directed to the selective immobilization of DNA fragments onto the photopatterned mixed layers (relevant for biochip applications) and the extension of the Bzn group to other functionalities.

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[14] For molecule **3** the nitroveratryl group is directly linked to the carboxylic acid function through an ester linkage (without a oxycarbonyl moiety), but for simplicity it is referred to as CO-Nvoc.
[15] See the Supporting Information for details.
[16] In analogy to the irradiated silane layers, nonirradiated reference substrates were also washed to identify and account for any intensity loss due to simple removal of the silane layer by washing. All absorbances remained constant after this procedure, corroborating the high stability of these silane layers.
[17] During irradiation a thin film of methanol was sandwiched between the substrate and a covering quartz plate to allow dissolution of the generated protecting-group fragments. In the case of the Nvoc-protected amine **1**, semicarbazide hydrochloride (55 mM solution in methanol) was added as a carbonyl scavenger to capture the photogenerated benzaldehyde and prevent potential imine formation with the free amino surface (Scheme 1).

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