Communication

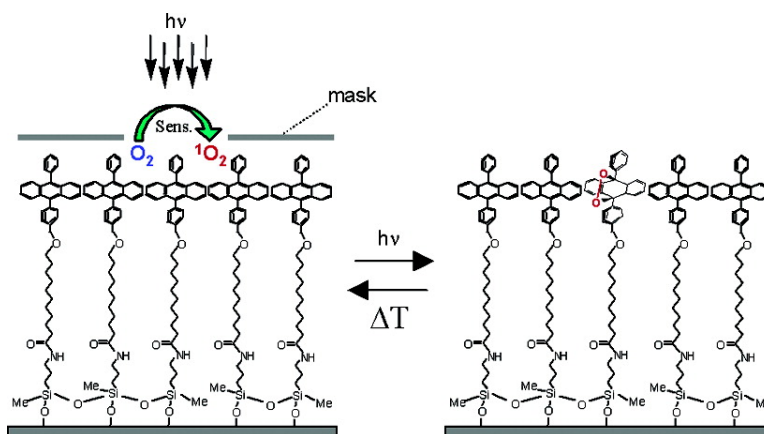# Reversible Light and Air-Driven Lithography by Singlet Oxygen

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Reversible Light and Air-Driven Lithography by Singlet Oxygen

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Tremendous work has been devoted to the design of micrometer-scale structures with applications ranging from electronic devices to bioassay arrays. Among the techniques employed, photolithography offers cheap and easily accessible equipment, where the structure originates from a prefabricated master.[1] As the exposed areas can undergo a broad range of chemical transformations, encompassing fragmentation, cross-linking, and photooxidations, the pattern motif, in general, is formed irreversibly as the material loses initial structural features.[2] Examples of introducing pattern structures by photooxidation involving singlet oxygen ($^1O_2$), the electronically excited form of O_2, are rare. Besides the variety of interesting reactions applied in organic synthesis,[3] photoresists, which were designed for $^1O_2$ chemistry, exploit only a few of the available chemical modes, that is, oxidation of furans, oxazoles, or alkenes.[4] In the course of our research, we developed the stereoselective synthesis of hydro- and endoperoxides from unsaturated carboxylic acids.[5] However, endoperoxides of anthracenes, which can be obtained by the [4 + 2]-cycloaddition with $^1O_2$, should be ideal substrates for patterning on surfaces since they reconvert in high yield to the parent hydrocarbon at elevated temperatures.[6] Here, we report the first example of creating defined micrometer structures into layers of anthracenes by the photosensitized generation of singlet oxygen from air on oxidized silicon surfaces. This technique offers a route to introduce new functional groups into a substrate, which can be either erased or used for further modification.

9,10-Diphenylanthracene (DPA) reacts rapidly to the corresponding endoperoxide in solution and can be restored upon heating. On assembling DPA on a surface, either as a monolayer or as a thin film (Scheme 1), the reacting species will be affected by the environment comprising (i) the support, (ii) the film, and (iii) the solid/air interface.

To be considered are competing photoreactions (vide infra) as well as following transformations of the endoperoxides.[7] Our first studies were carried out on monolayers on silicon wafers and glass slides (Scheme 1).[8] Incorporating an undecanoyl chain between DPA and the anchoring NH_2 group keeps the reaction center remote from the surface and provided a closer packing. The anthracene monolayer on glass was characterized by UV–vis (Figure 1) and fluorescence spectroscopy.[8]

The photooxidation of the monolayer with $^1O_2$ was carried out by incorporating methylene blue (MB) as sensitizer into the layer.[8] After subsequent irradiation by a sodium lamp, UV–vis and fluorescence spectra were taken to follow the course of the reaction. Both absorption (Figure 1) and fluorescence vanished completely after 15 min of irradiation, indicating that the anthracene chromophore has quantitatively reacted. After heating the samples at 120 °C for 30 min, the initial absorption and emission spectra reappeared without any loss of intensity. Recurring multiple cycles of irradiation and heating resulted in no significant changes in the spectra. Complete reversibility of the photooxygenation of conju-
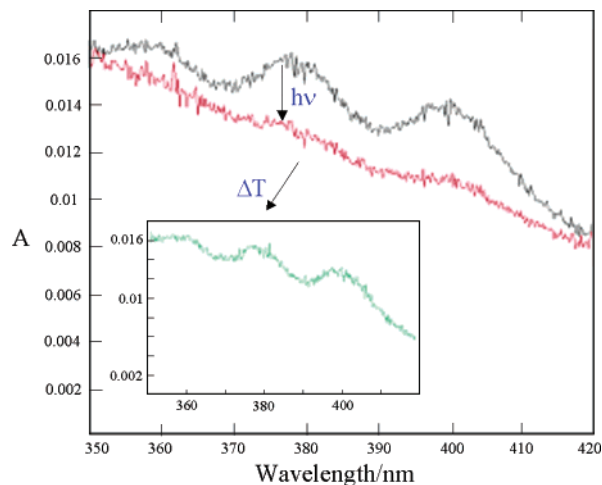

Figure 1. UV–vis spectra of a DPA monolayer, as shown in Scheme 1, after dipping into a solution of MB before and after irradiation with visible light and (inset) after heating the sample at 120 °C for 1 h.

Scheme 1. Pattern Generation into a Layer of Anthracenes

gated diens to endoperoxides by thermolytic oxygen cleavage accounts unambiguously for a single photoreaction pathway involving $^1O_2$ as the sole oxidizing species (Type II photooxidation). Alternatively, electron transfer processes involving the anthracene cation radical (Type I photooxidations) can be excluded as their products are irreversibly formed.[9] Thus, the DPA unit in the monolayer converts effectively into the corresponding endoperoxide, which reconverts to DPA and oxygen. Any interference with the adjacent underlying surface, comprised of Si–OH and aminopropylsilyl groups, can be thereby ruled out.

Proceeding with the investigation of the photooxygenation within a thin film, we deposited anthracene **1** on glass and silicon (Figure 2).[10]

After irradiation, in the presence of MB, the following thermal treatment only recovers about 88% of the starting material.[8] Repetition of multiple cycles of irradiation and subsequent heating revealed that the absorbance of anthracene in the UV spectra gradually declined, which became more pronounced as the thickness of the layer was increased. A spectroscopic analysis of the irradiated film indicates the formation of byproducts, which arise from

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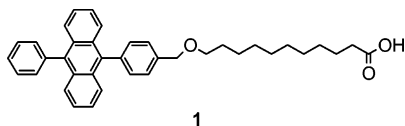[‡] Max-Planck-Institute of Colloids and Interfaces.
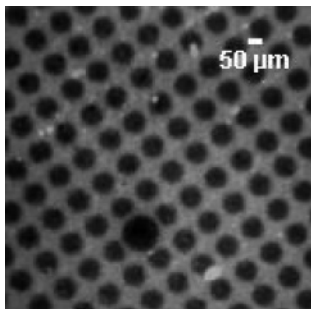
Figure 2. Molecular structure of anthracene **1**.

Figure 3. Fluorescence micrographs of pattern motifs imprinted into thin films of **1**.

Figure 4. Fluorescence images (transparent characters) of successive steps of writing (left), erasing, and rewriting (right) into a thin film of **1**.

irreversible Type I photooxidations, where $^1O_2$ is not involved.[8,11] Within a thin film, the mobility of $^1O_2$ and the anthracene moiety is expected to be very small, reducing the number of effective encounter complexes between DPA and $^1O_2$. The Type II pathway consequently slows down.[12] However, the reversible formation of endoperoxides was still the prevailing photooxidation pathway, which was also confirmed when 1,4-diazabicyclo[2.2.2]octane (DABCO), a $^1O_2$ quencher, was incorporated into the film, causing a longer time for conversion and a lower yield after thermal treatment. In a crucial control experiment under argon atmosphere, no reaction of anthracene **1** occurred.

Figure 3 shows microscopic images of 2D pattern motifs introduced into thin films consisting of 1×10^{-8} mol/cm^2 of **1** irradiated with visible light in the presence of MB through TEM grids. Those films bleached under the microscope since irradiated anthracene itself acts as sensitizer for $^1O_2$. The sharp black spots suggest that $^1O_2$ reacted almost exclusively at the light-exposed regions. Beyond the boundary, the cycloaddition arises only from $^1O_2$ generated at the exposed area. Considering a comparatively small diffusion coefficient in a solid matrix and a short lifetime for $^1O_2$ in a C−H containing media,[13] the mean displacement of $^1O_2$ should range below the resolution of the microscope. Since all pathways of photoreactions afford nonfluorescent products, the question arises whether the dark nonfluorescent regions correspond to endoperoxides. Endoperoxides, arisen from $^1O_2$, should return after annealing to fluorescent hydrocarbon, whereas all other photoproducts would remain nonfluorescent. Indeed, the motif introduced initially was not discovered after thermal treatment, and about 90% of the initial fluorescence intensity was restored. After erasing by heating, the samples could be used for the pattern generation again, as exemplified in Figure 4.

Finally, the endoperoxide patterns can be used as a master to transfer images to a reactive contact material, for example, by casting on a paper, which was impregnated with iodide.[8]
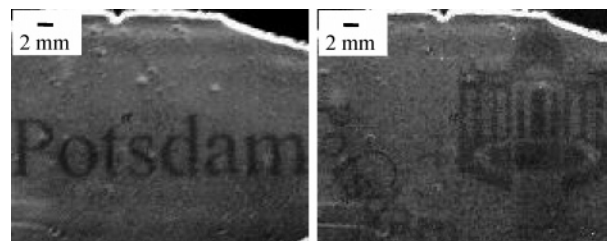
In summary, we have shown that pattern features can be introduced into thin films of anthracenes by photosensitized oxygenation and erased after short thermal treatment. The pathway leading to endoperoxides occurs exclusively in monolayers and dominates in thin films. This new methodology offers promising prospects for writing on surfaces under simple and ecological conditions. Future work will be focused on the reading process by scanning microscopy.

Supporting Information Available: Experimental details, UV−vis and fluorescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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