DOI: 10.1002/chem.200600387

Imaging by Sensitized Oxygenations of Photochromic Anthracene Films: Examination of Effects That Improve Performance and Reversibility

Werner Fudickar and Torsten Linker*[a]

Dedicated to Professor Siegfried Hünig on the occasion of his 85th birthday

Abstract: The aliphatic anthracene compound **1** and the oligomeric anthracene **2** were synthesized. Thin films of **1** and **2** mixed with the sensitizers tetraphenylporphyrin (TPP) and methylene blue (MB) were irradiated with visible light in air. Upon formation of singlet oxygen, the anthracene units were converted quantitatively to the corresponding endoperoxides. Heating of the irradiated samples afforded the parent anthracenes with high yields. Here, we demonstrate that the kinetics and reversibility of this reaction strongly depend on the microenvironment of the anthracene groups in the two compounds. The photooxidation of thin films of **1** is accompanied by interesting changes in the morphology of the film and allows the first application of **1** as a nondestructive negative-tone photoresist for lithography and as an oxidizing ink. The morphology of **2** remained unchanged after photooxidation as a result of the stabilizing oligomer backbone. This stabilizing effect significantly improves the photochromic performance of **2**. The reversibility of the photooxidation is very high (>90%) for oligomeric films of **2** after several cycles of irradiation and heating. Decomposition of the anthracene and a loss of the activity of the sensitizer diminish slightly the performance of the monomeric species.

Keywords: anthracenes · lithography · photochromism · singlet oxygen · thin films

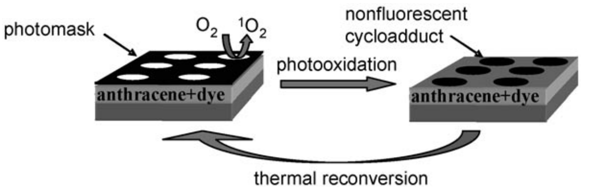
Introduction

Organic materials that undergo a reversible change in their optical characteristics upon irradiation have drawn increasing attention in the contest to develop advanced photonic devices.[1] The most profitable areas of application are optical switches and data storage. Though the first erasable optical memory media were manufactured from inorganic materials,[2] the organic counterparts are anticipated nowadays as promising candidates for future generations.[3] More generally speaking, the term photochromics (molecules that change color upon irradiation) includes any compound that can reversibly switch between two states by using light.[4] The changes of molecular properties may include, for example, their absorption spectra, dipole moment, or refractive index.[5,6] A vast contribution to research on photochromic materials deals with the families of diarylethenes and fulgides, characterized by photochemically allowed cyclization and ring-opening processes.[7,8] They exhibit both a striking resistance to fatigue and a thermal irreversibility.[9] In these systems, the wavelength of light that triggers the isomerization corresponds to the absorbance spectra of the initial species; reconversion, accordingly, requires the absorbance wavelength of the product. For some applications the use of the wavelength for writing and reading is inconvenient. Sensitized photoreactions, in which the energy of light is first transferred to a dye, become another alternative.[10] In addition, the scope of suitable photonic materials that may not depend on the fixed wavelength of the laser source becomes broader.

Singlet oxygen ($^1O_2$) is generated by dye-sensitization with high efficiency. It is used in organic chemistry as a powerful oxidant in regio- and stereoselective synthesis.[11] Surprisingly, there are only a few examples dealing with $^1O_2$ in photochemical surface chemistry.[12] During our studies on photooxidations of olefins with singlet oxygen ($^1O_2$)[13] we developed a photochromic system composed of a fluorescent anthracene and a sensitizing dye (Scheme 1).[14] Upon irradiation with visible light in the presence of air, $^1O_2$ is formed and reacts with the polyacene by a [4+2] cycloaddi-

---

[a] Dr. W. Fudickar, Prof. Dr. T. Linker
Department of Chemistry, University of Potsdam
14476 Potsdam (Germany)
Fax: (+49)331-977-5056
E-mail: linker@chem.uni-potsdam.de



Scheme 1. Photochromic system composed of a sensitizing dye and a polyacene. Singlet oxygen is formed exclusively at the light-exposed region and oxidizes the polyacene. The pattern, obtained by irradiation through a photomask, can be removed by heating.

tion forming a nonfluorescent endoperoxide.[15] Because the cycloaddition with $^1O_2$ is thermally reversible, heating afforded the fluorescent starting material with almost 100 % yield. Due to the short travel distance of singlet oxygen in solid matrices, the photoexcited form of oxygen exists and reacts only within the regions exposed to light, allowing a site-selective introduction of oxygen into the film.[16]

Although we succeeded to write, erase, and rewrite patterns into the film, we noticed a significant drop in the optical quality and the writing performance during the extension to multiple cycles of irradiation and thermal treatment.

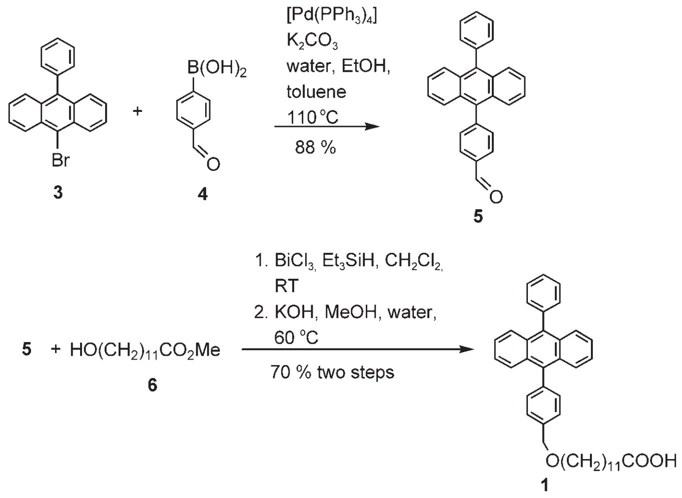
Furthermore, we were keen to learn whether the changes in chemical and physical properties of the exposed areas of the film could be exploited for successive applications, for example, lithography. To this end, we endeavored to improve the performance of the photoconversion and film stability of two different anthracene derivatives and investigated physical and chemical changes in their films. Our results demonstrate a significant improvement in this new class of photochromics.

Results and Discussion

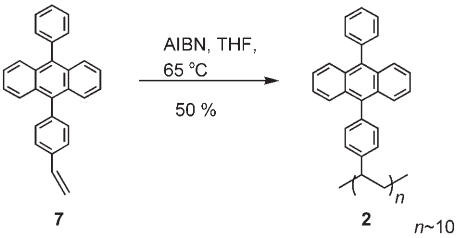
Synthesis of photochromic materials: Compound **1** was synthesized from 9-bromo-10-phenylanthracene (**3**) by Suzuki coupling with 4-formylphenylboronic acid (**4**), followed by reductive acetalization with 12-hydroxydodecanoic acid ester (**6**) and saponification (Scheme 2).

Suzuki coupling of the bromoanthracene **3** with 4-vinylphenylboronic acid afforded the vinylanthracene **7** that was homopolymerized to the oligomeric anthracene **2** (Scheme 3).

Thin films on glass were formed by either drop or spin coating from solutions of **1** and **2**. The long chain of **1** turned out to be a crucial entity for forming stable films. Glassy films were also obtained from homologues of **1** bearing a shorter chain. The formation of uniform and amorphous films failed if the pendant chain was omitted, for example, by using 9,10-diphenylanthracene, with a stronger tendency towards crystallization. Oligomers **2** (M_w~3100) provided smooth and glassy films of comparable quality. Compound **1** has a glass-transition temperature of 5 °C and melts at 126 °C, whereas the oligomer **2** exhibits no transition below 270 °C. Thus, the conditions for thermal treatment (see below) are slightly restricted for the monomeric anthracene **1** to avoid melting. Analysis of the film morphologies are provided below.

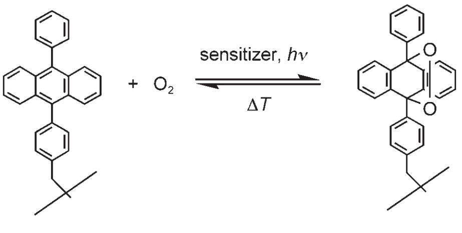


Scheme 2. Synthesis and structure of the anthracene **1**.



Scheme 3. Synthesis of the oligomeric anthracene **2**.

Kinetic studies on photooxidation: The anthracene moiety in **1** and **2** reacts with $^1O_2$ to give the endoperoxides **1**-O_2 and **2**-O_2 (Scheme 4). This reaction can be reversed either at elevated temperatures or upon irradiation with UV light. Thermolysis of 9,10-diphenylanthracene in dioxane, for example, affords almost 100 % of the parent anthracene and 35 % of the oxygen in the excited singlet state.[17]



Scheme 4. Reaction of the anthracenes **1** and **2** to give the endoperoxides **1**-O_2 and **2**-O_2.

The transformation of photosensitive thin films composed of anthracene **1** and sensitizing dyes on glass was investigated by UV-visible spectroscopy. Drop coating from solutions in dichloromethane gave reproducible samples with film thicknesses ranging between 0.5 and 1 μm, as determined from ellipsometric measurements. Irradiation with a halogen lamp caused a disappearance of the absorption bands of the anthracene chromophore (Figure 1).

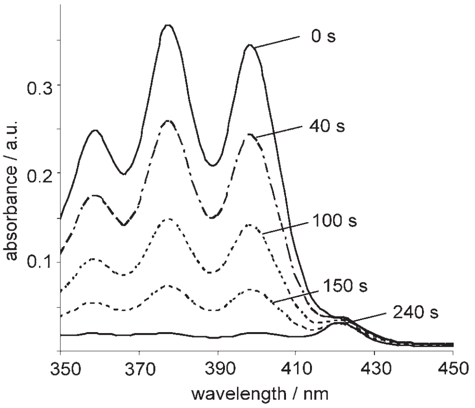


Figure 1. Spectral changes of a thin film of anthracene **1** doped with 0.12 mol% TPP upon exposure to visible light. Exposure times are indicated in seconds.

During our initial studies,[14] we encountered an irreversible decomposition of the deposited material that accumulated upon excessive duration of irradiation. NMR spectra of the dissolved material indicated the formation of unidentifiable products resulting from rearrangements or radical reactions (see below). Therefore, it is important to enhance the rate of the desired photoconversion to permit very short times of irradiation. This rate is dependent on the quantum efficiency of the sensitizer to produce singlet oxygen, the diffusion of oxygen in the film, and the reactivity of the substrate.

Two different sensitizers were employed, namely, tetraphenylporphyrin (TPP) and methylene blue (MB). The quantum yields for singlet-oxygen formation and the absorbance maxima of these two sensitizers are summarized in Table 1.[18]

Table 1. Physical data of the two sensitizers.

Sensitizer	$\Phi(^1O_2)$[a]	λ_{max} [nm] (ε)[b]
TPP	0.62 (benzene)	419 (4.8×10^5), 514 (19000), 549 (7700), 591 (5400), 647 (3400)
MB	0.23 (ethanol)	665 (89000)

[a] Values taken from ref. [18]. [b] Measured in solution (benzene, ethanol).

Excitation of the films within the absorbance region of the anthracene chromophore (350–400 nm) afforded undesired side products that are known to result from photoinduced rearrangement of endoperoxides or radical reactions (Type I photooxidations).[17] These side reactions were minimized further by using a filter that cut off all wavelengths below 515 nm (see Experimental Section). As expected, the rate of conversion of anthracenes increased as the amount of the sensitizers increased (Figure 2). Based on the molecular weight of the monomers, identical ratios of anthracene/sensitizer were employed. With both sensitizers, the anthracene units in the oligomeric film of **2** reacted faster than the monomeric film of **1**. The stronger sensitizer TPP, with the higher $^1O_2$ quantum yield (Table 1), is clearly mitigated, as its most intensive absorption bands are not effective within the operating-wavelength region. The effect on the sensitized $^1O_2$ production, the solute diffusion, and its chemical quenching in polymeric matrices has been studied intensively.[19] Although singlet-oxygen lifetimes are almost equal to those of their liquid analogues ($\tau \sim 20$ μs in polystyrene and $\tau \sim 30$ μs in toluene), oxygen diffusion is strongly restricted in polymers below their glass-transition temperature. For example, the diffusion coefficient (D) drops from $4.38\times10^{-5}\,cm^2s^{-1}$ in toluene (293 K) to $\sim 3\times10^{-7}\,cm^2s^{-1}$ in polystyrene (PS).[20] Interestingly, the reactivity of a strong quencher ($k_q > 10^8\,M^{-1}s^{-1}$) in a solid matrix is more affected than the reactivity of a weaker quencher ($k_q < 10^7\,M^{-1}s^{-1}$). For very weak quenchers, the rates observed are increased in polymers relative to the rate in liquids. This is explained by the increased number of collisions in the more rigid solvent cage of the oligomer. Within this relation, the moiety 9,10-diphenylanthracene ($k_q = 1\times10^6\,M^{-1}s^{-1}$)[21] has to be considered as a reactant, adopting only a moderate deceleration or acceleration in quenching in the solid environment. The matrix effects on the rate should have a weaker magnitude in the more fluid film of **1**, for which T_g is below room temperature. The slower conversion of the anthracene moiety in **1**, however, accounts for rather different properties in the intrinsic structural nature of the two films. The monomeric compound carries a long alkyl chain with a carboxylic acid group. The portion of the slower vibrational deactivation channel becomes more significant. Comparing the two sensitizers within the same film, a saturation limit at low conversion is reached in MB with a ratio of about one

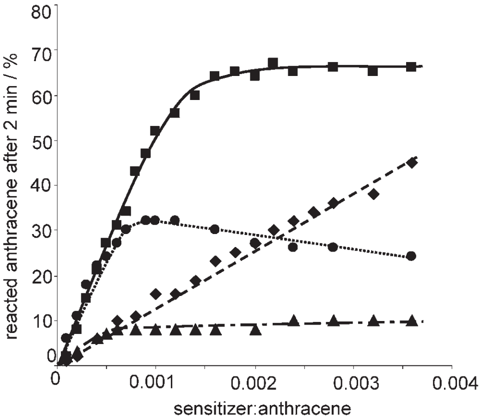


Figure 2. Conversion of anthracenes after 2 min at various concentrations of two sensitizers on glass. ■ = **2**, TPP; ◆ = **1**, TPP; ● = **2**, MB; ▲ = **1**, MB.

molecule of sensitizer per 1600 and 1200 molecules of anthracenes **1** and **2**, respectively. Beyond these concentration limits the efficiency of singlet-oxygen formation and subsequent oxygenation of anthracenes could not be increased further and the efficiency even decreased in the case of the doped films of oligomer **2**. This effect can be explained by sensitizer self-quenching and aggregation effects of MB at higher concentrations.[22] On the other hand, no limits appeared with TPP as sensitizer in thin films of **1** at low conversion ($<50\%$) and only at very high conversion ($>65\%$) in the oligomeric film of **2**. Because the two sensitizers cause different conversions at their optimum ratios, we can conclude that the quantum yields of photoconversion in the thin films of the two sensitizers are different and, under identical experimental conditions, TPP appeared to be more effective than MB.

During the initial stages, the photosensitized conversion of the anthracenes in the films investigated obey first-order kinetics with linear semilogarithmic slopes that can be rationalized by a steady-state concentration of $^1O_2$. Interestingly, as the reaction progresses the kinetics of the oligomeric anthracene **2** differ from those of the monomeric compound **1**. The latter exhibits a downward slope, whereas that of the oligomer is bent slightly upwards (Figure 3). This behavior was observed at various ratios between sensitizer and anthracene. If **1** was incorporated into a thin film of poly(methyl methacrylate) (PMMA), a clear first-order behavior was adopted if low concentrations of **1** were employed. The deviation from first-order kinetics and the acceleration of photoconversion of **1** as a neat film could arise from the phase changes of the film during irradiation, as such changes are prevented in a unreactive matrix, such as PMMA. This also conforms to a macroscopic alteration of the oxygenated film, which will be discussed in the next section. During the transition, oxygen diffusion may vary and the accessibility to reactive anthracene rings may be better facilitated. In contrast, the local environment within the oligomer maintains the anthracene units in the same relative orientation, due to the rigid oligomer chain. Motional freedom of the anthracene units is restricted and unreacted sites are shielded from the attacking $^1O_2$ by the nearby oligomer backbone or side-chain segments. No aggregation effects in oligomer **2** were observed by fluorescence spectroscopy of the film, as only a slight red shift distinguished it from a solution spectrum of 9,10-diphenylanthracene.[23] The two benzene rings may inhibit monomers from excimer formation, which would have been proved by a larger wavelength shift in the spectra. However, the close proximity of two reactive anthracene units is a definite consequence of the polyethylene chain.

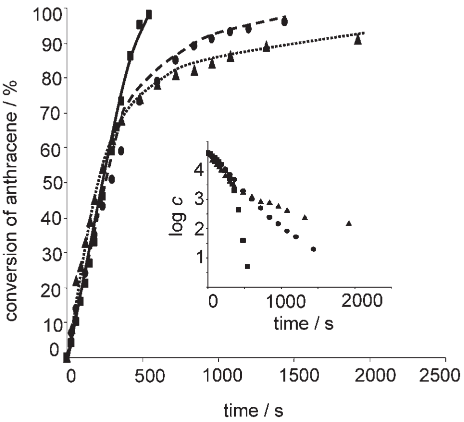


Figure 3. Conversion curves of anthracenes **1** and **2** versus time during irradiation in the presence of TPP at an anthracene/TPP ratio of $1{:}5\times10^{-3}$, plotted from the absorbance at 378 nm. ■ = **1**; ▲ = **2**; ● = **1**/PMMA. Inset: semilogarithmic plot of the absorbance of anthracenes. Molar ratio of **1**/PMMA = 1:4.

Investigation of physical changes during photooxidation: In addition to the disappearance of fluorescence and the changes in optical absorption, the photooxidation of the thin films is accompanied by some remarkable changes in physical properties. This should allow an imprint of visible two-dimensional structures into the material. Water contact angles increased from 95–97° at the unreacted surface to 97–100° after irradiation. Though the introduction of peroxo groups contributes to more polarity, the effect of a molecular reorientation prevails, in which changes in morphology cause a reduction in the wettability. These changes are compatible with the observed averaged increase in the thickness of spin-coating films by 5%, as measured by ellipsometry. The photooxygenated compound **1**-O_2 exhibited no glass transition below the onset of oxygen release at about 60 °C. If thin films of monomeric anthracene **1** and TPP were irradiated through photomasks, the boundary between the irradiated and nonirradiated region became visible, exactly congruent with the fluorescence image (Figure 4). During irradiation, the kinetic energy of the molecules increases and the exposed part of the film of **1** adopts a fluid state, in which molecular motions over a longer range occur. After complete conversion, the endoperoxides establish a more glassy film and movements of molecules during irradiation

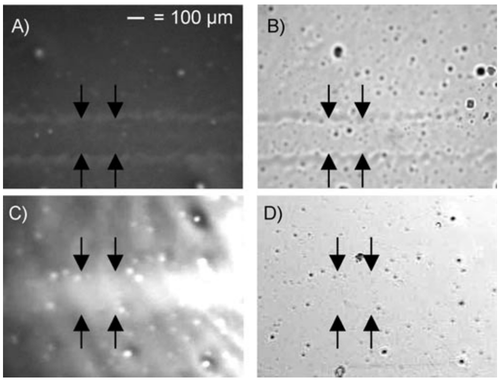


Figure 4. Photoimaging on thin films of anthracenes and TPP. Fluorescence images and optical images are compared and indicate boundaries for the monomeric species **1** and no boundaries for the oligomeric compound **2**. A) Fluorescence image of a thin film of **1**; B) optical image of the same region. C) Fluorescence image of a thin film of **2**; D) optical image of the same region.

will eventually cease. This results in the formation of two distinguishable phases at the surface with different refractive index values.

Interestingly, no boundary was visible if the imaging was carried out on a thin film of **2** mixed with TPP (Figure 4D). Only the fluorescence image was detectable. In this case, the rigid oligomer backbone impedes molecular motion and no phase separation is permitted.

This difference observed in morphology between irradiated and nonirradiated areas in the thin films of **1** is very important for lithographic applications. Therefore, we investigated the treatment of the samples with various solvents after the imaging step. Indeed, adhesion of the endoperoxide to the substrate was slightly stronger and the nonexposed regions exhibited selective flaking in hexane as the most suitable solvent for several minutes. The three steps of imaging, developing, and regeneration of the parent anthracene are demonstrated in Figure 5. After irradiation and developing in hexane, the sample was heated at 120 °C for two hours. The fluorescent anthracene returned to the exposed areas, thereby providing a **positive** image of the initial photoimage (Figure 5A and C).

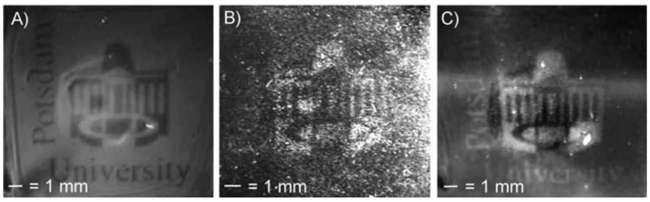


Figure 5. A) Fluorescence image of the irradiated thin film of **1**; B) optical image after dipping the sample into hexane for 1 min; C) fluorescence image after heating at 120 °C for 2 hr.

The patterns obtained from irradiation and subsequent developing were also studied by scanning force microscopy at micrometer resolution. The height of the remaining exposed region after dissolution of **1** was ~200 nm, with a mean roughness of 37 nm (Figure 6).

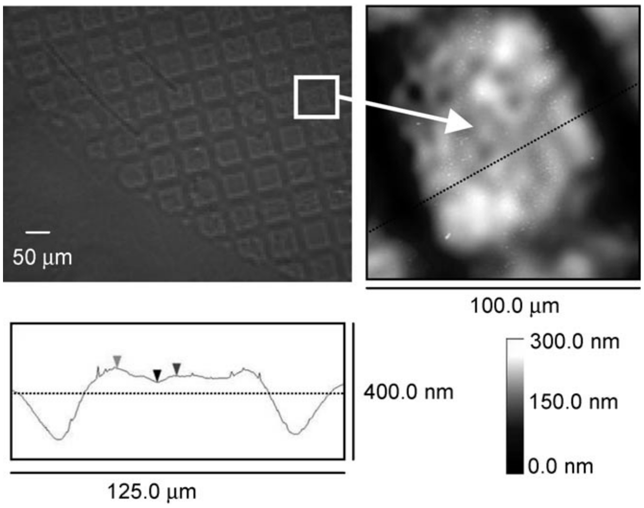


Figure 6. Imaging of a thin film of **1** after imaging and developing. Top left: microscope image; top right: tapping-mode AFM image of the area shown in the inset; bottom left: height profile.

Thus, anthracene **1** acts as a negative-tone photoresist that is finally unchanged after the developing process. In contrast to common techniques in photolithography that utilize solubility changes by cross-linking of the reactive material and are destructive, the photochromic compound **1** facilitates lithography with conservation of the material. Furthermore, this provides clear evidence for the reversibility of the [4+2] cycloaddition with singlet oxygen and the existence of endoperoxides as the sole photoproduct. Recurring fluorescence at the dark regions can arise only from endoperoxides that were reconverted to parent anthracenes by heating.

Finally, patterns that were introduced by photoimaging of the anthracene film of **1** and subsequent developing in hexanes could also be copied to another support, for example, a TLC slide. Thus, the glass slides that carried a pattern motif were used as stamps, in which the endoperoxide acts as an oxidizing ink. If the TLC slide was doped with iodide and brought into contact with the stamp, the pattern became visible on the TLC slide after gentle heating in response to the oxidation of iodide to iodine (Figure 7). Therefore, the oxidizing propensity of the endoperoxides is advantageous for lithographic applications because a **negative** image of the initial photoimage can be transferred directly to a peroxide-sensitive surface by means of an oxidizing ink. Such stamp technologies are often used in lithography and offer interesting perspectives for future applications.[24]

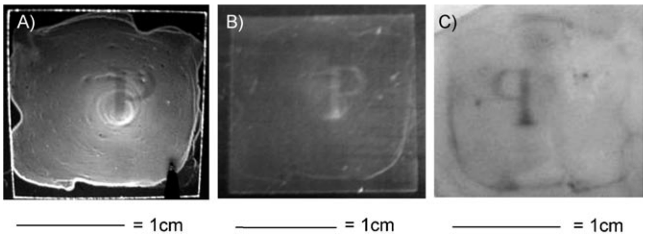


Figure 7. A) Fluorescence image of a thin film of **1** on a glass slide. B) Optical image after developing in hexane. C) Image of a TLC slide doped with KI after pressing against the glass slide and heating at 60 °C.

In conclusion, our new anthracene films allow the generation of a **positive** image by simply washing and heating, and a **negative** image through an iodide-developing process.

Investigation of thermoreversibility: Heating of irradiated samples afforded the initial anthracene species **1** and **2** accompanied by the release of dissociated oxygen. As the compounds studied have thermal transitions occurring in different regions, heating was carried out at different temperatures and, therefore, for different durations. The course of the thermolysis was monitored by recording the UV-visible spectra until the absorption intensity of the anthracene chromophore was same as that before irradiation and did not change upon further heating. The required time for a complete reconversion of the parent anthracene was 10, 120, and 600 min at 160, 120, and 100 °C, respectively. As we have reported previously,[14] the recovery of thin films of **1** doped with a sensitizer was not quantitative, and progressive decomposition of the photosensitive material was observed after repetitive irradiation and heating. We attained improvements in the quantitative degree of reversibility if excitation of the anthracene chromophore was strictly excluded (Figure 1). Thus, photooxidations starting from the excited state of anthracene and dimerizations by [4+4] photocycloaddition were eliminated.[25] Surprisingly, the first cycle afforded almost 99 % of **1** at 120 °C. A loss of parent anthracene, however, occurred in the second cycle, in which only 88 % of **1** was recovered (Figure 8). The progressive decrease was linear. If the cycles were carried out by using compound **1** and TPP, the time for irradiation required for almost (>95 %) complete photooxidation increased nonlinearly. After four cycles the performance was unsatisfactory. The reduction in performance for photoconversion is a result of an abating production of singlet oxygen by the sensitizer. Figure 9 depicts how the chromophore of TPP, namely the discernable Soret band at 423 nm, shifts to longer wavelengths and disappears during the cycles, subsequent to the heating process. The shift and disappearance of the Soret band could originate from a physical aggregation of the porphyrin dye.[26] Such aggregations are generally accompanied by a broadening and diminishing Soret band. Alternatively, a chemical decomposition is possible.[27] Notably, even trace amounts of oxygenation products could suffice to decompose a small portion of the sensitizer.

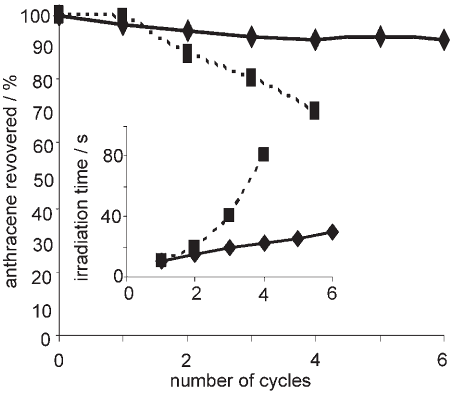


Figure 8. Percentage of recovered anthracene of films of **1** (◆) and **2** (■) during several cycles of complete photooxidation and thermolysis. Inset: time required for >95 % photooxygenation at each cycle.

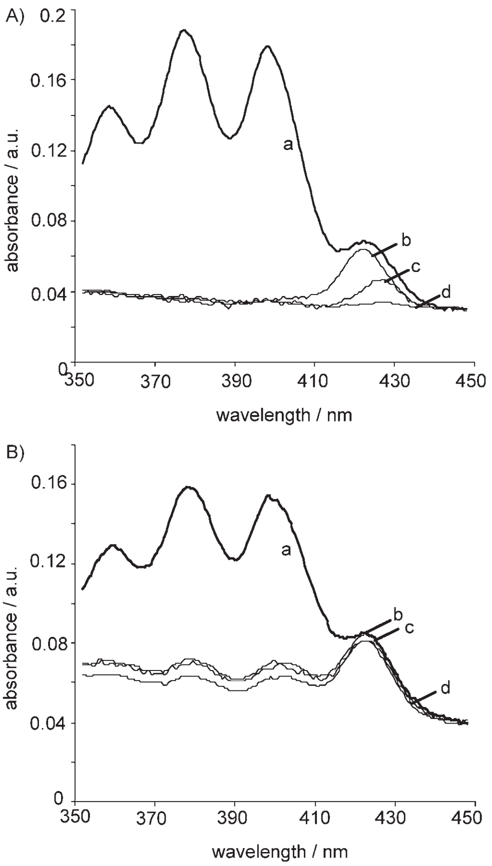


Figure 9. Absorbance spectra of a thin film of **1** (A) and **2** (B) mixed with TPP before irradiation (a), and directly after the first (b), second (c), and third (d) photooxygenation.

The observation that heating caused a red shift of the Soret band even with a nonirradiated film supports the first explanation of an aggregation of the sensitizer molecules. However, a complete disappearance occurred only if heating directly followed irradiation. Thus, we cannot exclude an additional chemical decomposition of the sensitizer. If oligomer **2** was employed under the same conditions, the decomposition of the anthracene species was almost negligible and the time required for a complete photooxygenation increased only slightly (Figure 8).

The Soret band of the sensitizer remained unchanged during the cycles of irradiation and heating (Figure 9).

This behavior is ascribed to the stabilizing effect of the oligomer backbone on the sensitizer molecules. Thus, the oligomeric compound **2** is superior to the monomer **1** for imaging by sensitized photooxygenations. These observations indicate the coherence between the decomposition of anthracene and the decreasing activity of the sensitizer during the cycles. Photooxidations proceed through two different pathways: the formation of $^1O_2$ and the subsequent [4+2] cycloaddition (Type II pathway), or through radical reactions from excited molecules (Type I pathway).[28] The first pathway produces endoperoxides and is reversible; the latter is responsible for irreversible decomposition and is usually slow and, thus, suppressed. We have discussed previously that the reduced lifetime of $^1O_2$ in a thin film is responsible for an increasing contribution from the undesired Type I pathway.[14] A higher proportion of the sensitizer may offset the physical quenching of $^1O_2$. If the production of $^1O_2$ drops due to the decreasing activity of the sensitizer, the conversion of the substrate will proceed along the second pathway, which also requires more irradiation time. However, the increasing contribution of light that is required for conversion is transferred to other channels of excitation in the film, for example, to exciplexes that do not sensitize the ground-state oxygen, but rather undergo chemical reactions. Thus, suitability as a photochromic material depends on properties that preserve the sensitizer, and this can be accomplished by using the oligomer **2**. Physical aggregation is clearly inhibited, but slight chemical decomposition of the sensitizer is still observed. We are currently synthesizing sensitizers with a higher stability to extend the lifetime of the photochromic materials.

Conclusion

Two anthracene derivatives were synthesized; one has a long alkyl chain, the other forms a side chain of an oligomer. Thin films of mixtures of each compound and a dye were applied as photochromic materials. Upon irradiation the monomeric compound exhibits remarkable changes in morphology. This behavior allowed the development of a new photoresist that produces **positive**, as well as **negative** patterns. Irradiation of thin films of the oligomer was accompanied by only reversible changes in the electronic structure. During multiple cycles, the oligomeric compound exceeds the photochromic performance of the monomeric species. The oligomer remains stable, whereas the monomeric anthracene and the sensitizer gradually decompose. Thus, the oligomer provides a firm and stable component for photochromic materials. On the other hand, the monomer displays interesting capabilities to act as a nondestructive negative-tone photoresist and as an oxidizing ink.

Experimental Section

General: Reagents of the highest commercial quality were purchased and were used without further purification. Flash chromatography was performed by using Merck silica gel 60 (230–400 mesh). NMR spectra were recorded by using a Bruker Avance 300 spectrometer. Molecular weights were measured by conducting gel-permeation chromatography (GPC) with THF as eluent and polystyrene as standard. Glass slides with a size of 1.8×1.8 cm were purchased from Roth, Germany. Before use, the slides were dipped into a mixture of ammonia/water/H_2O_2 (1:5:1) at 60°C for 10 min, then washed with triply distilled water, and dried at 120°C. Spin-coating films were prepared by using a SCI spin coater (Lot-Oriel) at 2000 rpm. Ellipsometry was performed by using a Multiskop Ellipsometer (Optrel) with a He:Ne laser at 70°C. The thickness was calculated by using a computer program and assuming a refractive index of 1.45 for the films. Static contact angles were measured by using a G10 (Kruss) contact-angle measurement instrument. UV/Vis and fluorescence spectra were recorded by using a Unicam UV3 spectrometer. Fluorescence microscopy measurements were recorded by using a Zeiss Axiostar (Zeiss, Germany) with an Hg-vapor lamp as light source. The excitations and emissions were filtered at 365 nm and 420 nm, respectively. All other fluorescence images were recorded by using a consumer digital camera and a 364-nm Hg light source. Atomic force microscopy (AFM) was performed by using a Nanoscope IIIa instrument operating in tapping mode. Commercial silicon nitride tips were used.

Syntheses

9-Bromo-10-phenylanthracene (3): 9-Bromo-10-phenylanthracene, (3), was synthesized according to a published procedure.[29]

4-(10-Phenylanthracen-9-yl)benzaldehyde (5): A two-phase solution of 9-bromo-10-phenylanthracene **3** (1 g, 3.0 mmol),[29] 4-formylphenylboronic acid (495 mg, 3.3 mmol), tetrakis(triphenylphosphine)palladium (240 mg, 0.02 mmol), and K_2CO_3 (2.4 g) in a solvent mixture of benzene (40 mL), water (16 mL), and ethanol (8 mL) was refluxed under argon for 24 h. The organic phase was separated, washed with brine, and dried over sodium sulfate. After evaporation of the solvent the crude product was precipitated in hexanes and was used for the next step without further purification. Yield: 945 mg (88%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 10.23$ (s, 1H), 8.16 (d, $J = 8.3$ Hz, 2H), 7.77–7.68 (m, 4H), 7.67–7.55 (m, 5H), 7.50 (d, $^3J = 8.0$ Hz, 2H), 7.41–7.34 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): $\delta = 192.41$ (d), 139.50 (d), 139.18 (d), 138.38 (d), 136.09 (d), 136.68 (d), 132.61 (d), 131.61 (d), 130.24 (s), 130.22 (s), 129.84 (s), 128.85 (s), 128.01 (s), 127.58 (s), 126.66 (s), 125.91 (s), 125.53 ppm (s).

9-[4-(10-Phenylanthracen-9-yl)benzyloxy]dodecanoic acid (1): Compound **5** (650 mg, 1.8 mmol) and 12-hydroxydodecanoic acid methyl ester (405 mg, 1.8 mmol) were dissolved in dry $CHCl_3$ (20 mL). Under an argon atmosphere, anhydrous $BiCl_3$ (140 mg, 0.4 mmol) and Et_3SiH (310 mg, 2.7 mmol) were added and the solution was stirred at RT for 12 h and quenched by addition of a saturated aqueous solution of NH_4Cl (10 mL). After the organic phase was separated and dried over sodium sulfate, the solvent was evaporated off and the residue was subjected to flash chromatography (hexane/EtOAc 10:1). Yield: 720 mg (70%) of a yellow solid. $R_f = 0.40$ (hexane/EtOAc 10:1).

The methyl ester was saponified in a refluxing solution of MeOH (10 mL) and water (2 mL) in the presence of NaOH (1 g) for 4 h. After evaporation of the solvent and acidification to pH 2, the aqueous solution was extracted three times with CH_2Cl_2. Drying and evaporation of the combined organic layers afforded 390 mg (98%) of **1**. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 7.71$–7.68 (m, 4H), 7.65–7.55 (m, 5H), 7.53–7.46 (m, 4H), 7.37–7.31 (m, 4H), 4.71 (s, 2H), 3.66 (t, $^3J = 6.6$ Hz, 2H), 2.36 (t, $^3J = 7.3$ Hz, 2H), 1.80–1.60 (m, 4H), 1.55–1.24 ppm (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): $\delta = 184.73$ (s), 139.49 (s), 138.64 (s), 138.35 (s), 137.49 (s), 137.33 (s), 131.74 (s), 131.72 (s), 130.31 (d), 130.27 (d), 128.79 (d), 128.09 (d), 127.85 (d), 127.39 (d), 127.35 (d), 125.38 (d), 125.35 (d), 73.27 (t), 71.39 (t), 34.33 (t), 30.22 (t), 29.96 (t), 29.91 (t), 29.90 (t), 29.80 (t), 29.61 (t), 29.44 (t), 26.64 (t), 25.08 ppm (t); IR (KBr): $\tilde{\nu} = 3061$, 2923, 2851, 1706, 1439, 1392, 1293, 1132, 1098, 1029, 942 cm^{-1}; MS: m/z (%): 558 (100) [$M^+ + 1$]; elemental analysis calcd (%) for $C_{39}H_{42}O_3$ (558.3): C 83.87, H 7.52; found: C 83.58, H 7.17.

9-[4-(10-Phenylanthracen-9-yl)benzyloxy]hexanoic acid: This compound was synthesized under identical conditions to those described above by using **5** (1.7 g, 4.7 mmol), 6-hydroxyhexanoic acid ethyl ester (1.04 g, 4.7 mmol), $BiCl_3$ (346 mg, 1.0 mmol), and Et_3SiH (565 mg, 7.0 mmol) in CH_2Cl_2 (20 mL). Yield after chromatography (hexane/EtOAc 10:1): 1.6 g (68%).

Saponification was carried out with 1 g of the ester under the same conditions as for **1**. Yield: 870 mg (95%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 7.69$–7.78 (m, 4H), 7.57–7.64 (m, 5H), 7.46–7.52 (m, 4H), 7.31–7.37 (m, 4H), 4.69 (s, 2H), 3.66 (t, $^3J = 6.5$ Hz, 2H), 2.43 (t, $^3J = 7.3$ Hz, 2H), 1.7–1.81 (m, 4H), 1.49–1.6 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): $\delta = 179.4$ (s), 139.4 (s), 138.6 (s), 138.2 (s), 137.5 (s), 137.2 (s), 131.7 (d), 131.7 (d), 130.3 (s), 130.2 (s), 128.7 (d), 128.0 (d), 127.8 (d), 127.3 (d), 127.3 (d), 125.3 (d), 125.3 (d), 73.3 (t), 70.9 (t), 34.2 (t), 29.8 (t), 26.1 (t), 24.9 ppm (t); elemental analysis calcd (%) for $C_{35}H_{34}O_3$ (502.3): C 83.66, H 6.77; found: C 83.14, H 6.26.

9-Phenyl-10-(4-vinylphenyl)anthracene (7): A solution of 4-vinylphenylboronic acid (1 g, 6.75 mmol), **3** (1.8 g, 5.4 mmol),[29] tetrakis(triphenylphosphine)palladium (240 mg, 0.02 mmol), and K_2CO_3 (2.4 g) in a solvent mixture of benzene (40 mL), water (16 mL), and ethanol (8 mL) was refluxed under argon for 24 h. The organic phase was separated, washed with brine, and dried over sodium sulfate. After evaporation of the solvent the crude product was precipitated in hexanes and was used for the next step without further purification. The product was purified by flash chromatography (hexane/EtOAc 10:1) to afford 1.27 g (66%) of the anthracene **7**. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.56–7.78 (m, 9H), 7.44–7.52 (m, 4H), 7.32–7.39 (m, 4H), 6.92 (dd, ^3J_a=10.8 Hz, ^3J_b=17.6 Hz, 1H), 5.95 (d, ^3J_b=17.6 Hz, 1H), 5.39 ppm (d, ^3J_a=10.8 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=139.4 (s), 139 (s), 137.5 (s), 137.1 (s), 137.0 (d), 131.9 (d), 131.7 (d), 130.2 (s), 130.2 (s), 128.7 (d), 128.7 (d) 127.8 (s), 127.3 (d), 127.2 (d), 126.6 (d), 125.4 (d), 125.3 (d), 114.5 ppm (t); elemental analysis calcd (%) for $C_{28}H_{20}$ (356.0): C 94.38, H 5.61; found: C 93.42, H 5.66.

Oligomerization from monomer 7 to compound 2: Monomer **7** (200 mg, 0.6 mmol) and azobisisobutyronitrile (AIBN) (5 mg) were dissolved in anhydrous THF (10 mL) and refluxed under argon for 6 h. The precipitate formed was filtered off and was dissolved in CH_2Cl_2. Yield of precipitate: 80 mg (40%). Average molecular weight (M_w): 3120 g mol^{-1}; weight dispersity: 2.53; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=6.8–7.8 (br, 17H), 1.8–2.5 (br, 1H), 1.0–1.5 ppm (br, 2H).

Sample preparation: For UV/Vis absorption measurements, **1** or **2** (40 μmol, ~20 mg) were dissolved in CH_2Cl_2 (4 mL). Solutions of 1.6×10^{-3} M of the sensitizers methylene blue (MB) and *meso*-tetraphenylporphyrin (TPP) were prepared in CH_2Cl_2. Aliquots of the sensitizer solutions were added to the solutions of the anthracenes and a volume of 60 μL was dropped onto a glass slide. After evaporation of the solvent, the samples were placed into a sample holder.

Imaging: Samples were prepared from either drop coating or spin coating.

Drop coating: The sensitizer solution (30 μL) was added to the anthracene (20 mg) dissolved in CH_2Cl_2 (4 mL). An amount (60 μL) of this solution was dropped onto the glass slide and the solvent was allowed to evaporate.

Spin coating: Films were prepared from solutions of the anthracene (20 mg) in CH_2Cl_2 (1 mL) and the sensitizer solution (30 μL).

Samples were covered with a transparent film and irradiated with a 20 W halogen lamp for 10 min at a distance of 10 cm, with a high-pass filter with a 515 nm cut-off placed between the sample and the light source. The sample for AFM measurement was obtained by irradiation through a TEM grid of 50 μm grid size, with a blank transparent film between the grid and the sample.

Development: Immediately after irradiation, the samples were dipped into hexanes for 2 min and dried in air. AFM was carried out in tapping mode on a glass slide.

Thermolysis: Heating of the irradiated glass slides was carried out in a protective glass vial in an oven at constant temperature.

Acknowledgements

We thank Anne Heilig for AFM measurements. Generous financial support from the Deutsche Forschungsgemeinschaft (DFG, Li 556/9-1) and from the Graduate School "Confined Interactions and Reactions in Soft Matter" is acknowledged.

---

[1] For a comprehensive overview, see: *Photochromism Molecules and Systems* (Eds.: H. Durr, H. Bouas-Laurent), Elsevier, Amsterdam, **2003**; "Photonic and Optoelectronic Polymers": ACS Symp. Ser. **1997**, *672*.

[2] M. Emmelius, G. Pawlowski, H. W. Vollmann, *Angew. Chem.* **1989**, *101*, 1475–1502; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1445–1471.

[3] M. Heilemann, E. Margeat, R. Kasper, M. Sauer, P. Tinnefeld, *J. Am. Chem. Soc.* **2005**, *127*, 3801–3806; R. Hagen, T. Bieringer, *Adv. Mater.* **2001**, *13*, 1805–1810; G. H. Springer, D. A. Higgins, *Chem. Mater.* **2000**, *12*, 1372–1377; S. Kawata, Y. Kawata, *Chem. Rev.* **2000**, *100*, 1777–1788.

[4] M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716.

[5] A. Romani, G. Chidichimo, P. Formoso, S. Manfredi, G. Favaro, U. Mazzucato, *J. Phys. Chem. B* **2002**, *106*, 9490–9495.

[6] K. Horie, S. Murase, S. Takahashi, M. Teramoto, H. Furukawa, *Macromol. Symp.* **2003**, *195*, 201–208; E. Kim, Y.-K. Choi, M.-H. Lee, *Macromolecules* **1999**, *32*, 4855–4860.

[7] K. Higashiguchi, K. Matsuda, N. Tanifuji, M. Irie, *J. Am. Chem. Soc.* **2005**, *127*, 8922–8923; K. Matsuda, M. Matsuo, M. Irie, *J. Org. Chem.* **2001**, *66*, 8799–8803; J. Biteau, F. Chaput, K. Lahlil, J.-P. Boilot, G. M. Tsivgoulis, J.-M. Lehn, B. Darracq, C. Marois, Y. Levy, *Chem. Mater.* **1998**, *10*, 1945–1950.

[8] Y. Yokoyama, *Chem. Rev.* **2000**, *100*, 1717–1740.

[9] S. Nakamura, M. Irie, *J. Org. Chem.* **1988**, *53*, 5136–5138.

[10] R. Schmidt, W. Drews, H. D. Brauer, *J. Phys. Chem.* **1982**, *86*, 4909–4913.

[11] For reviews on singlet-oxygen chemistry, see: W. Adam, D. V. Kazakov, V. P. Kazakov, *Chem. Rev.* **2005**, *105*, 3371–3387; E. L. Clennan, A. Pace, *Tetrahedron* **2005**, *61*, 6665–6691; W. Adam, M. Prein, *Acc. Chem. Res.* **1996**, *29*, 275–283; A. G. Griesbeck, T. T. El-Idreesy, A. Bartoschek, *Pure Appl. Chem.* **2005**, *77*, 1059–1074.

[12] H. Ito, T. Ikeda, K. Ichimura, *Macromolecules* **1993**, *26*, 4533–4538; E. Takeuchi, Y. Tajima, K. Takeuchi, T. Hosomi, *J. Photopolym. Sci. Technol.* **2000**, *13*, 351–356.

[13] T. Linker, L. Fröhlich, *Angew. Chem.* **1994**, *106*, 2064–2066; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1971–1972; T. Linker, L. Fröhlich, *J. Am. Chem. Soc.* **1995**, *117*, 2694–2697; T. Linker, F. Rebien, G. Tóth, *Chem. Commun.* **1996**, 2585–2586; V. Nardello, J.-M. Aubry, T. Linker, *Photochem. Photobiol.* **1999**, *70*, 524–530.

[14] W. Fudickar, A. Fery, T. Linker, *J. Am. Chem. Soc.* **2005**, *127*, 9386–9387.

[15] J.-M. Aubry, C. Pierlot, J. Rigaudy, R. Schmidt, *Acc. Chem. Res.* **2003**, *36*, 668–675.

[16] C. Schweitzer, R. Schmidt, *Chem. Rev.* **2003**, *103*, 1685–1758; I. Zebger, L. Poulsen, Z. Gao, L. K. Andersen, P. R. Ogilby, *Langmuir* **2003**, *19*, 8927–8933.

[17] K. B. Eisenthal, N. J. Turro, C. G. Dupuy, D. A. Hrovat, J. Langan, T. A. Jenny, E. V. Sitzmann, *J. Phys. Chem.* **1986**, *90*, 5168–5173; N. J. Turro, M. F. Chow, *J. Am. Chem. Soc.* **1981**, *103*, 7218–7224; N. J. Turro, M.-F. Chow, J. Rigaudy, *J. Am. Chem. Soc.* **1979**, *101*, 1300–1302.

[18] R. Schmidt, E. Afshari, *J. Phys. Chem.* **1990**, *94*, 4377–4378; J. J. M. Lamberts, D. R. Schumacher, D. C. Neckers, *J. Am. Chem. Soc.* **1984**, *106*, 5879–5883.

[19] P. R. Ogilby, M. P. Dillon, M. Kristiansen, R. L. Clough, *Macromolecules* **1992**, *25*, 3399–3405; R. L. Clough, M. P. Dillon, K.-K. Iu, R. R. Ogilby, *Macromolecules* **1989**, *22*, 3620–3628; P. R. Ogilby, K.-K. Iu, R. L. Clough, *J. Am. Chem. Soc.* **1987**, *109*, 4746–4747; N. J. Turro, M.-F. Chow, M. Blaustein, *J. Phys. Chem.* **1981**, *85*, 3014–3018.

[20] A. Schumpe, P. Lüring, *J. Chem. Eng. Data* **1990**, *35*, 24–25.

[21] B. Stevens, S. R. Perez, J. A. Ors, *J. Am. Chem. Soc.* **1974**, *96*, 6846–6850.

[22] E. Braswell, *J. Phys. Chem.* **1968**, *72*, 2477–2482.

[23] J. S. Hargreaves, S. E. Webber, *Macromolecules* **1984**, *17*, 235–240.

[24] B. D. Gates, Q. Xu, M. Stewart, D. Ryan, C. G. Willson, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1823–1848.

[25] H.-D. Becker, *Chem. Rev.* **1993**, *93*, 145–147.

[26] K. Procházková, Z. Zelinger, K. Lang, P. Kubát, *J. Phys Org. Chem.* **2004**, *17*, 890–897; C. Tanielian, C. Wolff, M. Esch, *J. Phys. Chem.* **1996**, *100*, 6555–6560.

[27] M. Krieg, D. G. Witten, *J. Am. Chem. Soc.* **1984**, *106*, 2477–2479.

[28] E. L. Clennan, *Tetrahedron* **1991**, *47*, 1343–1382.

[29] X.-M. Zhang, F. G. Bordwell, J. E. Bares, J.-P. Cheng, B. C. Petrie, *J. Org. Chem.* **1993**, *58*, 3051–3059.

Received: March 17, 2006