Experimental Section

Liquid 60% hydrogen peroxide (3 mmol H_2O_2 min^{-1}) was sucked through fine teflon tubing into a flash evaporator at 90°C. The peroxide vapor mixed with gaseous silane (0.1–03 mmol min^{-1}) a few centimeters below where the template (substrate) was suspended in a pyrex glass reaction chamber. The sample and all internal surfaces of the reaction chamber became coated with silica at a rate of 50–200 nm min^{-1}. The layer thickness was adjusted through the amount of silane precursor and the reaction time. Subsequent pumping on the reaction chamber at 0.01 hPa assisted in removing side products as well as giving a highly condensed silica network. The organic template was removed by calcination at 500°C in air. As known from earlier studies of the deposition on silicon wafers, silane can be replaced by the less pyrophoric methylsilane to give silica containing only a very small amount of organic groups.[6]

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Patterned Polymer Brushes

Surface-Initiated Polymerization on Self-Assembled Monolayers: Amplification of Patterns on the Micrometer and Nanometer Scale**

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The application of highly ordered self-assembled monolayers (SAMs) as initiator systems for surface-initiated polymerization (SIP) allows the preparation of uniform and densely grafted polymer brushes. This so-called "grafting from" technique was demonstrated for nearly all types of polymerization,[1] including living anionic[2] and cationic SIP.[3] One important aspect offered by the use of SAM systems as two-dimensional initiator systems is the possibility to control the locus of the initiator sites within a SAM, for example, to finetune the grafting density of the resulting polymer brush by using mixed SAMs,[4] to prepare two-component gradients,[5] or to fabricate complex spatial structures at various length scales. The latter can be formed by various techniques, in particular by microcontact printing (µCP) for structures ranging from 0.1 to several hundred micrometers.[6, 7] For patterning on the nanometer scale, SPM-based techniques for the manipulation of SAMs such as "dip-pen nanolithography",[8] "nanografting", or "nanoshaving"[9] were recently developed.

A combination of directed deposition of functionalized areas of SAMs and consecutive SIP allows a superior control of pattern formation and amplification of the patterns by creating polymer-brush layers at predefined sites. Surface defects, present in all SAM systems, as well as topological features of the substrate are covered by a significantly thicker layer of a flexible polymer brush. The resulting structures display a better contrast between the functionalized and

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unfunctionalized areas in terms of their chemical and physical properties (e.g. interfacial roughness, wetting behavior, thermal stability, etch resistance, etc.). The wide variety of recently developed combined SAM/SIP systems allows the production of tailor-made surfaces for a given technological application.

This approach was first demonstrated by using contact-printed SAMs of ω-functionalized alkane thiols, passivation of the uncovered areas by inert n-alkyl thiols, and subsequent SIP of N-carboxy anhydrides,[10] ε-caprolactone,[11] or norbornene derivatives.[12] The created polymer-brush layers amplified the originally printed SAM structures. The lateral resolution of features obtained with this technique ranged from 2–50 μm. With the same technique, spatially resolved free[13] and controlled[14] radical SIP as well as step polymerization for the preparation of hyperbranched polymers[15] was carried out on printed SAMs. The advantages of SAM structure amplification by SIP was demonstrated by an improved etch resistance as a function of the brush-layer thickness and by the selective adsorption of cells.

In another approach, surface patterns can be created by selective UV irradiation of homogeneous SAMs of photoinitiators through a mask or processed photo resists.[16] Although the lateral resolution is limited, this approach allows a repetitive SIP on the same substrate, resulting in chemically heterogeneous polymer-brush surfaces.[17] Both techniques, however, are intrinsically limited by means of the obtainable structure size and the stability of the original SAM system.

Recently, some of us developed chemical lithography, a technique that utilizes specific reactions between the SAMs and electron beams for nanopatterning.[18, 19] The name was chosen, since electron irradiation of SAMs of, for example, 4′-nitro-1,1′-biphenyl-4-thiol (NBT) results in selective and quantitative reduction of the nitro functionalities to amino groups,[20] while the aromatic biphenyl layer is dehydrogenated and cross-linked.[21] Hence, the local irradiation of SAMs can be used for the chemically selective binding of functional entities by using the terminal amino group.

In contrast to the above-mentioned techniques based on scanning probe microscopy and microcontact printing, chemical lithography is not restricted to any length scale since the use of electron-flood guns in combination with adequate stencil masks allows an efficient patterning of large areas. For high-resolution patterning, electron beams can be focused to nanometer-sized spots, and the resolution is only limited by secondary electrons that are generated during irradiation. The smallest SAM structures that have been generated with electron beams are about 5 nm in size;[22] thus far, the smallest chemical nanostructures obtained by chemical lithography had lateral dimensions of ~20 nm.[18, 19]

The selectivity, flexibility, high throughput, and superior resolution of chemical lithography make it an ideal technological platform for the preparation of structured, functionalized SAM patterns that can be amplified by SIP. Herein we present a facile method for the conversion of patterns created by irradiation of NBT SAMs through a mask into patterned polymer-brush systems.

The preparation of initiator sites and a consecutive polymerization was first carried out without structuring: A SAM of NBT on Au(111) was converted into cross-linked 4′-amino-1,1′-biphenyl-4-thiol (cABT) SAM by irradiation with electron beams, as previously reported (50 eV with an electron dose of 20000 μC cm^{-2} or 300 eV with 40000 μC cm^{-2}).[20] The terminal amino groups were then diazotized and treated with methylmalonodinitrile to give a surface-bound monolayer of the 4′-azomethylmalonodinitrile-1,1′biphenyl-4-thiol (cAMBT) (Figure 1). Phenyldiazenylalkylmalonodinitriles and their derivatives are suitable second-generation initiators for the radical polymerization of a broad variety of vinyl compounds to prepare graft copolymers in solution,[23] as well as for SIP.[17, 24] In contrast to commonly used symmetric azo initiators, thermal or photoinitiated decomposition yields a highly reactive, bound (in our case) phenyl radical and a free, stable malonodinitrile radical, which is not capable of initiating radical polymerization owing to its resonance stabilization. In other words, by the decomposition of the surface-bound, asymmetric phenylazoalkyl initiator, the polymerization is only initiated at the surface and not by a cleaved free radical in solution, as is the case with dialkylazo initiators.[25] Furthermore, previous results indicate that the radical polymerization initiated by phenylazomethylmalonodinitrile follows a controlled polymerization mechanism: in "grafting from" reactions the degree of polymerization of the side chains can be varied with the reaction time and the typical polydispersity index is significantly lower ($M_w/M_n \sim 1.4$) than in free-radical polymerization.[26]

The monolayer of cAMBT was then exposed to a solution of styrene in toluene and heated to 80°C, and the polymerization was thus started by thermal decomposition of the SAM initiator system. After a reaction time of 6 hours, unbound polystyrene was removed from the substrate surface by Soxhlet extraction. Inspection of the substrate surface with FTIR spectroscopy, scanning probe microscopy (SPM), and ellipsometry revealed that the surfaces were homogeneously covered by a polystyrene brush layer of 6.3 nm.[27, 28] The surface modification proved to be surprisingly stable at elevated temperatures and resistant to solvent extraction (Soxhlet) as a result of the cross-linked SAM support and the known stabilization effect of the polymer brush itself.[2, 3a] The SPM scans of the polymer brush, contrary to those of the native polycrystalline gold substrate, showed the rendering of the single gold crystals, with a decrease in the step height of individual crystals from ~2.5 nm to approximately 1 nm and a small decrease in the root-mean-square roughness value to 0.7 nm (from 0.9 nm for the original surface roughness of the gold substrate).

The structured polystyrene brushes were prepared by following the same procedures (Figure 1a–d), but the irradiation was performed through a stencil mask with circular openings of 800-nm radii[29] which was placed on the NBT-covered substrate. Figure 2a shows an scanning electron micrograph recorded at an electron energy of 3 keV using the "in-lens" detector, which is particularly sensitive to secondary electrons emitted from the sample surface. The contrast results from the differences in the secondary electron yield from the original SAM/gold substrate and the thin polystyrene film. The dark dots represent areas where NBT was
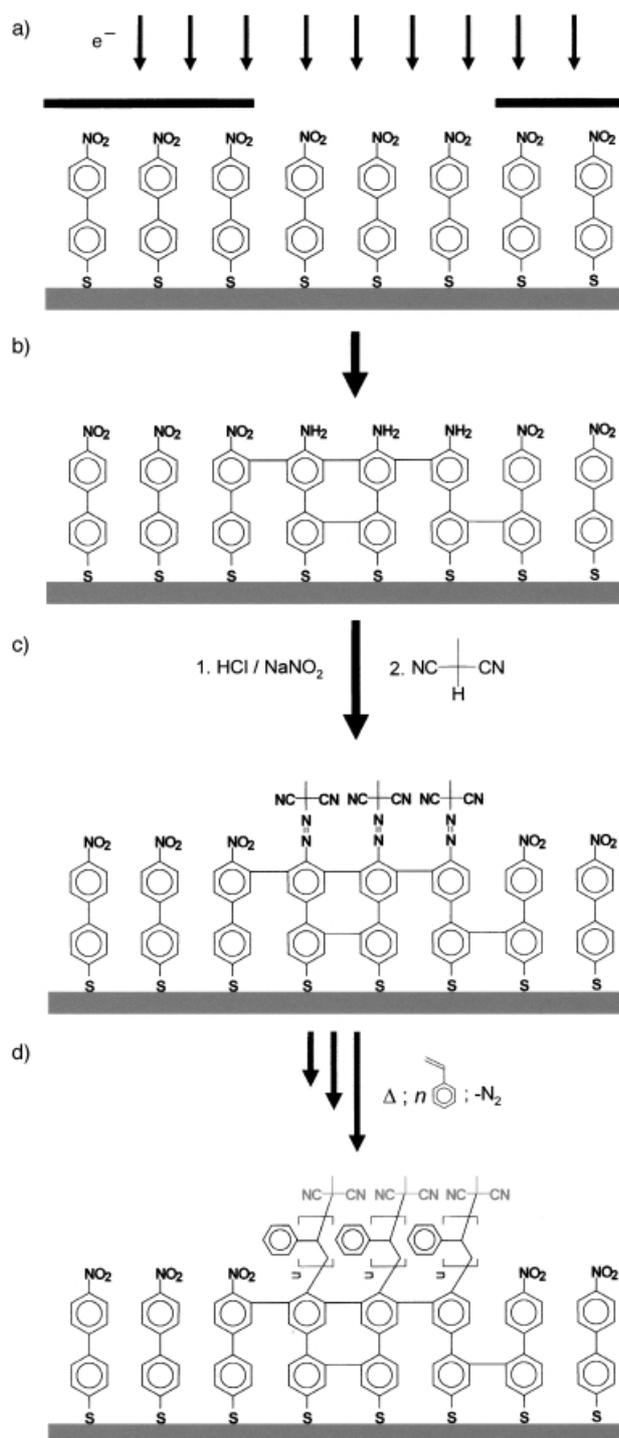
Figure 1. Reaction scheme starting from SAMs of NBT on Au(111). a) Exposure of the monolayer to electron beams. b) This irradiation results in intralayer cross-linking and conversion of the terminal nitro groups into amino groups, thus forming cABT. c) Diazotization and coupling with malonodinitrile gives a SAM that bears an asymmetric azo initiator (cAMBT). d) Finally, by exposure to a vinyl monomer (styrene) and heating at 80°C, the radical polymerization results in a polymer brush layer at the irradiated areas.

Figure 2. a) Scanning electron micrograph of polystyrene brushes generated by SIP on a substrate that was irradiated through a stencil mask with a coarse grid with a 60-μm periodicity. Each square contains an array of circular holes (1.6-μm diameter, 2.5-μm periodicity). b) SPM image of a small area of the same substrate, together with a height profile along the indicated line.

converted into cABT by irradiation, which reacted further to form cAMBT, and where SIP of styrene took place. The selectivity and uniformity of the process on this large scale is significant. We further investigated the surface topography by SPM (Figure 2b), which revealed typical heights of the polystyrene spots of 6 nm, a diameter of 1.6 μm; the spots were spaced with a periodicity of 2.5 μm. This pattern reflects a one-to-one translation of the original mask at the surface. Investigation of different areas by SPM showed nearly no variation of the structures.

As a test of the potential of our approach, a stencil mask made by focused ion-beam milling[21] with slits between 50 and 300 nm wide, was also used for the selective irradiation and amplification by SIP. The SPM micrographs of the

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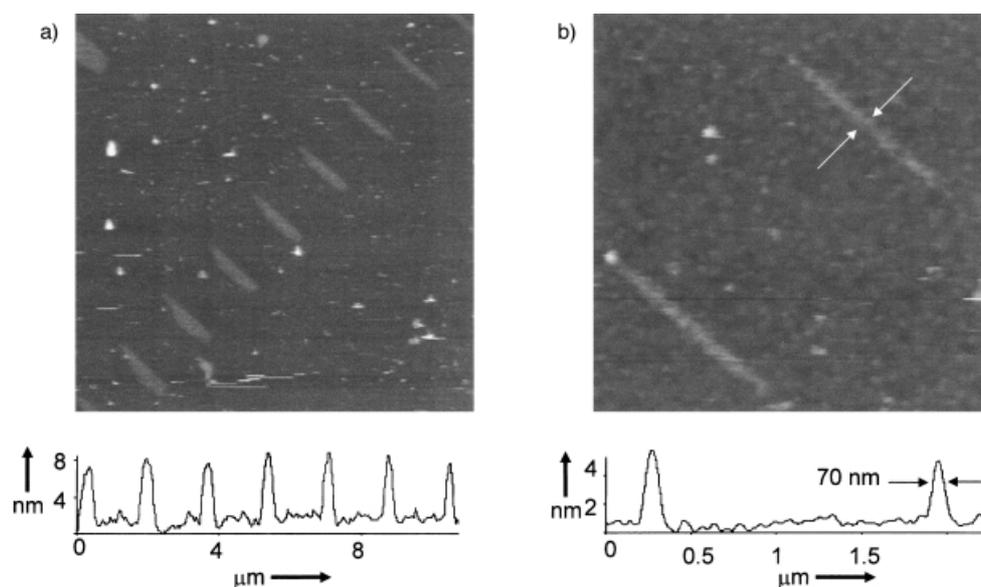
Figure 3. AFM micrographs of polystyrene brushes, which were generated by irradiation of an NBT SAM with a stencil mask with a slit pattern and subsequent SIP. The height profiles show an average profile with lines of width ~200 nm (a) and ~70 nm (b).

resulting polystyrene brush-line structures together with averaged height profiles are depicted in Figure 3. Again, SIP was limited to the NBT SAM originally exposed to radiation, resulting in a one-to-one translation of the mask pattern in the nanometer range.

These structures created by the combination of chemical lithography and SIP are significantly smaller than features produced by using previously known techniques.[10–15] This approach allows the choice of surface structures that can be created and the material contrast that can be realized by the combination of chemical lithography and amplification with SIP. Furthermore, micrometer- as well as nanometer-sized features can be generated in a single step.

Experimental Section

The polycrystalline gold films on silicon were obtained from Albert Coatings.[30] The preparation of the SAMs as well as the irradiation by low-energy electrons was performed as previously reported.[18,20,21] FTIR spectra were recorded on a Bruker IFS55 spectrometer equipped with an FT-80 external reflection setup from SpectraTech. AFM images were obtained in the tapping mode with a Nanoscope IIIa scanning probe microscope from Digital Instruments or with an Autoprobe CP scanning probe microscope from Park Scientific. Scanning electron micrographs were obtained with a LEO 1530 electron microscope with a primary electron energy of 3 kV and an in-lens detector for secondary-electron detection.

Preparation of the cAMBT/Au initiator system: The irradiated substrates bearing SAMs of cross-linked cABT were diazotized at 4°C by treatment with an aqueous solution of HCl (0.5 mL HCl$_{conc.}$ in 2 mL water) and subsequent treatment with sodium nitrite (1 mmol) in water (2 mL). Finally, the azo initiator was prepared by the reaction of the substrate with methylmalonodinitrile[31] and sodium acetate (1 g) in water/ethanol (2.5 mL:1.5 mL) for at least 15 min.

Polymerization: A freshly prepared functionalized substrate was added to an oxygen-free solution of toluene (2 mL) and styrene (1 mL) and heated at 80°C (for polymerization times, see text). After the reaction, all substrates were cleaned by Soxhlet extraction with toluene for at least 12 h.

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[27] The external reflection FTIR spectra of the purified surfaces (Soxhlet extraction, toluene, 12 h) confirmed that in all cases a layer of covalently attached polystyrene was formed (typical absorption bands: ($\tilde{v}$ in cm^{-1}): CH aromatic stretching: 3102, 3018, 3060, 3026, 2999; CH aliphatic stretching: 2922, 2848; overtones of CH out-of-plane fundamentals for monosubstituted aromatic rings: 1945, 1867, 1795; ring breathing: 1602, 1493, 1452, CH deformation modes (out-of-plane): 758, 698.

[28] Quantitative analysis of the film thickness as a function of the polymerization time and irradiation conditions are currently underway. However, the film thickness steadily increases with the time of polymerization, although not as rapidly as reported in reference [17] for the photoinitiated polymerization in the presence of a similar initiator.

[29] The stencil mask was obtained from Quantifoil Micro Tools, Jena, Germany.

[30] Georg Albert PVD-Coatings, Heidelberg, Germany (GeorgAlbert@web.de).

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Radical Anion Complexes

Coordinated *o*-Dithio- and *o*-Iminothiobenzosemiquinonate(1−) π Radicals in [M^{II}(bpy)(L·)](PF$_6$) Complexes**

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Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday

o-Benzosemiquinonate(1−) π-radical anions are archetypical open-shell, bidentate ligands in the coordination chemistry of transition-metal ions[1] but for their *o*-dithio derivatives the situation is not clear. The existence of S,S-coordinated *o*-dithiobenzosemiquinonate(1−) radical anions (rather than their closed-shell, aromatic *o*-dithiolate dianions) has occasionally been suggested[2] to occur in some complexes but—at times—has also been explicitly denied.[3] Clear experimental evidence is lacking to date. Similarly, recently it has been shown indirectly that *o*-iminobenzosemiquinonate(1−) π radical ions[4] and their sulfur analogues[5] as well as *o*-diiminobenzosemiquinonate(1−)[6] π radical anions (Scheme 1) are coordinated in diamagnetic, square-planar complexes [Ni^{II}(X·)$_2$]. Density functional theoretical (DFT) calculations have shown that the electronic structure of these species is in accord with the description as singlet diradicals.[7]

Here we report the synthesis and characterization of diamagnetic square-planar neutral complexes of Pd^{II} and Pt^{II} containing a *single* aromatic (L)$^{2−}$ ligand and a 2,2′-bipyridine ligand (Scheme 1): [M^{II}(bpy)(X)]^0 (**1–5**). We show that complexes **1–5** undergo a reversible, ligand-centered one-electron oxidation yielding paramagnetic complexes [M^{II}(bpy)(X·)](PF$_6$) (**1a–5a**) with a $S = \frac{1}{2}$ ground state and a coordinated π radical anionic ligand (L·)$^−$.

The following complexes have been isolated as solid materials: [Pd^{II}(bpy)(A)] (**1**), [Pd^{II}(bpy)(A·)](PF$_6$) (**1a**), [Pd^{II}bpy)(B·)](PF$_6$) (**2a**), [Pd(bpy)(C)] (**3**), [Pd^{II}(bpy)(D)] (**4**), [Pd^{II}(bpy)(D·)](PF$_6$) (**4a**), [Pt^{II}(bpy)(E)] (**5**), and [Pt^{II}(bpy)(E·)](PF$_6$) (**5a**).

The reaction of [M(bpy)Cl$_2$] (M = Pd, Pt) and the respective ligand H$_2$[A], ...H$_2$[E] (1:1) in CH$_3$CN or THF in the presence of two equivalents of a base (NaOCH$_3$, BH$_4$$^−$, or NEt$_3$) under argon led to the formation of the neutral species **1, 3**, and **5**, which were isolated as dark blue needles (**1**) or dark green crystals (**3** and **5**). The oxidized species **1a** (dark

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