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Grafting a homogeneous transition metal catalyst onto a silicon AFM probe: a promising strategy for chemically constructive nanolithography†

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We report a novel approach to chemically selective lithography using an atomic force microscope (AFM) probe with immobilized homogeneous catalyst, potentially giving access to diverse nanoscale transformations of the surface-bound functional groups. This new concept was proven for the local epoxidation of an alkene-terminated self-assembled monolayer on silicon using H₂O₂ as an oxidant and a catalytic silicon AFM tip charged with manganese complexes with 1,3,7-triazacyclononane type ligands.

Introduction

Scanning probe lithography (SPL) is actually one of the most promising tools for the creation of specific nanosized patterns on a surface, within spatial resolutions in the range of 10–100 nm.¹ The majority of SPL methods are based on the controlled diffusion transfer of a reagent from an atomic force microscope (AFM) tip to a surface *via* water meniscus (dip-pen nanolithography (DPN)²), electrical (local oxidation nanolithography³) or mechanical (nanoshaving and nanografting^{3a,4}) interaction of the AFM probe with the surface. Combinations of these techniques are also possible, for instance electrochemically assisted DPN⁵ or DPN combined with nanografting,⁶ or nanoshaving coupled with AFM tip induced metal electrodeposition.⁷

In spite of the rapid progress of SPL techniques during the past two decades, spatially controlled chemically selective transformations of organic functional groups of the self-assembled monolayers (SAMs) are still quite rare and remain highly challenging. In this way AFM driven electro-oxidation of the terminal vinyl,⁸ methyl,⁹ or thiol¹⁰ groups of SAMs have been performed to prepare, respectively, carboxylic acid and thio-sulfinate/thiolsulfonate surface domains. Local deprotection of α,α -dimethyl-3,5-dimethoxybenzyloxycarbonyl moieties using

positive and negative voltage bias was shown to give, respectively, free thiol¹¹ and primary amine¹² groups. Electrochemical aryl nitroso/arylamine transformation was reported to even take place reversibly using a regular AFM tip.¹³ Modified AFM tips coated with noble metals (Pd, Pt) or native copper(i) oxide allowed the catalysis of, respectively, local azide hydrogenation,¹⁴ alkene hydrosilylation^{14b} and 1,3-dipolar Huisgen cycloaddition reaction.¹⁵ Similarly AFM tips with adsorbed acid and palladium nanoparticles were used for silyl ether hydrolysis,¹⁶ Suzuki–Miyaura and Mizoroki–Heck cross coupling processes, respectively.¹⁷

Despite the great interest in such AFM-driven surface nanochemistry, the scope of these SPL methods is actually limited to redox-induced transformations, acidic hydrolysis, and reactions catalyzed by proper heterogeneous catalysts. The combination of AFM with homogeneous catalysis could provide new opportunities for a wide variety of chemically selective surface reactions with high spatial resolution. We report herein the first example of the SPL approach using an AFM probe with an immobilized homogeneous transition metal catalyst, illustrated by spatially controlled surface alkene epoxidation (Scheme 1).

Results and discussion

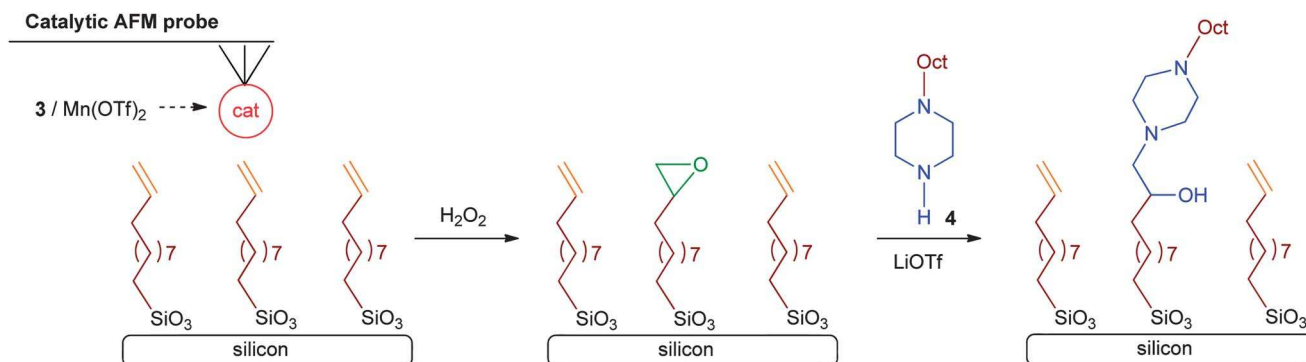
Alkene epoxidation belongs to the most important reactions in organic chemistry because of possible highly regio- and stereoselective nucleophilic opening of the epoxide ring.¹⁸ To our knowledge, no examples of local alkene epoxidation on SAMs have been reported to date using either SPL techniques or microcontact printing. The development of such a process could provide new perspectives in materials science and nanotechnology since the surface-bound epoxide moieties are extensively used as anchoring sites for the covalent grafting of simple peptides,¹⁹ proteins and enzymes,²⁰ as well as for the

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† Electronic supplementary information (ESI) available: Complete experimental procedures, AFM characterization data of the 3/Mn(OTf)₂ pre-catalyst immobilized on the silicon wafer, description of the home-built AFM liquid cell. See DOI: 10.1039/c3sc50979f



Scheme 1 Local alkene SAM epoxidation by a catalytic AFM probe, loaded with $\text{Mn}(\text{OTf})_2$ /ligand **3** and H_2O_2 as co-oxidant in acetonitrile, followed by AFM-free nucleophilic ring-opening reaction of epoxide sites with amine **4**.

fabrication of highly ordered thin layers of zeolites,²¹ polymers²² and cyclodextrins.²³

Irreversible self-assembly of various organosilanes onto a silicon support to form well-ordered and mechanically robust SAMs²⁴ prompted us to choose in our epoxidation nanolithography the SAM of commercially available 10-undecenyltrichlorosilane (Scheme 1) as an alkene substrate²⁵ and regular silicon AFM probes as homogeneous catalyst carriers, both protected from leaching to ensure the best spatial reaction control. The use of an appropriate AFM tip should allow facile switching between the epoxidation (writing) procedure in the AFM contact mode^{14–17} and characterization (reading) in the AFM tapping mode, which is less destructive for the surface and prevents undesired background epoxidation.²⁶

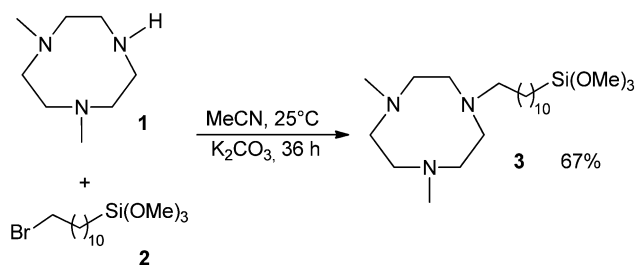
Owing to the wide variety of known supported transition metal alkene epoxidation catalysts,²⁷ and in order to target the catalytic system well adapted to AFM experiments 1,4,7-triazacyclononane (tacn) ligated manganese complexes were selected. These have been shown to be highly active and selective for the epoxidation of terminal aliphatic alkenes at 0–25 °C in acetonitrile both in homogeneous²⁸ and immobilized on silica²⁹ versions using aqueous H_2O_2 as an oxygen atom source (and alone absolutely unreactive towards alkenes). In addition, this catalytic system is stable towards air and moisture and could be easily immobilized on a silicon support.

For an AFM driven epoxidation process and in order to facilitate the mutual penetration of the catalyst and alkene SAM fragments in such a doubly heterogeneous process, a tacn-type ligand **3** (Scheme 2) bearing a long flexible alkyl chain between

the silane anchoring group and macrocyclic core was designed. After thorough tuning of the reaction conditions,³⁰ compound **3** was prepared in 67% yield by the selective alkylation of the secondary amine function in the known macrocyclic precursor **1** with 11-bromoundecyltrimethoxysilane **2**.

A set of preliminary experiments confirmed the covalent grafting of **3** to a polished silicon wafer (5 mM solution of **3** in toluene, 25 °C, 72 h) and the successful doping of immobilized ligand **3** with $\text{Mn}(\text{II})$ triflate (MeOH, 25 °C, 1.5 h) by XPS analysis.³¹ It was also shown that $\text{3}/\text{Mn}(\text{OTf})_2$ immobilized on amorphous silica according to a literature procedure (90 °C, 15 h)²⁹ is active in the epoxidation of 1-octene as a model substrate for an alkene SAM (see ESI†). The same protocol was then used for the preparation of silicon AFM probes with immobilized $\text{3}/\text{Mn}(\text{OTf})_2$ pre-catalyst, which can be stored under air for a period of 1–2 weeks without any loss of activity. The formation of catalytically active manganese species on the probe surface takes place in the presence of H_2O_2 during AFM epoxidation experiments.

In the representative AFM nanolithography experiment, AFM catalysis and AFM characterization were performed at identical positions before and after each indicated chemical treatment. The working area of the 10-undecenyltrichlorosilane SAM on Si/SiO₂ prepared according to a known procedure^{25b} (see ESI†) was first imaged in acetonitrile with a catalytic AFM tip in tapping (reading) mode (see Fig. 1, for the corresponding phase image (Fig. 1a), topography (Fig. 1b) and height profile (Fig. 1c)). Then, a local AFM-catalyzed epoxidation process was conducted: the solvent in the AFM cell was replaced by a 50 mM solution of H_2O_2 in acetonitrile and five $1 \times 1 \mu\text{m}^2$ squares (256 lines per square) were scanned in contact (writing) mode with constant rate $0.3 \mu\text{m s}^{-1}$ and gradually increasing force (*ca.* 200, 400, 600, 1200 and 2500 nN). The characterization of the resulting surface in reading mode is presented in Fig. 1d–g. At this point the local surface modification is tricky to confirm by topography image (Fig. 1e, objects no. 1–3) but a clear mechanical degradation of the SAM by the AFM tip occurs using high values of the applied force (Fig. 1e, objects no. 4 and 5). The height profile of object no. 5 shows a depressed area (Fig. 1f), but the profile of object no. 2 (Fig. 1g) does not reveal any evident topography change from alkene to epoxide.



Scheme 2 Synthesis of the tacn-type ligand **3**.

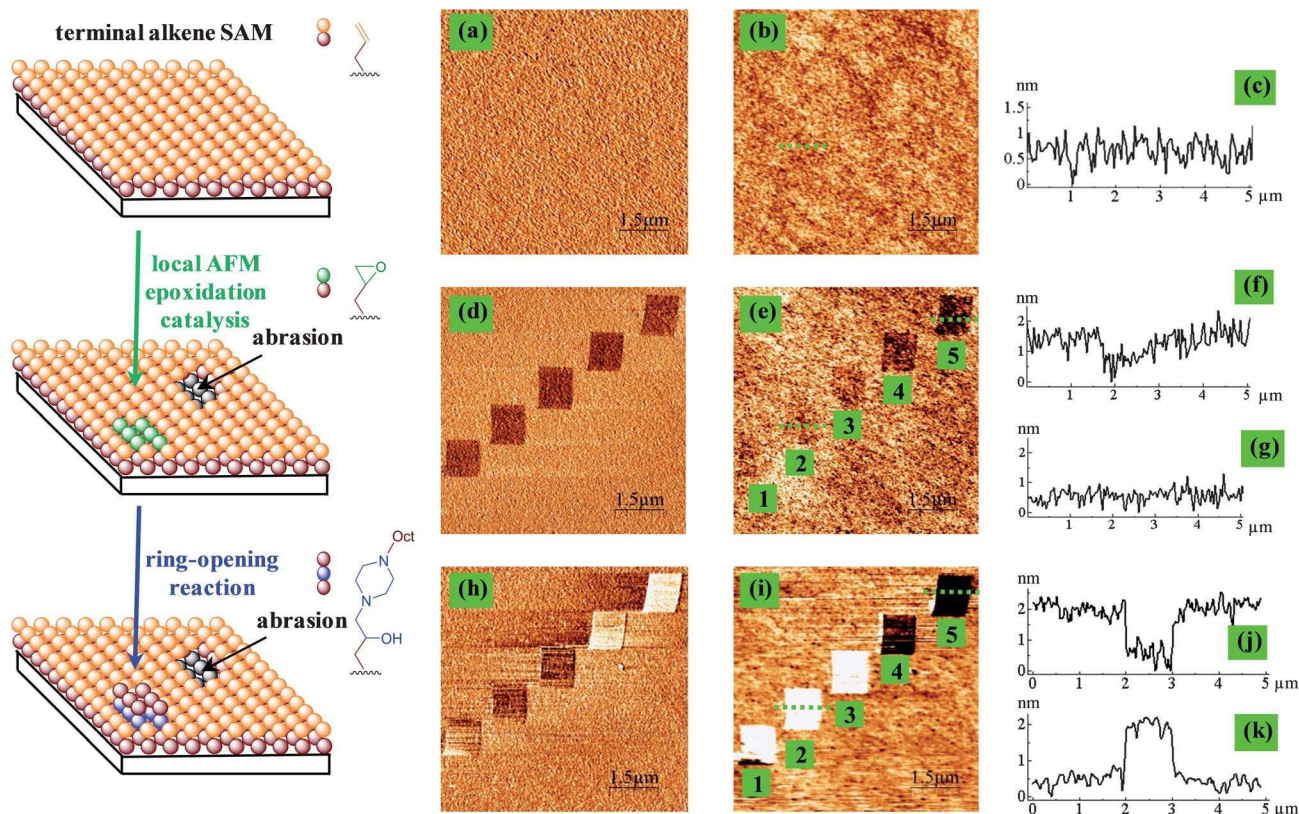


Fig. 1 Tapping mode AFM of the initial 10-undecenyltrichlorosilane SAM (MeCN, 25 °C, $10 \mu\text{m s}^{-1}$, Z colour scale 0.8 nm): phase image (a), topography (b) and height profile (c). SAM area after catalytic spatially-resolved AFM epoxidation (writing) of five $1 \times 1 \mu\text{m}^2$ squares in contact mode (50 mM solution of H_2O_2 in MeCN, $0.3 \mu\text{m s}^{-1}$, applied force ca. 200, 400, 600, 1200 and 2500 nN for objects no. 1 to 5 respectively): phase image (d), topography (e) and height profiles for objects no. 2 (g) and no. 5 (f). The same area after treatment of the modified SAM with a MeCN solution of *N*-octylpiperazine **4** (2 mM) and LiOTf (4 mM): phase image (h), topography (i) and height profiles for the raised (object no. 2 (k)), and depressed (object no. 5 (j)) features obtained. All AFM measurements were performed in acetonitrile (MeCN) at 25 °C using scan rates 15–20 $\mu\text{m s}^{-1}$, with Z colour scale 1.0, 1.0 and 1.6 nm for (b), (e) and (i) respectively.

Nevertheless, a clear signature is observed on the corresponding phase image (Fig. 1d), demonstrating well pronounced surface modifications in all patterned areas. In order to reveal the local surface alkene epoxidation, we explored the reactivity of the epoxide moiety by the addition of a nucleophile that could be easily detected in an AFM topography image. For this purpose, a ring opening reaction of the epoxide function with amine **4**, under soft Lewis acid activation,³² was performed.

First, the sample was thoroughly liberated from H_2O_2 and rinsed with pure acetonitrile, then treated in the AFM cell with a 2 mM solution of *N*-octylpiperazine **4** in MeCN (25 °C, 20 h) in the presence of a two-fold excess of LiOTf as the Lewis acid catalyst. An AFM topography image of the derivatized sample showed unambiguously a well pronounced surface growth for the first three squares no. 1–3 (Fig. 1i). The formed patterns were found to be completely stable towards repetitive washing with acetone, ethanol and water, which allowed us to propose a covalent character of the amine attachment onto the epoxidized areas. The height of the objects formed (1.4 ± 0.2 nm, Fig. 1k) agrees well with the length of amine **4**.³³ The observed raised patterns can be attributed to the amino alcohol surface domains with hydrophobic self-assembly of the long alkyl chains in a polar solvent such as MeCN, which are certainly rigidified by the possible occurrence of a 2D hydrogen bond

framework including alcohol and amine groups in the middle of the chains. As a counter reaction, no growth was observed on the patterned areas no. 4–5 (Fig. 1i), but a nanoshaving of the SAM is now clearly identifiable, and probably revealed by the washing process. The measured depth of object no. 5 (-1.7 ± 0.2 nm, Fig. 1j) corresponds to the SAM thickness (ca. 1.5 nm) which was previously determined by ellipsometry^{25a} and evaluated by semi-empirical calculations (see ESI†) thus being consistent with complete elimination of silane molecules at high values of applied force.

All attempts to observe the formation of characteristic raised features by treatment of the SAM with amine **4** after writing with a noncatalytic bare AFM silicon tip under the same conditions (Fig. 2), as well as experiments with an AFM tip bearing grafted ligands **3** without coordinated Mn(II) cations (Fig. 3) were unsuccessful. These experiments demonstrate no change (Fig. 2b and f, object no. 3), or local degradation (Fig. 2b and f, object no. 4) of the SAM at different values of applied force, and also, the absence of grafting of the nucleophile after amine treatment. In addition, no phase contrast was created by the writing (Fig. 2a, e and 3a, d). All these control experiments confirm that no adsorption of materials coming from experimental reagents, or AFM tip ligand/metal degradation, occurred at the surface after the AFM tip scan. Furthermore,

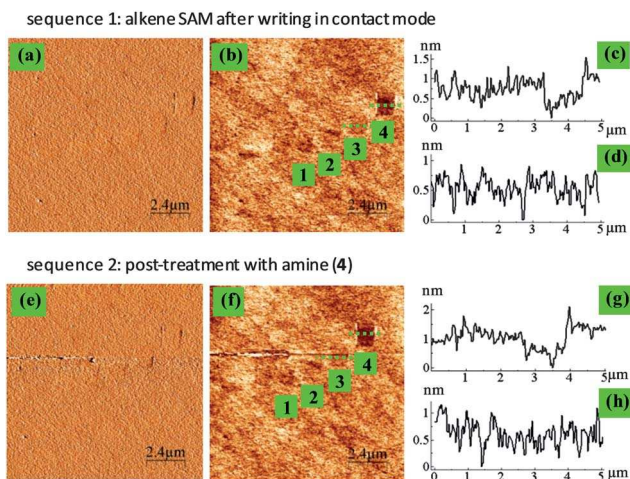


Fig. 2 Control experiment with standard commercial tip (non-modified): alkene SAM after writing of four $1 \times 1 \mu\text{m}$ squares in contact mode with a bare non-catalytic AFM tip (50 mM solution of H_2O_2 in MeCN, $0.3 \mu\text{m s}^{-1}$, applied force ca. 200, 400, 600, 900 nN from objects no. 1–4) (sequence 1, a–d), and subsequent treatment with an MeCN solution of *N*-octylpiperazine **4** (2 mM) and LiOTf (4 mM) (25 °C, 15 h) (sequence 2, e–h). AFM phase (a and e), and topography images (b and f) in tapping mode (MeCN, scan rates $20 \mu\text{m s}^{-1}$, Z colour scale 1.0 nm) and corresponding height profiles of non-degraded object no. 3 (d and h) and degraded object no. 4 (c and g).

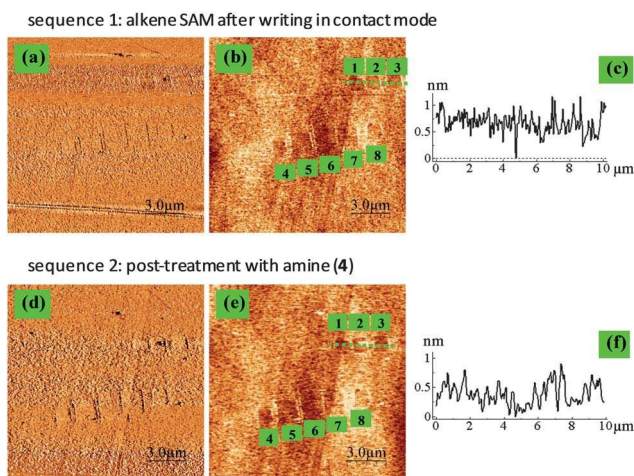


Fig. 3 Control experiment with ligand modified noncatalytic tip: alkene SAM area after writing of the objects in contact mode with an AFM tip having immobilized ligand **3** without doping with manganese(II) triflate (50 mM solution of H_2O_2 in MeCN, $0.5 \mu\text{m s}^{-1}$) (sequence 1, a–c), and subsequent treatment with MeCN solution of *N*-octylpiperazine **4** (2 mM) and LiOTf (4 mM) (25 °C, 15 h) (sequence 2, d–f). AFM phase (a and d) and topography images (b and e) in tapping mode (MeCN, scan rates $15\text{--}20 \mu\text{m s}^{-1}$, Z colour scale 1.0 nm). Objects no. 1–3 were written at ca. 200, 400, 600 nN respectively, the others (no. 4–8) were made at ca. 400 nN. The height profiles of objects no. 1–3 did not reveal any topography change (c and f).

post-treatment with amine **4** did not modify, under these conditions, both abraded or not SAM areas (see height profiles Fig. 2c, d, g, h and 3c, f).

Importantly, and similar to other AFM-based lithographic methods, the control of force applied to the SAM plays one of the key roles in the AFM driven epoxidation process: the

reaction proceeded with similar efficiency in the 200–600 nN force range but at higher force values ($>700\text{--}800$ nN), an increase of height resulting from amine addition was never observed, even if the observed alkene SAM mechanical deformation after AFM lithography did not exceed 2–3 Å. It was also found that the application of such a high force led to the loss of catalytic activity, suggesting, as for the SAM, a partial or complete degradation of the supported manganese pre-catalyst at the surface of the AFM tip.

Nevertheless, in a good range of applied force, the catalytic AFM tip is sufficiently active to produce a dozen $1 \times 1 \mu\text{m}^2$ squares even with a scan rate of $4.8 \mu\text{m s}^{-1}$ (Fig. 4a), which is 16 times faster than used initially (ca. 1 vs. 16 min scanning time). The height of the nanoobjects formed is reproducible (Fig. 4b) even if the shapes of the square areas are more difficult to control with such fast scanning conditions. The absence of any significant difference in the morphology of the objects obtained at the different scan rates, *i.e.* different reaction times, and excellent homogeneity of the amino alcohol surface domains, shows that both consecutive chemical alkene to epoxide to amino alcohol transformations at the surface proceed in very good yield, though it is very difficult to estimate quantitatively in this case.³⁴

Preliminary tests on the possible space resolution which could be achieved with this chemical nanolithography demonstrated the formation of features having a line width ca. 150–200 nm in the AFM phase image of epoxide (Fig. 4c), as well as the topography image after treatment of the sample with **4** (Fig. 4d). Despite the current spatial resolution obtained with rigid AFM probes (50N m^{-1} average spring constant), we believe that better resolution should be obtained using softer catalytic AFM probes still suitable for tapping mode³⁵ and/or upon more precise force control during the epoxidation procedure. The optimization of spatial resolution, grafting of different nucleophiles to surface epoxide domains as well as the use of catalytic 3/Mn(II) AFM tips for selective local oxidation of other surface-bound functional groups is in progress in our group.

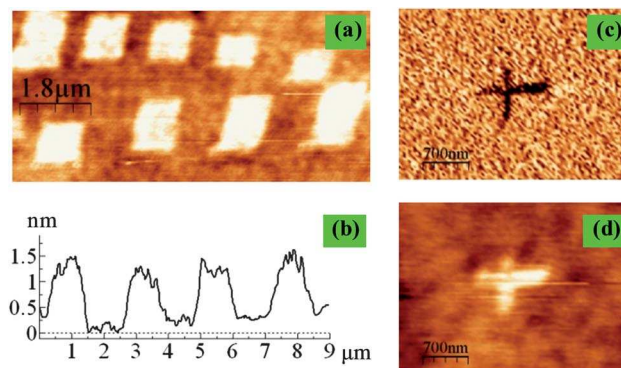


Fig. 4 Tapping mode AFM topography images for two series of local SAM epoxidations with a constant force of ca. 400 nN and different scan rates ($0.3 \mu\text{m s}^{-1}$ for upper and 1, 1.5, 3, $4.8 \mu\text{m s}^{-1}$ for lower sequence from left to right) after treatment with **4**/LiOTf (a) and height profile for the lower series of amino alcohol surface domains (b). Phase image of a cross written by the catalytic AFM tip with ca. 400 nN force (c) and topography image of the same surface after treatment with **4**/LiOTf (d). AFM imaging was performed in MeCN with a scan rate of $15\text{--}20 \mu\text{m s}^{-1}$ and a Z colour scale of 1.0 nm for (a) and (d).

Conclusions

In conclusion, a novel approach to chemically selective AFM lithography based on the immobilization of a homogeneous catalyst bearing a silane anchoring group onto a silicon AFM probe has been introduced, and is illustrated by local alkene SAM epoxidation as a proof-of-concept experiment. The proposed grafting protocol is very simple and does not require any specific modification of cheap commercially available AFM probes. We believe that the AFM chemical lithography method outlined here can be easily generalized to a wide variety of well-known homogeneous metal catalyzed reactions, opening the door to local nanoscale organic synthesis and spatially controlled creation of molecular objects on a surface.

Experimental section

All compounds used were purchased from commercial sources or prepared according to published procedures (1, 2, 4 for details see ESI†). Semiconductor quality polished silicon wafers (P-Bore type, 100 orientation, 0.1–100 Ω cm) were purchased from Siltronic, and cut into *ca.* 5 × 10 mm pieces for the preparation of 10-undecyltrichlorosilane SAM as previously described.^{25b} Silicon AFM probes (model ACT-20, nominal spring constants 25–75 N m⁻¹, resonance frequency range 200–400 kHz, tip radius < 10 nm) were purchased from AppNano. All AFM experiments were carried out on an Agilent Technologies 5500 microscope using the PicoView 1.6 software package in a home-built Teflon liquid cell allowing facile and complete replacement of the solution inside without any sample shift using flexible plastic tubing and syringes (see ESI†, page S11). AFM measurements were performed in acetonitrile (LC/MS quality, Fischer Scientific) inside a hermetic glass vessel under an air atmosphere saturated with MeCN vapour in order to minimize solvent evaporation in the cell during long experiment times. Forces applied by the AFM tip to the surface were calculated using the average cantilever spring constant value (50 N m⁻¹) given by the manufacturer. All AFM images were treated by standard processing protocols including image flattening and contrast enhancement using free WSxM software (Nanotec Electronica, Spain).³⁶

Synthesis of tacn ligand 3

K₂CO₃ (500 mg, 3.6 mmol), freshly dried under vacuum at 250 °C, was suspended in MeCN (3 mL) at room temperature. To this, 11-bromoundecyltrimethoxysilane (2) (178 mg, 0.5 mmol) and 1,3-dimethyl-1,3,7-triazacyclononane (1) (79 mg, 0.5 mmol) were added consecutively *via* syringe. The suspension was vigorously stirred for 36 h at room temperature, then the solution was filtered and the precipitate was washed with MeCN (3 × 1 mL). The combined extracts were evaporated to dryness and the resulting viscous pale-yellow oil was extracted with hexane (3 × 2 mL). The solution was separated from the oily precipitate by filtration through Celite to give after solvent removal compound 3 (145 mg, 67%) as a pale-yellow liquid. Ligand 3 should be stored under an argon atmosphere in the freezer at –20 °C to minimize oligomerization processes.

3: ¹H NMR (400.1 MHz, CDCl₃) δ 3.53 (s, 9H), 2.71 (s, 4H), 2.63 (s, 8H), 2.42 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 6H), 1.45–1.35 (m, 4H), 1.30–1.20 (m, 14H), 0.61 (t, *J* = 8 Hz, 2H); ¹³C {¹H} NMR (100.6 MHz, CDCl₃) δ 59.4, 57.6, 57.0, 56.3, 50.5, 46.8, 33.2, 29.7, 29.65, 29.60, 29.5, 29.3, 28.0, 27.6, 22.6, 9.1; HRMS (ESI) 432.3607 [M + H]⁺. Calculated for [M + H]⁺ 432.3616.

Preparation of catalytically active AFM probes

A flat bottomed glass vessel (volume *ca.* 2.5 mL) containing a small stirring bar was dried at 100 °C overnight, capped with a rubber septum and cooled to room temperature under an argon atmosphere. Toluene (2 mL) and ligand 3 (4.3 mg, 0.01 mmol) were added *via* syringe and the solution was stirred for 10 min. The stirring bar was removed and two AFM probes were placed on the bottom of the vessel and incubated under an argon atmosphere for 3 days. The resulting probes with grafted 3 were accurately washed with toluene in the little glass beaker (volume *ca.* 10 mL) and placed into another glass vessel containing 0.5 mL of a 1 mM stock solution of manganese(II) triflate in anhydrous methanol for 1.5 h. Finally AFM probes with the immobilized pre-catalyst were washed with methanol and dried under ambient conditions.

General procedure for catalytic AFM epoxidation nanolithography and sample derivatization with amine 4

The sample of 11-undecyltrichlorosilane SAM was installed in the sample holder, the AFM cell was filled with MeCN and the SAM surface was imaged by AFM in tapping mode using a probe with immobilized 3/Mn(OTf)₂ pre-catalyst. After localizing a good SAM area the solvent in the cell was very carefully removed by syringe and then replaced in the same manner with freshly prepared 50 mM H₂O₂ solution prepared from a non-stabilized 30% aqueous solution of H₂O₂ (26 μ L, 0.25 mmol) in MeCN (5 mL). After catalytic alkene epoxidation of the SAM in AFM contact mode, the solution of H₂O₂ was syringed off and the cell was washed twice with pure MeCN, keeping the solvent in the cell during 5–10 min before removal. Then a freshly prepared solution of 4 (4.75 μ L, 0.02 mmol) and LiOTf (6.25 mg, 0.04 mmol) in MeCN–H₂O 95 : 5 (10 mL) was introduced in the cell and the sample was kept overnight (15–20 h) at room temperature. The solution was then removed and the sample was washed consequently with MeCN, 95% ethanol, and water, keeping each solvent in the cell during 5–10 min before removal. Finally the cell was filled with MeCN and the sample after chemical derivatization was imaged in AFM tapping mode to characterize the nanoobjects formed.

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Notes and references

- For a general review on SPL methods see: (a) R. M. Nyffenegger and R. M. Penner, *Chem. Rev.*, 1997, **97**, 1195; (b) R. Garcia, R. V. Martinez and J. Martinez, *Chem. Soc. Rev.*, 2006, **35**, 29; (c) L. G. Rosa and J. Liang, *J. Phys.: Condens. Matter*, 2009, **21**, 483001; (d) C. Haensch, N. Herzer, S. Hoepfener and U. S. Schubert, in *Nanotechnology*, ed. H. Fuchs, M. Grätzel, H. Krug, H. Schmid, V. Vogel and R. Waser, Wiley-VCH, Weinheim, 2010, pp. 49–124; (e) S. H. Lee, T. Ishizaki, K. Teshima, N. Saito and O. Takai, in *Recent Advances in Nanofabrication Techniques and Applications*, ed. B. Cui, InTech, Shanghai, 2011, ch. 24, pp. 475–504.
- D. S. Ginger, H. Zhang and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2004, **43**, 30.
- (a) D. Wouters and U. S. Schubert, *Angew. Chem., Int. Ed.*, 2004, **43**, 2480; (b) D. Wouters, S. Hoepfener and U. S. Schubert, *Angew. Chem., Int. Ed.*, 2009, **48**, 1732.
- G.-Y. Liu, S. Xu and Y. Qian, *Acc. Chem. Res.*, 2000, **33**, 457.
- (a) Y. Li, B. W. Maynor and J. Liu, *J. Am. Chem. Soc.*, 2001, **123**, 2105; (b) B. W. Maynor, S. F. Filocamo, M. W. Grinstaff and J. Liu, *J. Am. Chem. Soc.*, 2002, **124**, 522; (c) G. Agarwal, R. R. Naik and M. O. Stone, *J. Am. Chem. Soc.*, 2003, **125**, 7408; (d) Y. Cai and B. M. Ocko, *J. Am. Chem. Soc.*, 2005, **127**, 16287; (e) O. Y. Loha, A. M. Ho, J. E. Rima, P. Kohlib, N. A. Patankara and H. D. Espinosa, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 16438; (f) J.-W. Jang, R. G. Sanedrin, D. Maspoch, S. Hwang, T. Fujigaya, Y.-M. Jeon, R. A. Vega, X. Chen and C. A. Mirkin, *Nano Lett.*, 2008, **8**, 1451.
- N. A. Amro, S. Xu and G. Liu, *Langmuir*, 2000, **16**, 3006.
- K. Seo and E. Borguet, *Langmuir*, 2006, **22**, 1388.
- R. Maoz, S. R. Cohen and J. Sagiv, *Adv. Mater.*, 1999, **11**, 55.
- R. Maoz, E. Frydman, S. R. Cohen and J. Sagiv, *Adv. Mater.*, 2000, **12**, 725.
- E. Pavlovic, S. Oscarsson and A. P. Quist, *Nano Lett.*, 2003, **3**, 779.
- Z. M. Fresco and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2005, **127**, 8302.
- (a) Z. M. Fresco, I. Suez, S. A. Backer and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2004, **126**, 8374; (b) S. A. Backer, I. Suez, Z. M. Fresco, M. Rolandi and J. M. J. Fréchet, *Langmuir*, 2007, **23**, 2297; (c) D. A. Unruh, C. Mauldin, S. J. Pastine, M. Rolandi and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2010, **132**, 6890.
- (a) N. Saito, N. Maeda, H. Sugimura and O. Takai, *Langmuir*, 2004, **20**, 5182; (b) N. Saito, S.-H. Lee, I. Takahiro, J. Hieda, H. Sugimura and O. Takai, *J. Phys. Chem. B*, 2005, **109**, 11602.
- (a) W. T. Müller, D. L. Klein, T. Lee, J. Clarke, P. L. McEuen and P. G. Schultz, *Science*, 1995, **268**, 272; (b) C. Blackledge, D. A. Engebretson and J. D. McDonald, *Langmuir*, 2000, **16**, 8317.
- W. F. Paxton, J. M. Spruell and J. F. Stoddart, *J. Am. Chem. Soc.*, 2009, **131**, 6692.
- M. Péter, X.-M. Li, J. Huskens and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 2004, **126**, 11684.
- (a) J. J. Davis, K. S. Coleman, K. L. Busuttill and C. B. Bagshaw, *J. Am. Chem. Soc.*, 2005, **127**, 13082; (b) J. J. Davis, C. B. Bagshaw, K. L. Busuttill, Y. Hanyu and K. S. Coleman, *J. Am. Chem. Soc.*, 2006, **128**, 14135; (c) J. J. Davis and Y. Hanyu, *Nanotechnology*, 2010, **21**, 265302.
- E. N. Jacobsen and M. H. Wu, in *Comprehensive Asymmetric Catalysis*, ed. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, Springer, New York, 1999, vol. 2, pp. 649–677.
- D. Leipert, D. Nopper, M. Bauser, G. Gauglitz and G. Jung, *Angew. Chem., Int. Ed.*, 1998, **37**, 3308.
- (a) C. Mateo, V. Grazú, J. M. Palomo, F. López-Gallego, R. Fernández Lafuente and J. M. Guisán, *Nat. Protoc.*, 2007, **2**, 1022; (b) C. Mateo, V. Grazú, B. C. C. Pessela, T. Montes, J. M. Palomo, R. Torres, F. López-Gallego, R. Fernández Lafuente and J. M. Guisán, *Biochem. Soc. Trans.*, 2007, **35**, 1593 and references therein.
- A. Kulak, Y.-J. Lee, Y. S. Park and K. B. Yoon, *Angew. Chem., Int. Ed.*, 2000, **39**, 950.
- I. Luzinov, D. Julthongpipit, A. Liebmann-Vinson, T. Cregger, M. D. Foster and V. V. Tsukruk, *Langmuir*, 2000, **16**, 504.
- S. Busse, M. DePaoli, G. Wenz and S. Mittler, *Sens. Actuators, B*, 2001, **80**, 116.
- S. Onclin, B. J. Ravoo and D. N. Reinhoudt, *Angew. Chem., Int. Ed.*, 2005, **44**, 6282.
- (a) S. R. Wasserman, Y.-T. Tao and G. M. Whitesides, *Langmuir*, 1989, **5**, 1074; (b) C. Wendeln, S. Rinnen, C. Schulz, H. F. Arlinghaus and B. J. Ravoo, *Langmuir*, 2010, **26**, 15966.
- The sole reported example of the reaction in tapping mode concerned the reduction of an imine SAM by an AFM tip with a glued chunk of NaBH(OAc)₃ during 1–4 h, see: L. K. Blasdel, S. Banerjee and S. S. Wong, *Langmuir*, 2002, **18**, 5055.
- S. Shylesh, M. Jia and W. R. Thiel, *Eur. J. Inorg. Chem.*, 2010, 4395 and references therein.
- (a) D. E. De Vos, B. F. Sels, M. Reynaers, Y. V. S. Rao and P. A. Jacobs, *Tetrahedron Lett.*, 1998, **39**, 3221; (b) A. Berkessel and C. A. Sklorz, *Tetrahedron Lett.*, 1999, **40**, 7965.
- D. E. De Vos, S. De Wildeman, B. F. Sels, P. J. Grobet and P. A. Jacobs, *Angew. Chem., Int. Ed.*, 1999, **38**, 980.
- The use of inorganic base (K₂CO₃) is found to be crucial in this case, since even 10-fold excess of Et₃N or *i*Pr₂NEt never gave complete conversion of **2** at room temperature leading to the partial oligomerization of silane even at 40 °C. The attempt to discriminate NH and NMe moieties in **2** towards addition of **1** by formation of the corresponding lithium amide also failed due to preferred Si(OMe)₃ fragment degradation.
- The analysis of the silicon surface with immobilized 3/Mn(OTf)₂ pre-catalyst by X-ray photoelectron spectroscopy revealed the signals for all expected atoms: (binding energies, eV) C (1s) 286.4; O (1s) 533.6; N (1s) 401.3, 403.7; F (1s) 690.2; S (2s) 233.9, 229.3; Mn (2p_{3/2}) 653.7, 654.9.
- In order to follow compatible reaction conditions with our AFM liquid cell (room temperature, air and water tolerant reagents), we have selected an effective ring-opening procedure for aliphatic epoxides with secondary amines

- using LiOTf as a Lewis acid catalyst. For details see the ESI† and references: (a) M. Chini, P. Crotti and F. Macchia, *Tetrahedron Lett.*, 1990, **31**, 4661; (b) J. Augé and F. Leroy, *Tetrahedron Lett.*, 1996, **37**, 7715.
- 33 According to semi-empirical calculations (PM3, Gaussian 2009) the length of model 11,10-epoxyundecyltrimethoxysilane molecule is increased by 1.5 nm after addition of *N*-octyl-piperazine 4 (see the ESI† for details).
- 34 We believe that metal leaching from the catalyst is not significant in the working force range since the AFM tip remains active after patterning ten objects with no apparent AFM imaging erosion.
- 35 We suppose that the sample characterization with such an active catalytic AFM probe like in our case has to be carried out in tapping mode in order to avoid undesired background reactions, which could proceed to some extent in contact mode even at the scan rate of $64 \mu\text{m s}^{-1}$ (ref. 15).
- 36 I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero and A. M. Baro, *Rev. Sci. Instrum.*, 2007, **78**, 013705.