

## Molecular Graph Paper\*\*

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*Dedicated to Professor Dieter Fenske on the occasion of his 75th birthday*

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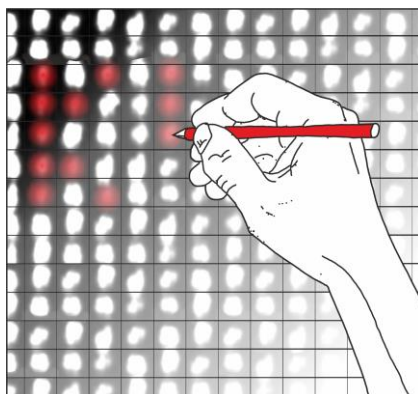
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[\*\*] The authors acknowledge financial support by the Research Network »Functional Nanostructures« of the Baden-Württemberg Stiftung and by the Helmholtz Research Program STN (Science and Technology of Nanosystems).

**Abstract:** We present a self-assembled template of tetraphenylmethane-based variants on a Au(111) surface which feature a periodic lateral arrangement of acetyl groups sticking out of the molecular film. Using the tip of a scanning tunneling microscope, this acetyl group can be removed in a spatially controlled way **without a significant effect on the remaining molecular assembly**. The chemically modified molecule can readily be distinguished from the original ones such that information can be engraved in the molecular film. **Both the modified nature of an individual molecule and the order of the molecular film are shown to persist at room temperature.** We show that the mesh size of this molecular graph paper can be tuned by varying the length of the molecular spacer group so that writing and reading information on the nanoscale with variable letter size becomes possible.

**TOC Graphic:**

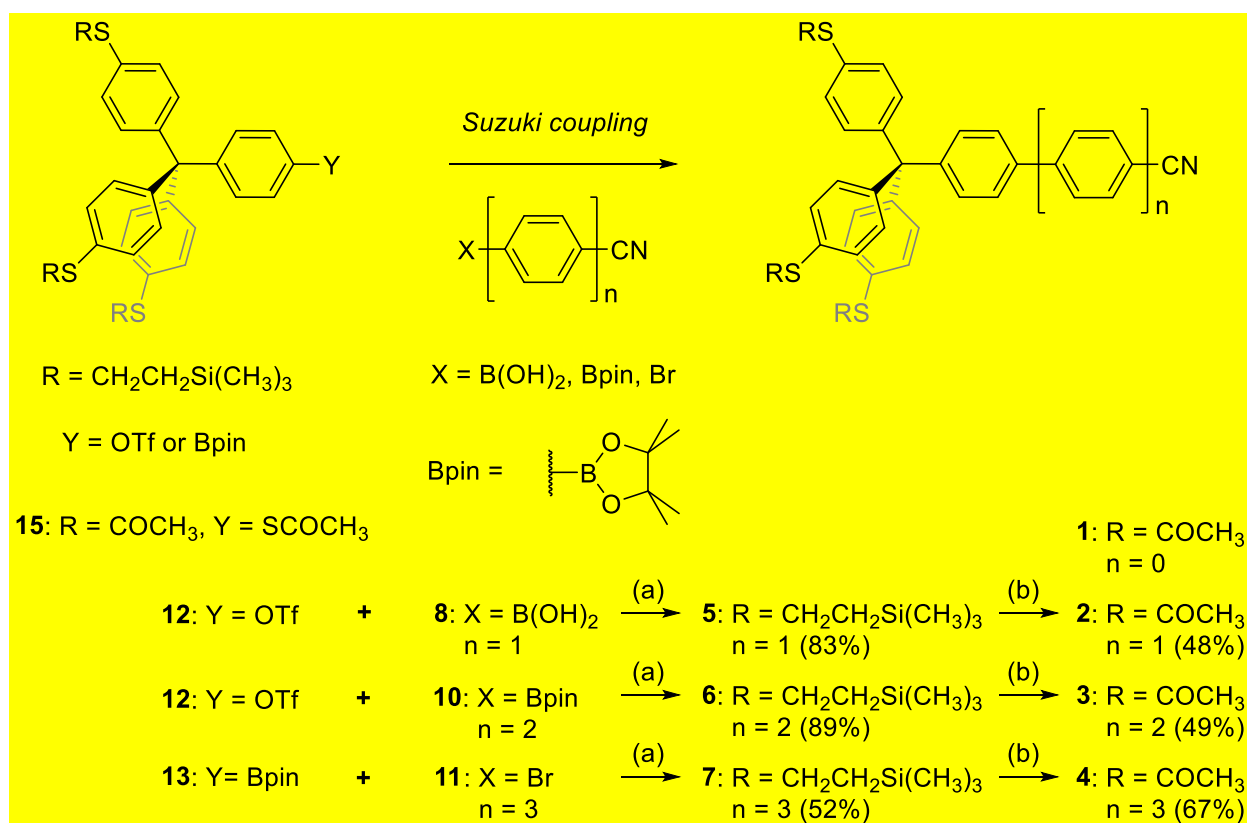


Words of human language have been stored and transmitted in written form on paper since its invention in ancient China about 2000 years ago. Over the time, printing, micro-photography and electron beam writing pushed the smallest possible size of individual letters to the nanoscale. Feynman's challenge of writing the entire Encyclopædia Britannica on the head of a pin [1] is long achieved, and writing letters with atoms arranged by the tip of a scanning tunneling microscope (STM), as first was shown by Eigler et al. [2,3], has become common practice [4] and even kilobyte atomic memories have been realized [5]. However, atomic manipulation is an intrinsically slow technique and truly nanoscale writing with tunable mesh sizes is still demanding. Typically, single atoms arranged at low temperatures start to diffuse well below room temperature and any predefined order like e.g. arranged characters will vanish. Therefore, bistable atomic switches at room temperature are rare [6]. Supramolecular self-assembly in two dimensions on metal surfaces is meanwhile a reasonably well understood process providing laterally ordered structures with nanoscale precision which can be stable at room temperature [7-12]. In order that such self-assembled patterned structures can serve as a writable template, a suitable, modifiable marker must be implemented such that it can be addressed in a spatially controlled manner by an external stimulus. While the self-assembly of molecules has been used to organize reactants for subsequent intermolecular reactions [13], as markers only locally resolved molecular events triggered by the STM tip like e.g. single molecule switches [14, 15] or even single molecule reactions [16-20] are suited.

Here we present a new approach of molecularly defined graph paper which can be written on with the STM tip. The graph paper consists of tailor-made tetraphenylmethane-based molecules deposited on a Au (111) surface. As the molecules were initially designed to study the dimensionality of the molecular rod arranged perpendicular to the surface mounted on tripodal foot structures [21], the here presented study is first of all another example of the limited comprehension we have about molecular behavior at interfaces. However, the unexpected molecular arrangement upon the applied deposition method enabled the observation of the phenomenon enabling the here reported molecular graph paper. The molecular structures arrange in regular patterns in which the mesh size is controlled by the length of the molecular spacer group consisting of a *para*-oligophenyl rod with a terminal nitrile group. The terminal nitrile groups

ensure a strong enough interaction with the gold surface that upon deposition on the substrate and subsequent annealing, only two of the three thiol groups decorating the tetraphenylmethane subunit interact with the gold surface and are deprotected, while the third one is exposed in its acetyl protected form. Furthermore, the interaction in the densely packed self-assembled pattern with the substrate is strong enough to prevent thermally activated diffusion at room temperature. The surface pattern results in a periodic lateral arrangement of exposed acetyl protected thiophenol groups reminding the periodic squares of graph paper. However, acetyl protected thiophenol rods have been reported to be cleavable by voltage pulses in STM experiments from single molecules [22]. We here present molecular graph paper by demonstrating that the acetyl groups sticking out from the surface can be selectively cleaved by application of voltage pulses with the STM tip positioned above the acetyl group. The molecules without the acetyl protecting groups typically appear darker in STM, which allows an easy identification and opens the possibility of writing and retrieving information on the nanoscale with a predefined spacing of the mesh. The contrast of this molecular graph paper is based on the cleavage of chemical bonds and the applicability of this mechanism at room temperature is demonstrated for the case of an individual molecule.

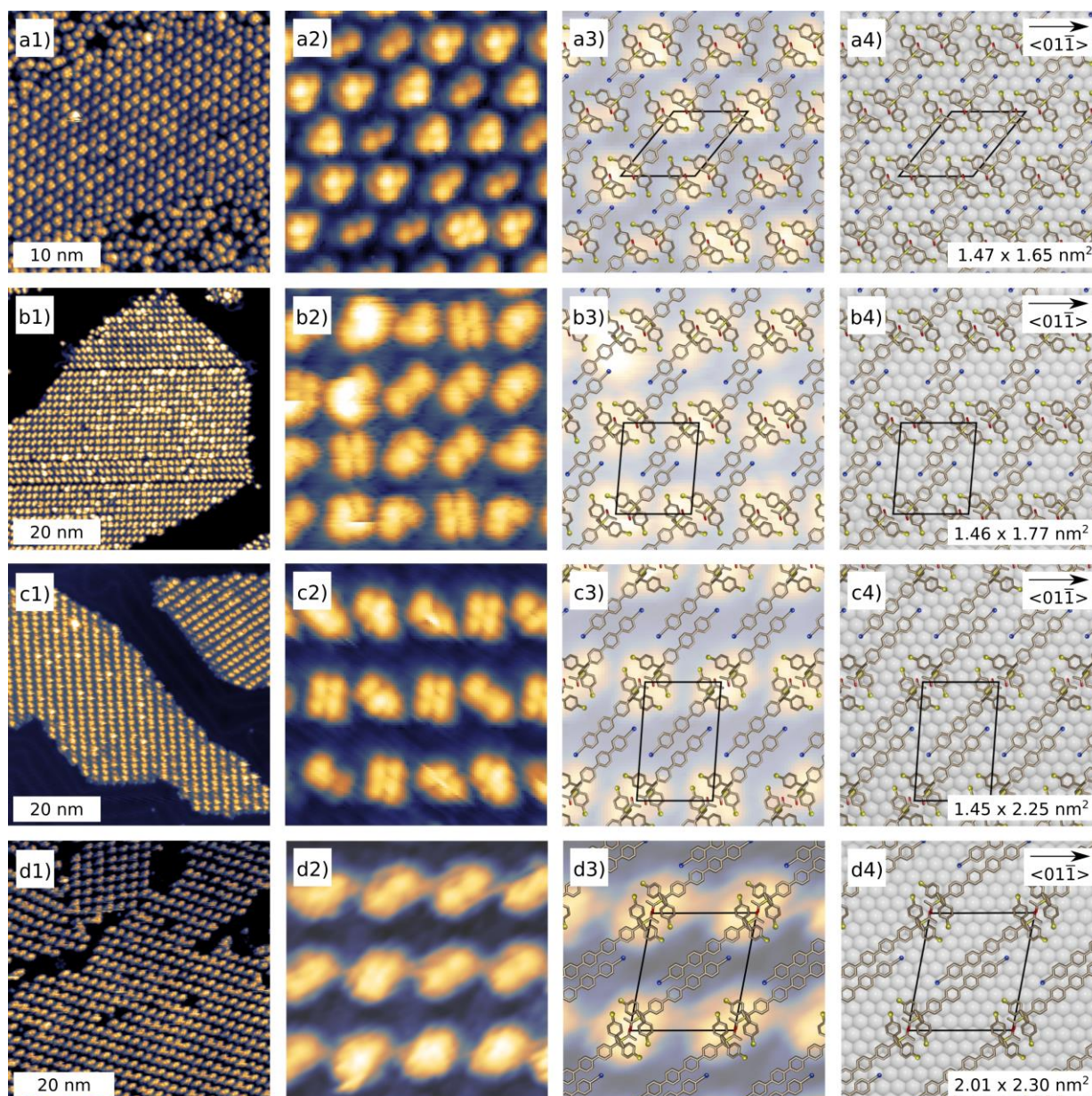
In Scheme 1, the syntheses of the four members of the tetraphenylmethane family **1-4** are displayed. While the synthesis of the shortest derivative **1**, as well as of the triflate **12** and the pinacol boronate **13** derivatives of tetraphenylmethane as common precursors of the entire family were already reported [23], all longer derivatives **2-4** were assembled by Pd catalyzed *Suzuki* coupling between **12**, **13** respectively and the corresponding bromo-aryl **11** or aryl pinacol boronate derivatives **8**, **10** [24], from which **10** was itself assembled by sequence of *Suzuki* coupling and *Miyaura* borylation [25] protocols and **11** was assembled via *Suzuki* cross-coupling reaction. Final transprotection of the 2-(trimethylsilyl)ethyl protected thiols **5-7** has been successfully performed using silver tetrafluoroborate and acetyl chloride to afford the desired thioacetates **2-4**. Detailed synthetic protocols of all new compounds are provided in the supporting information and the identity of all new compounds was corroborated by their full characterization.



**Scheme 1:** The members of the tetraphenylmethane family **1-4** and the syntheses of the longer derivatives **2-4**. Reagents and conditions: a)  $[\text{Pd}(\text{PPh}_3)_4]$ ,  $\text{K}_2\text{CO}_3$ , dioxane (THF)/ $\text{H}_2\text{O}$  (5/1, v/v), reflux, 16 h; b)  $\text{AgBF}_4$ ,  $\text{AcCl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ -RT.

The molecules **1-4**, **15** were deposited from a dichloromethane solution that was sprayed onto clean Au(111) surfaces as described previously [23,26]. In order to promote proper arrangement in regular pattern, the samples were mildly annealed to  $165^\circ\text{C}$  in ultra-high vacuum (UHV) and transferred in situ into the STM working at 5.3 K if not indicated otherwise.

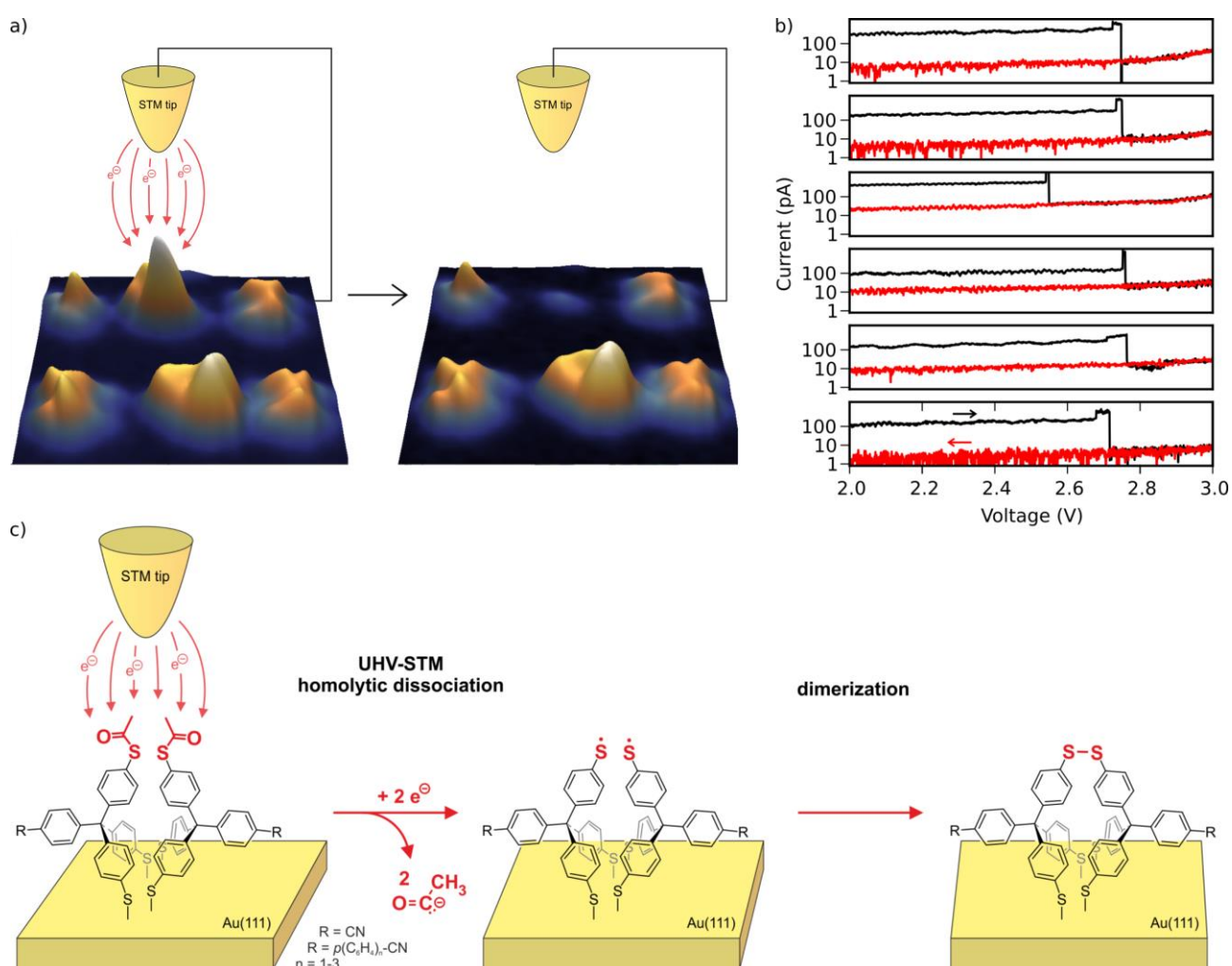




**Figure 1:** Adsorption configuration of the tetraphenylmethane variants **1-4** with different spacer groups: row a) phenyl **1** (tunnelling conditions: 0.8 V, 5 pA), row b) biphenyl **2** (1.3 V, 4 pA), row c) terphenyl **3** (1.3 V, 6 pA), row d) quarterphenyl **4** (1.4 V, 21 pA). Column 1 shows large scale overview images, column 2 shows images of 7 nm in width with the motifs of individual acetyl groups of the corresponding variant, columns 3 and 4 show STM images of 5 nm in width with the molecular models superimposed to scale and the corresponding model of the Au(111). The size of the experimentally determined unit cell is given in column 4.

All four tetraphenylmethane derivatives **1-4** arrange in regular islands with almost square-like unit cells (see Fig. 1). The appearance of one bright feature can take three different basic motifs while all four variants show the very same three motifs (column 2 in Fig. 1). The size of the unit cell varies with the length of the *p*-oligophenylene spacer and is indicated by a black rhomboid in the columns 3,4 in Fig. 1. We propose the

following adsorption model which is supported by superposition of our STM measurement with the molecular models and which assumes a molecular film that is commensurate with the Au(111) lattice (see Fig. 1, column 4). All molecules **1-4** are arranged in a close-packed pairwise fashion. The brightest spot within the unit cell is formed by the acetyl groups of two adjacent tetraphenylmethanes (see Fig. 1, columns 3, 4). The presence of different motifs within one island is explained by different conformations of the paired acetyl groups (see Figure SI-24). Thus, we obtain a density of protruding acetyl pairs of between 0.21 and 0.55 per square nm.



**Figure 2:** a) Modification of the molecular motif (variant **2**) by application of a voltage of 3 V across the tunneling junction. The molecular motif is reduced to a single blob of drastically lower intensity. b) Tunneling current as a function of the applied voltage recorded for six individual experiments analogous to a) with the tip positioned above a molecular motif. The modification is reflected by a small increase in the current followed by a sudden drop to a



drastically lower value. The voltage sweep from 2 to 3 V is shown in black, the sweep back to 2 V is shown in red. c)

The proposed mechanism of acetyl groups cleavage by applying a voltage pulse from the STM tip.

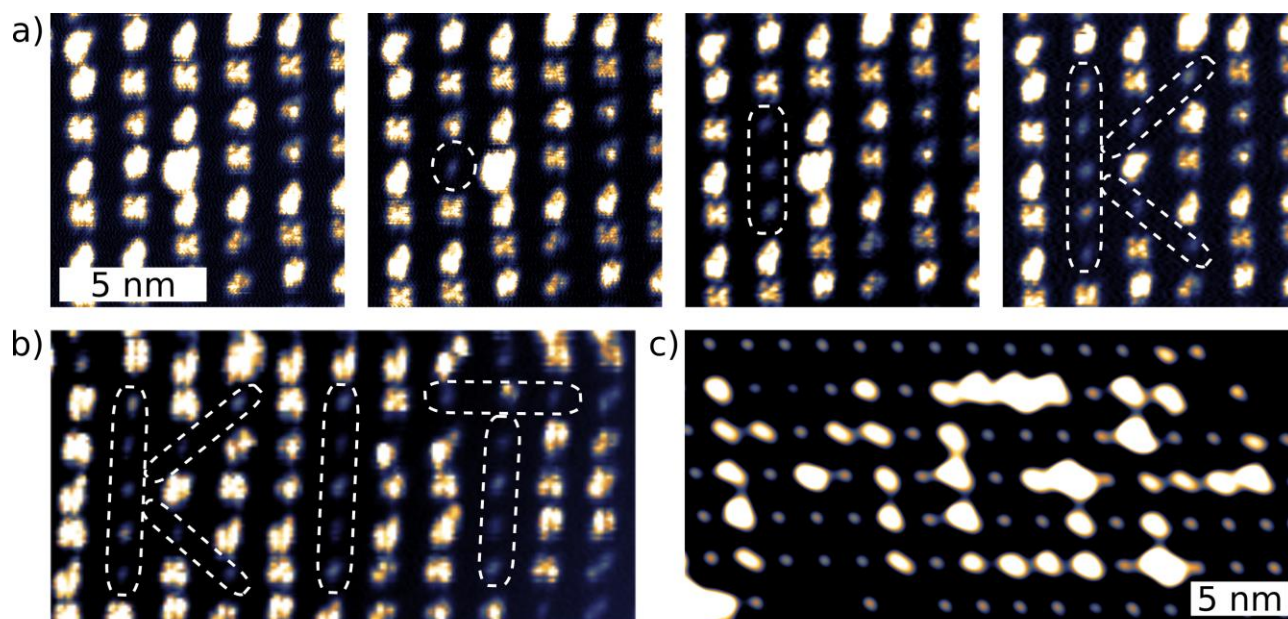
As the acetyl groups point away from the surface and are arranged in laterally separated pairs, they can be freely addressed with the STM tip. Because this part of the molecule is decoupled from the metal surface by the central  $sp^3$ -hybridized carbon atom of the tetraphenylmethane center, it is particularly suited for electron-induced single molecule chemistry. It is known that in thiol-based molecules which adsorb flat on a metal substrate, voltage pulses from the STM tip can dissociate the end group by selective breaking of the sulfur-acetyl (S-Ac) bond [22]. We show that also freestanding acetyl groups can be removed by selective bond dissociation using tunneling electrons from the STM tip at precisely defined locations above the molecules. As is shown in Fig. 2a, voltage pulses of about +3 V applied across the tunneling junction lead to a clear modification of the molecular motif and a drastic reduction of the intensity in the STM image. Pulses of opposite polarity were less successful and required higher voltages. The threshold voltage for this process can be determined more precisely by ramping the voltage and simultaneously recording the tunneling current. The modification of the molecule under the STM tip is then accompanied by a drop in the tunneling current (see Fig. 2b) which can be associated with the sulfur-acetyl (S-Ac) dissociation event. In such I-V curves, we found critical values of the voltage in the range of 2.55 to 2.73 V for a ramp speed of 1 V/s. The observed modification of the protruding motif was irreversible in all cases. Also, the application of voltages of opposite polarity did not allow to reverse the process. In the view of these high energies and the irreversibility of the process, conformational changes seem to be very unlikely. Furthermore, application of even harsher conditions, that is higher voltages of 3 V or more and reduced distance between tip and sample, leads to further reduction of the apparent height which might be attributed to the additional sulfur atom abstraction (see Figure SI-25). We did, however, not look into the details of this second modification process, because at these conditions it is very likely to modify the tip as well, which makes systematic experiments difficult.



Although the cleavage mechanism of individual acetyl groups is not fully understood and a number of mechanisms can play a role in the same molecule [27], our currently favored hypothesis is based on a radical mechanism which seems most likely considering the UHV surrounding of the reaction (see Fig. 2c). The STM tip induced cleavage of thioacetate may involve a homolytic cleavage of the S-Ac bond with the injected electrons forming thiyl (phenylsulfanyl) radicals ( $\text{RS}\cdot$ ). Due to their proximity in the self-assembled molecular arrangements we further assume that the two neighboring thiyl radicals ( $\text{RS}\cdot$ ) immediately form the corresponding disulfide ( $\text{RS-SR}$ ). As side product of the homolytic cleavage labile acyl anions ( $\text{COCH}_3^-$ ) are formed. Whether these anions are immediately adsorbed by the positively charged substrate or they undergo rapid decarbonylation providing methyl anions, which subsequently are attracted by the substrate is beyond the scope of the present study. After deacetylation at low temperatures, we neither observe a change of the tip nor find isolated acetyl groups in the vicinity of the writing position. As additional experimental indication for the formation of disulfide bonds ( $\text{RS-SR}$ ) stabilizing the structure we rate our unsuccessful attempts to separate an isolated dimer with the STM tip. Instead of separating, the whole isolated dimer simply rotates (see Figures SI-27b,c).

The described cleavage process is highly reproducible and selective to the acetyl groups in the tunneling junction such that the self-assembled molecular layers can be modified molecule by molecule. Fig. 3a shows a sequence of four images of the same area of a self-assembled monolayer of **2**. Step by step, acetyl groups are removed in order to engrave the letter “K” and finally writing “KIT” (see Fig. 3b). The self-assembled template functions as a molecular graph paper that allows us to write information on the nanoscale in a well-controlled manner as is also shown in Fig. 3c by writing “MGP”. In order to proof our concept of deacetylation, we performed controlled writing on the fully thiol-terminated tetraphenylmethane **15** which is similar to **1** (see Figure SI-23 b). We successfully wrote the letter “S” on a molecular array with a density as high as 0.59 pixels per  $\text{nm}^2$  (see Figure SI-26c), which clearly shows that the effect is highly localized. The grid spacing of the molecular graph paper depends on the length of the spacer group. Figures SI-26a,b show the letters “KIT”, written on self-assembled monolayers of derivative **4** (grid spacing is  $2.01 \times 2.30 \text{ nm}^2$ , see Fig. SI-26a) and derivative **2** (grid spacing of  $1.46 \times 1.77 \text{ nm}^2$  see Fig SI-

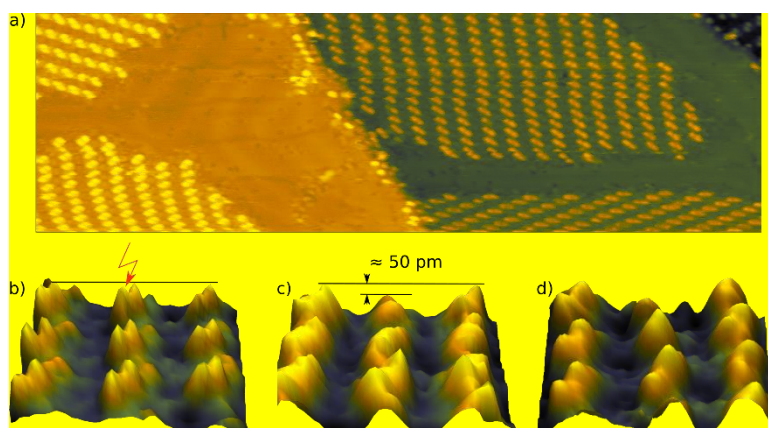
26b). In principle, the writing process works in the same way for all variants presented, however a larger intermolecular spacing allows to address single molecule even with a blunt but stable STM tip.



**Figure 3:** Writing experiments at 5.3 K. a) Writing the capital letter “K” on a 12x12 nm area of a monolayer of **2** by sequential removing the acetyl groups. b) “KIT” written on a monolayer of **2** (Constant height mode, 1.5 V). c) “MGP” as acronym for molecular graph paper, written on a monolayer of **4** (1.5 V, 6 pA). All acetyl groups are cleaved off, except for those forming the letters “MGP”.

A particularly interesting feature is the thermal stability of the molecular graph paper. The practical applicability requires that the mechanisms of writing and reading remain functional at room temperature and a written bit remains stable, i.e. does not diffuse. Therefore, in order to test for room temperature performance of the proposed writing concept, we directly performed room temperature STM on a layer of derivative **3** deposited as described above. The ordered islands can clearly be imaged with sub-molecular resolution revealing the same motif as at low-temperature (see Fig. 4a), which shows the room temperature stability of the self-assembly (see also Figure SI-27). Furthermore, we show that modification of a single molecule by a voltage pulse (+2.5 V applied to the sample) and readout is possible at room temperature (see Fig. 4b-d). Furthermore, we did not observe that the written information diffuses in the molecular layer (see Fig. 4d). However, writing clearly works better at low temperature. At room temperature the application of voltage pulses is very likely to lead to modifications of the STM tip (see

slight changes of the molecular motif from Fig. 4b to Fig. 4c), which hampered the creation of more complex structures.



**Figure 4:** STM at room temperature: a) Ordered islands of tetraphenylmethane-derivative **3** imaged at room temperature. The size of the image is 100 x 30 nm<sup>2</sup>. Array of **3** before (b) and after (c) application of a voltage pulse (+2.5 V applied to the sample) at the position indicated with a red arrow. d) An image acquired 2 min later still shows the same structure. The width of the images is 9 nm. Tunneling parameters are 1.5 V, 5 pA for all panels.

In conclusion, we have realized a novel type of nanostructurization with room temperature stability. The key to making this molecular graph paper work lies in the combination of the self-assembled molecular layer and the possibility to manipulate individual molecular groups with voltage pulses in the STM junction. The clear separation of the molecular spacer and the marker group allows us to engrave information by chemically modifying single molecular groups without interfering with the well-ordered mesh. The idea of conceptual separation of the substrate-molecule interaction and the manipulatable marker is likely to be transferable to similar molecular structures and allows to explore a huge variety of molecular groups. Finally, this method allows chemical functionalization on the nano-scale such that in a second step, other molecules may selectively react with the molecular graph paper only at positions that were engraved.

## Keywords

nanostructures, scanning probe microscopy, self-assembly, surface chemistry, tetraphenylmethane

## References

- [1] R. P. Feynman, *Engineering and Science* **1960**, 22-36.
- [2] D. M. Eigler, E. K. Schweizer, *Nature* **1990**, 344, 524-526.
- [3] J. A. Strosio, D. M. Eigler, *Science* **1991**, 254, 1319-1326.
- [4] K. Morgenstern, N. Lorente, K.-H. Rieder, *Phys. Status Solidi B* **2013**, 250(9), 1671-1751.
- [5] F. E. Kalff, M. P. Rebergen, E. Fahrenfort, J. Girovsky, R. Toskovic, J. L. Lado, J. Fernández-Rossier, A. F. Otte, *Nat. Nanotech.* **2016**, 11, 926-929.
- [6] U. J. Quaade, K. Stokbro, C. Thirstrup, F. Grey, *Surface Science* **1998**, 415(3), L1037-L1045.
- [7] J. Teyssandier, S. De Feyter, K. S. Mali, *Chem. Commun.*, **2016**, 52, 11465-11487.
- [8] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, 105, 1103-1169.
- [9] C. Vericat, M. E. Vela, G. Benitez, P. Carro, R. C. Salvarezza, *Chem. Soc. Rev.* **2010**, 39, 1805-1834.
- [10] F. Klappenberger, *Prog. Surf. Sci.* **2014**, 89, 1-55.
- [11] W. Auwärter, D. Ćija, F. Klappenberger, J. V. Barth, *Nat. Chem.* **2015**, 7, 105-120.
- [12] X. Bouju, C. Mattioli, G. Franc, A. Pujol, A. Gourdon, *Chem. Rev.* **2017**, 117, 1407-1444.
- [13] J. A. W. Münninghoff, J. A. A. W. Elemans, *Chem. Commun.* **2017**, 53, 1769-1788.
- [14] J. L. Zhang, J. Q. Zhong, J. D. Lin, W. P. Hu, K. Wu, G. Q. Xu, A. T. S. Wee, W. Chen, *Chem. Soc. Rev.* **2015**, 44, 2998-3022.
- [15] L. Gerhard, K. Edelmann, J. Homberg, M. Valášek, S. G. Bahoosh, M. Lukas, F. Pauly, M. Mayor, W. Wulfhekel, *Nat. Commun.* **2017**, 8, 14672.
- [16] S.-W. Hla, L. Bartels, G. Meyer, K.-H. Rieder, *Phys. Rev. Lett.* **2000**, 85, 2777-2780.
- [17] A. Zhao, S. Tan, B. Li, B. Wang, J. Yang, J. G. Hou, *Phys. Chem. Chem. Phys.* **2013**, 15, 12428-12441.
- [18] L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters, S. Hecht, *Nat. Nanotechnol.* **2007**, 2, 687-691.
- [19] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Müllen, R. Fasel, *Nature* **2010**, 466, 470-473.
- [20] D. Zhong, J. -H. Franke, S. K. Podiyanachari, T. Blömker, H. Zhang, G. Kehr, G. Erker, H. Fuchs, L. Chi, *Science* **2011**, 334, 213-216.

[21] M. Valášek, M. Lindner, M. Mayor, *Beilstein J. Nanotechnol.* **2016**, 7, 374–405.

[22] Y. Jiang, Q. Huan, L. Fabris, G. C. Bazan, W. Ho, *Nat. Chem.* **2013**, 5, 36–41.

[23] M. Lindner, M. Valášek, J. Homberg, K. Edelman, L. Gerhard, W. Wulfhekel, O. Fuhr, T. Wächter, M. Zharnikov, V. Kolivoška, L. Pospíšil, G. Mészáros, M. Hromadová, M. Mayor, *Chem. Eur. J.* **2016**, 22, 13218-13235.

[24] A. Suzuki, *Angew. Chem. Int. Ed.* **2011**, 50, 6723-6737; *Angew. Chem.* **2011**, 123, 6854-6869.

[25] T. Ishiyama, M. Murata, N. Miyamura, *J. Org. Chem.* **1995**, 60, 7508-7510.

[26] M. Valášek, K. Edelman, L. Gerhard, O. Fuhr, M. Lukas, M. Mayor, *J. Org. Chem.* **2014**, 79, 7342-7357.

[27] S.-W. Hla, K.-H. Rieder, *Annu. Rev. Phys. Chem.* **2003**, 54, 307–330.