

Direct writing of N-heterocyclic carbene nanostructures

M. Kubicki,¹ P. Chahar,² D. Schmidt,¹ A. Das,² M.-L. Fraser,¹ A. Doronina,¹ G. Lorenz,¹ C. Kühn,¹ J. Troger,¹ Ph. Gruber,¹ V. Balfanz,¹ M. Dähne,¹ C. Hogan,^{3,4} F. Glorius,² and M. Franz¹

¹ Technische Universität Berlin, Institut für Physik und Astronomie, Hardenbergstraße 36, D-10623 Berlin, Germany

² Universität Münster, Organisch-Chemisches Institut, Corrensstraße 36, 48149 Münster, Germany

³ CNR-Istituto di Struttura della Materia (CNR-ISM), Via del Fosso del Cavaliere 100, 00133 Rome, Italy

⁴ Dipartimento di Fisica, Università di Roma 'Tor Vergata', Via della Ricerca Scientifica 1, 00133 Rome, Italy

To date, various scanning probe lithography (SPL) techniques already exist, in which scanning probe microscopes are used to directly create nanostructures on surfaces. Thereby, different physical and chemical effects are used to locally change the structure of the sample surface beneath the probe. Examples include thermal or thermochemical SPL, oxidation SPL, and dip-pen nanolithography [1].

Here, we present a method allowing the direct writing of nanostructures consisting of monolayers of N-heterocyclic carbene (NHC) molecules. NHCs constitute a well-established class of organic compounds with applications in homogeneous catalysis, main-group chemistry, and functional materials [2]. In recent years, they have also emerged as important ligands for surface modification and functionalization. While initial research focused mainly on noble metal surfaces, other substrates such as semiconductors have recently come into focus [3,4].

In the NHC-SPL method demonstrated here, the writing is induced by the electric field between the STM tip and the surface, thus it can be regarded as a sort of bias-induced SPL. During writing, molecular precursors, which are present on the surface as a highly mobile molecular gas are attracted towards the tip-sample gap and immobilized underneath the tip. This is accompanied by a covalent bonding to the surface resulting in the formation of highly stable NHC monolayers. The method allows for the creation of arbitrary structures with resolutions in the range of single nanometers. The writing furthermore works on a variety of (modified) semiconductor surfaces and with different NHC molecules, making a wide range of applications conceivable.

[1] R. Garcia. et al., Nat. Nanotechnol. **9**, 577 (2014).

[2] M. N. Hopkinson et al., Nature **510**, 485 (2014).

[3] M. Franz et al., Nat. Chem. **13**, 828 (2021).

[4] M. Franz et al., Angew. Chem. Int. Ed. **64**, e202511094 (2025).

⁺ Author for correspondence: martin.franz@physik.tu-berlin.de

Supplementary information

Figure 1 shows STM images of structures written by the NHC-SPL method developed here. The writing is demonstrated for two different NHC molecules and three different substrates underpinning the high degree of universality of the method.

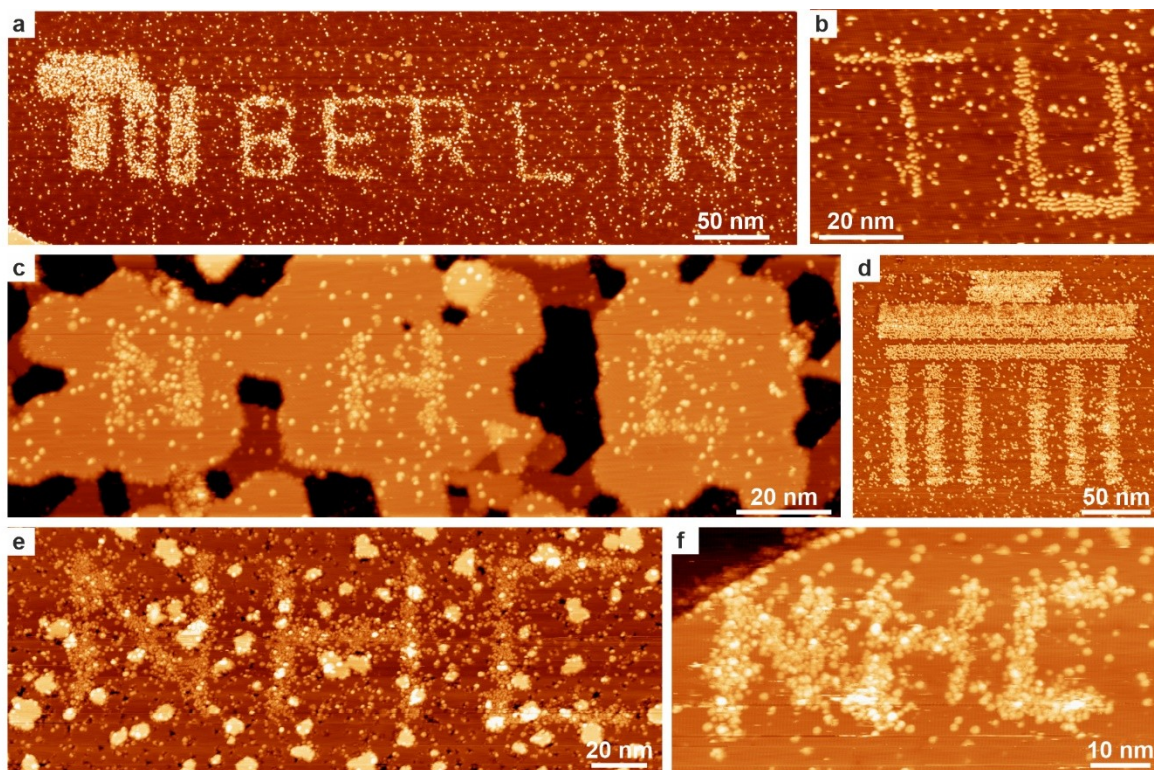


Figure 1: STM images of structures written with the NHC-SPL method developed here using two different NHC molecules and three substrates: (a) BIme-NHC on B-modified Si(111), (b) BIme-NHC on GaAs(110), (c) BIme-NHC on rare earth modified Si(111), (d) IPr-NHC on B-modified Si(111), (e) IPr-NHC on rare earth modified Si(111), and (f) IPr-NHC on GaAs(110).