

Achieve Desired Alkanedithiol Self-assembled Monolayers on Gold by Regulating the Surface Reaction Mechanism via an AFM-based Approach

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Outline

❖ Introduction

- *Background and Motivation*
- *Our proposed approach- using scanning probe lithography method known as nanografting performed in an alkanedithiol solution*

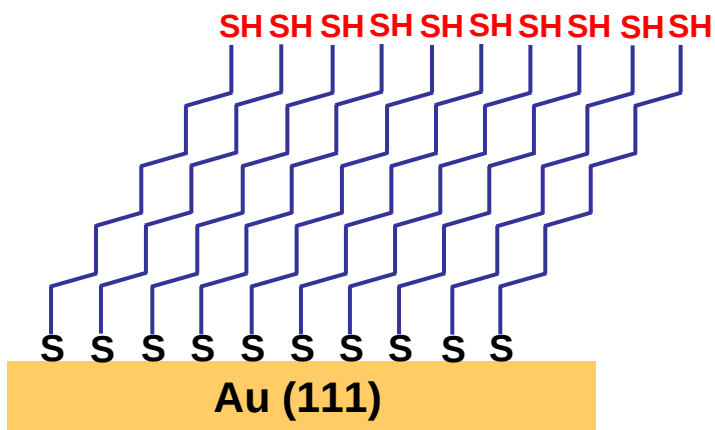
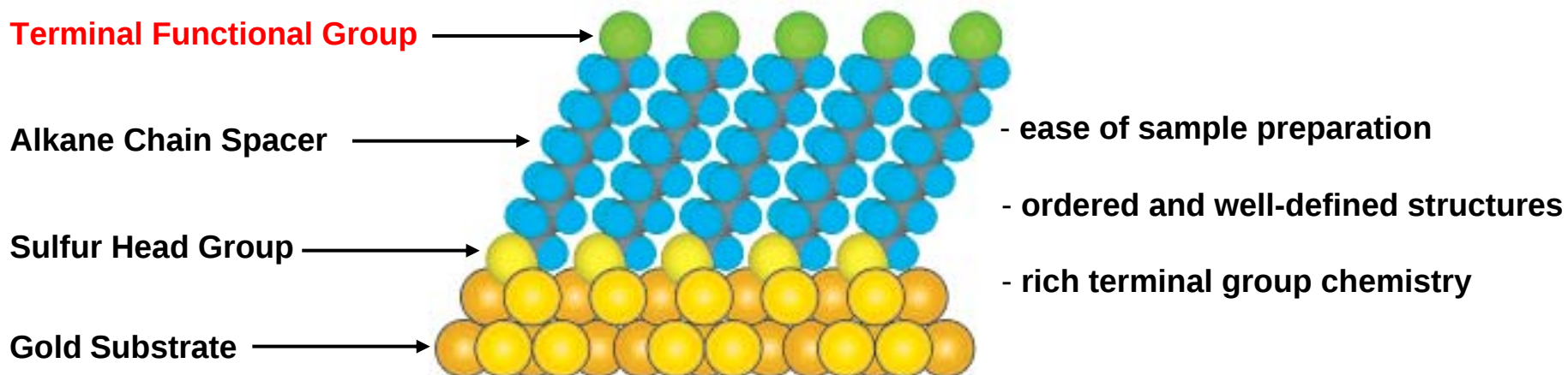
❖ Results

- *AFM studies to probe the molecular orientation of naturally grown alkanedithiol SAMs*
- *Nanofabrication of high-quality thiol-terminated SAMs using nanografting*

❖ Conclusions



Self-assembled Monolayers of Organothiols on Gold



- Self-assembled monolayers exhibiting free thiol functional groups provide the possibility to anchor metal atoms and particles, fabricate metal films on organic substrates, or construct molecular electronics.

- α , ω - organodithiols on gold are good candidates to generate thiol-terminated surfaces if these dithiol molecules adopt a upright or standing-up configuration and are packed densely in the SAM

Love et al. *Chem. Rev.* **2005**, 105, 1103-1169.

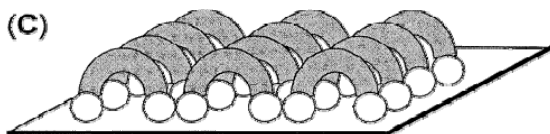
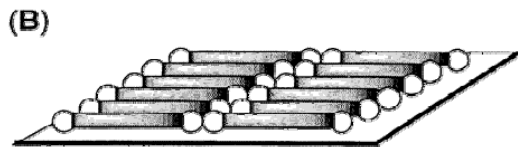
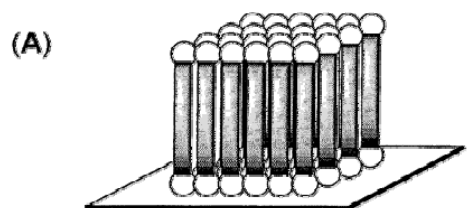


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Challenges



Schematic representations of three possible orientations of α,ω -organodithiols on the metal surface corresponding to the (A) stand-up, (B) lie-down, and (C) looped monolayer assembly structures.

Yang et al. *J. Org. Chem.* **2000**, 65, 871-877.

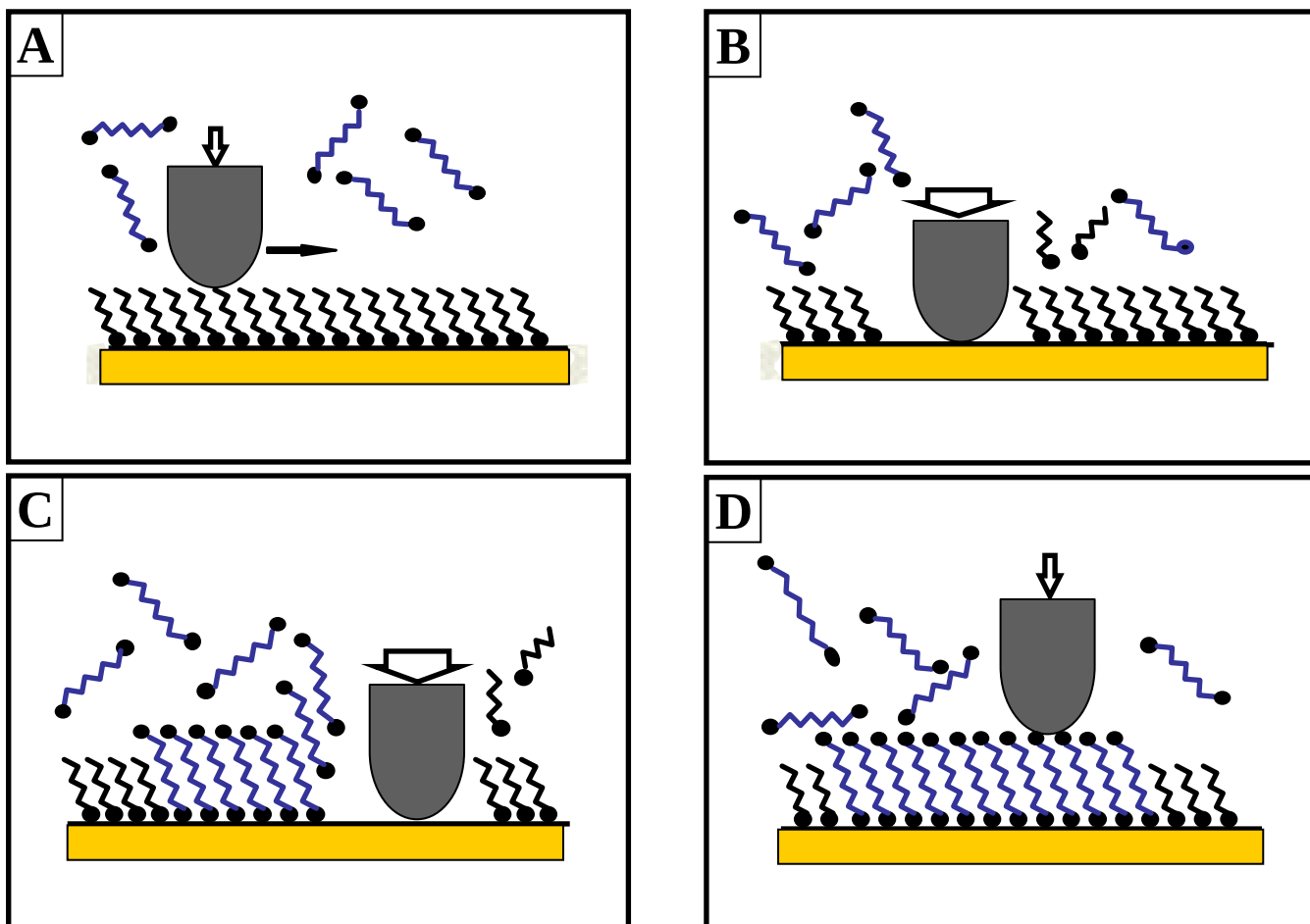
Natural growth approach (the most common preparation method, namely, soaking gold substrates in the corresponding organodithiol solutions) typically result into the formation of disordered, ill-defined surfaces based on pervious IR spectroscopy and scanning tunneling microscopy (STM) studies.

Our Motivation

Develop new methodology to fabricate high-quality thiol-terminated surfaces at nanometer scale using simple organodithiols such as n-alkanedithiols.



Nanografting*- the Proposed Approach to Produce Thiol-terminated SAMs



Nanografting enabling aspects:

- *Producing nanostructures with designed size and geometry*
- *Surface structural characterization*
- *Regulation of the surface reaction mechanism*

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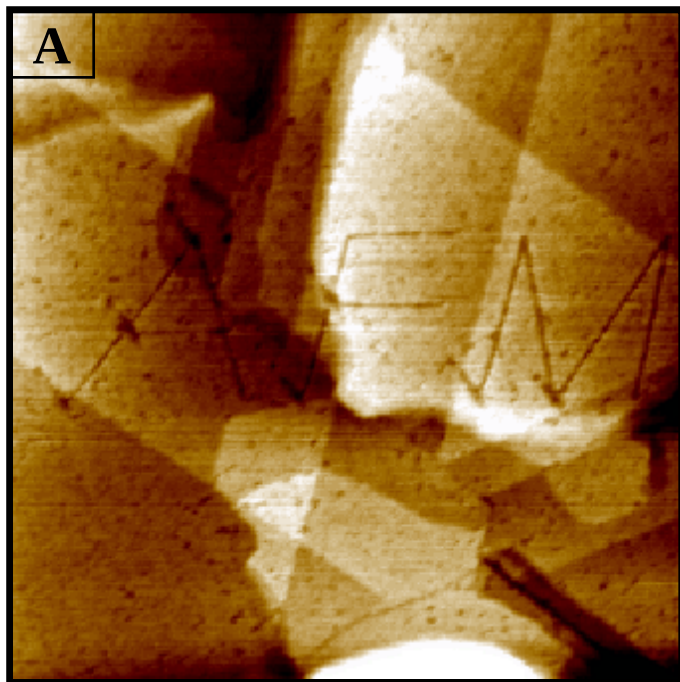
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Abbreviations of the Thiol Molecules Used in This Talk

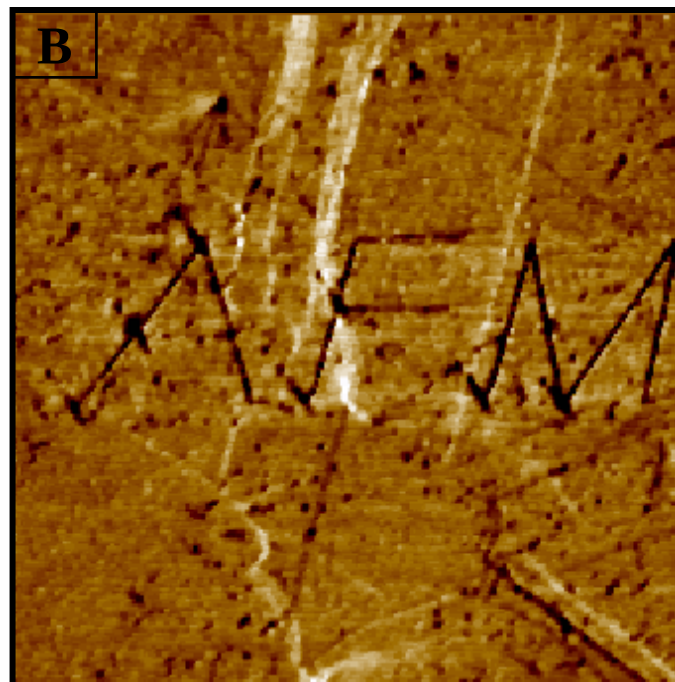
C6:	$\text{HS}-(\text{CH}_2)_5\text{CH}_3$	1-Hexanethiol
C8:	$\text{HS}-(\text{CH}_2)_7\text{CH}_3$	1-Octanethiol
C10:	$\text{HS}-(\text{CH}_2)_9\text{CH}_3$	1-Decanethiol
C2COOH:	$\text{HS}-(\text{CH}_2)_2\text{COOH}$	3-Mercaptopropionic acid
C8DT:	$\text{HS}-(\text{CH}_2)_8\text{-SH}$	1,8-Octanedithiol
C16DT:	$\text{HS}-(\text{CH}_2)_{16}\text{-SH}$	1,16-Hexadecanedithiol



SAM Fabrication with High Spatial Resolution Using Nanografting



scan size: 600 nm × 600 nm



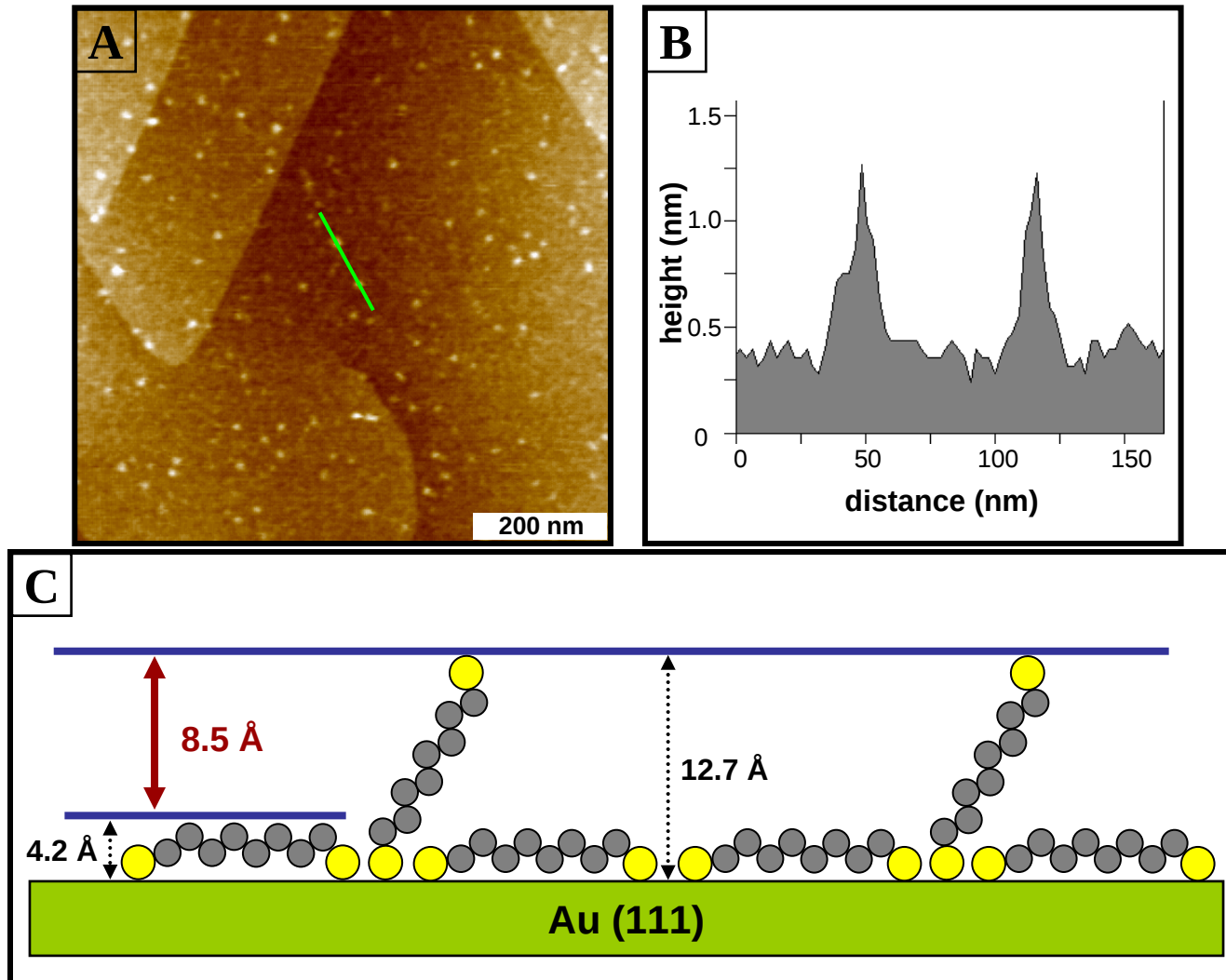
scan size: 600 nm × 600 nm

[A] Topographic, and [B] Friction images showing that a fabricated “AFM” logo composed of C2COOH molecules and with the line width less than 10 nm is produced successfully within a C10 matrix on gold. The pattern is negative with respect to the surrounding matrix in topographic image due to the shorter molecular length of 3-mercaptopropionic acid. In addition, the two terminal functionalities (carboxylic acid versus methyl) are differentiated in lateral force (friction) image.



AFM Capability of Differentiation of Alkanedithiol Molecular Orientations

(a naturally grown C8DT SAM prepared by soaking in a 0.02 mM solution for 7 days)

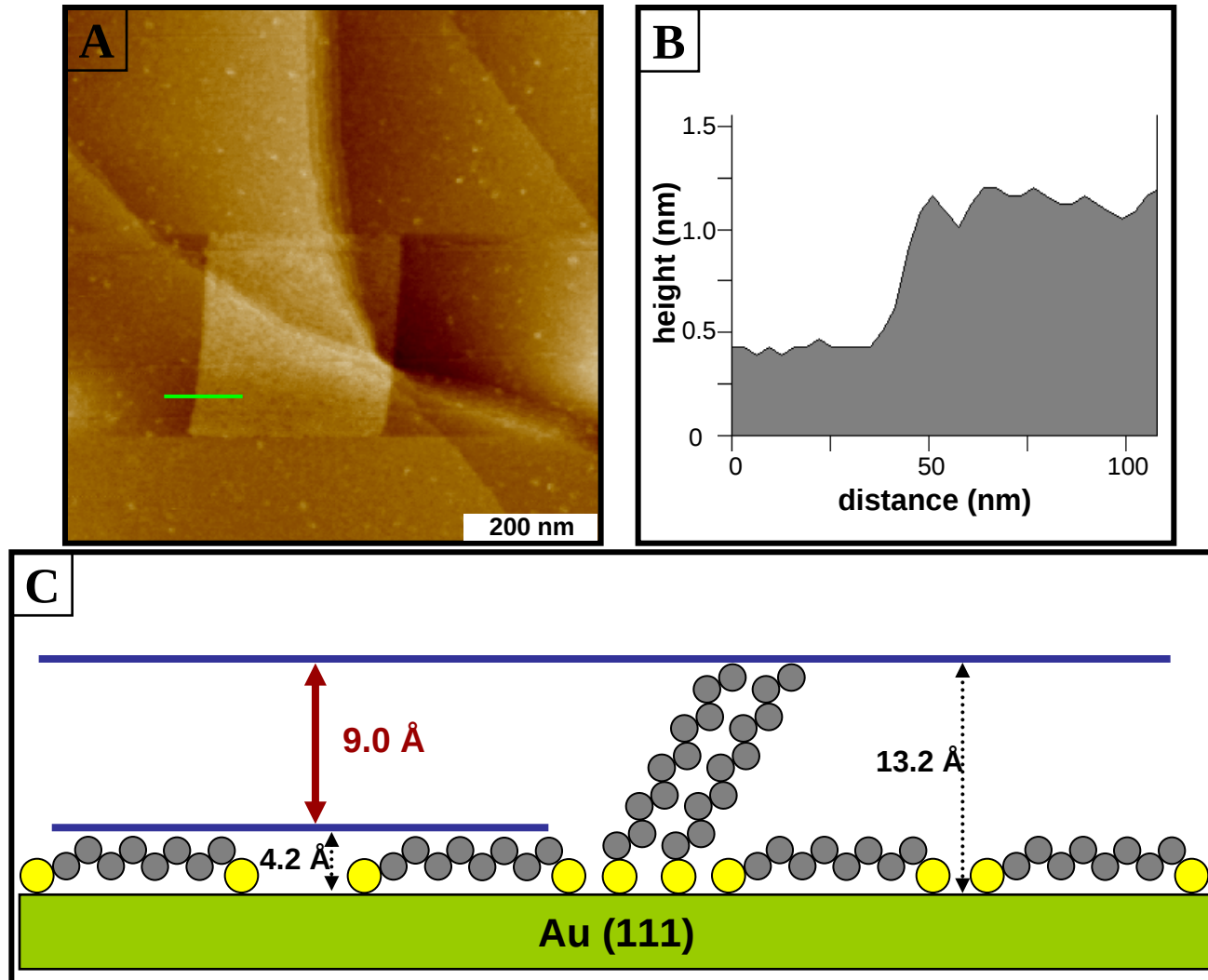


[A] Topographic image showing protrusion dots sparsely distributed on the surface. [B] Cursor profile corresponding to the line drawn in [A]. [C] A model showing the theoretical height difference between a lying-down C8DT monolayer and a standing-up C8DT SAM. *Yu et al. Langmuir 2008, 24, 11661-11668.*



AFM Capability of Probing the Alkanedithiol Layer Thickness

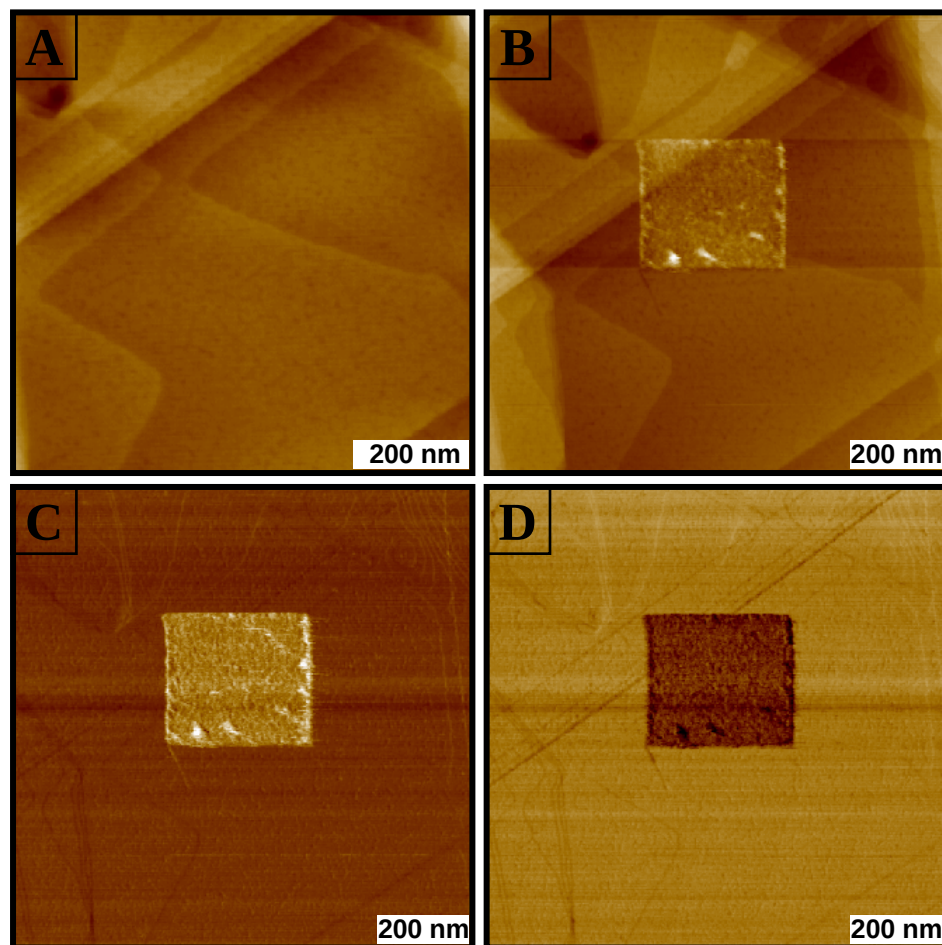
(a naturally grown C8DT SAM prepared by soaking in a 0.02 mM solution for 7 days)



[A] The *in situ* topographic image showing fabrication of a C10 SAM into the C8DT SAM matrix. [B] Cursor profile corresponding to the line drawn in [A]. [C] A Model showing the theoretical height difference between a lying-down C8DT monolayer and an upright C10 SAM.



Construction of a SH-terminated SAM via nanografting (using a 0.02 mM C8DT solution)



[A] Topographic image of the C6 SAM matrix before fabrication. [B] After nanografting the resulting pattern of C8DT layer is taller than the surrounding C6 SAM. The corresponding friction trace [C] and retrace [D] images of [B].

Yu et al. Langmuir **2008**, 24, 11661-11668.

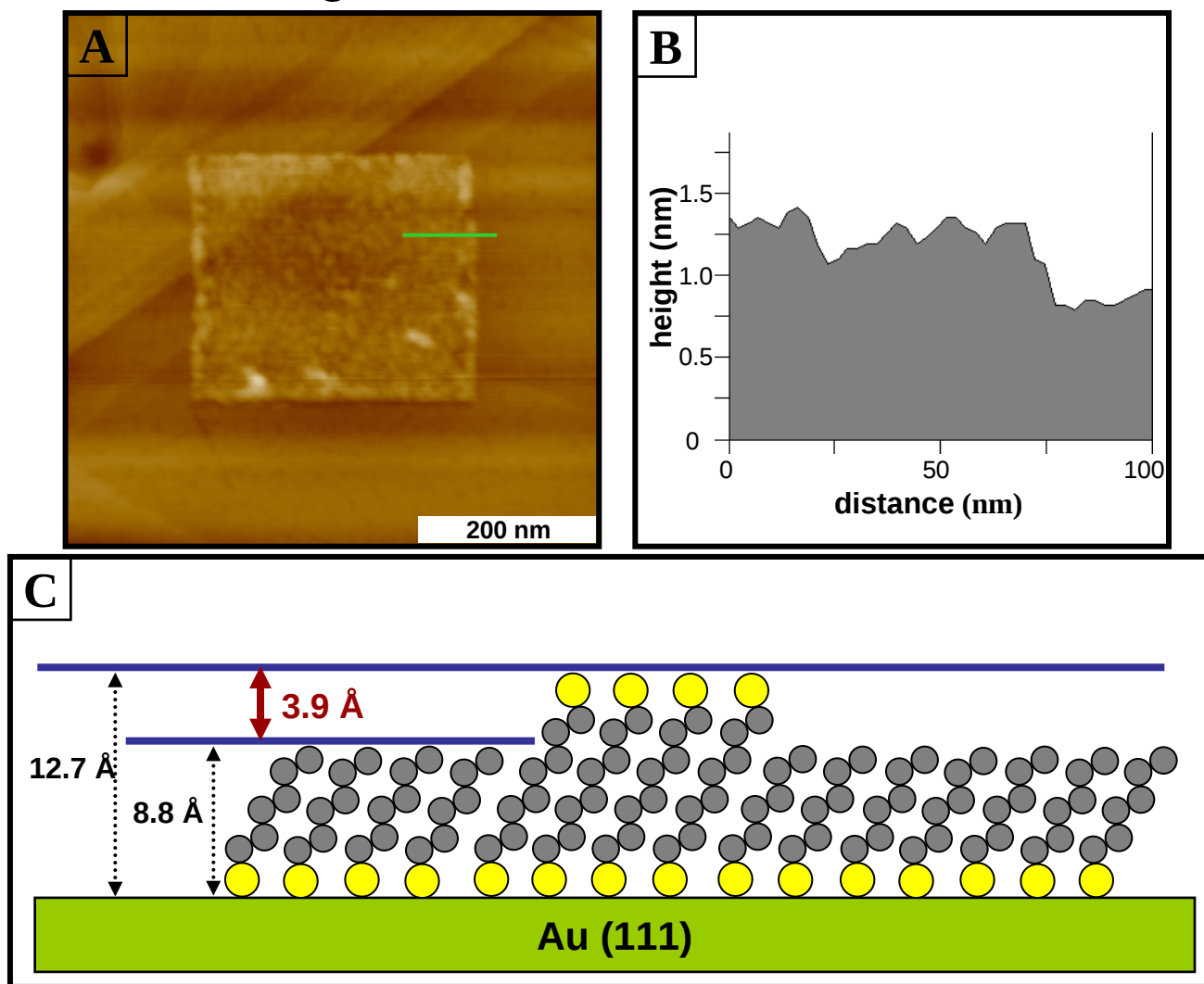


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Quantitative Height Measurement of Fabricated C8DT SAM



[A] A high-resolution topographic image showing that dithiol molecules are densely packed in the pattern. [B] Cursor profile corresponding to the line drawn in [A]. [C] A model showing the theoretical height difference between a stand-up C8DT monolayer and a standing-up C6 SAM.

Yu et al. Langmuir 2008, 24, 11661-11668.

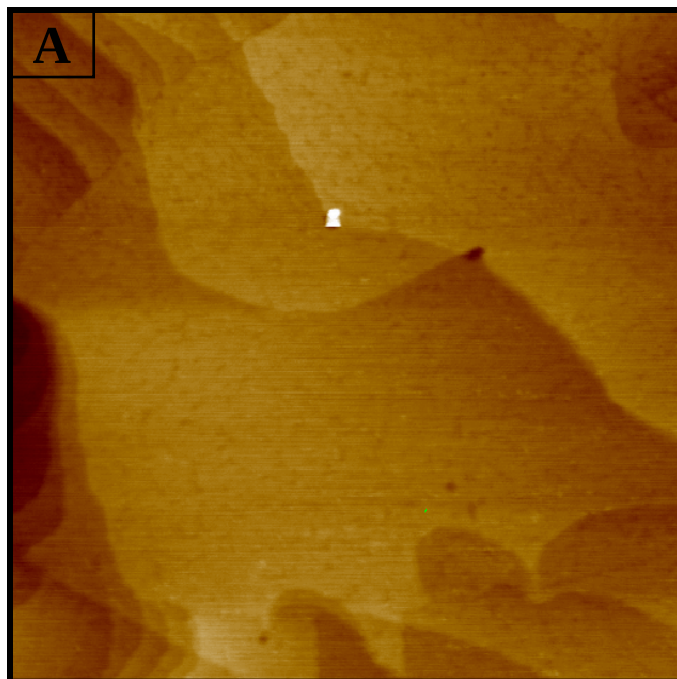


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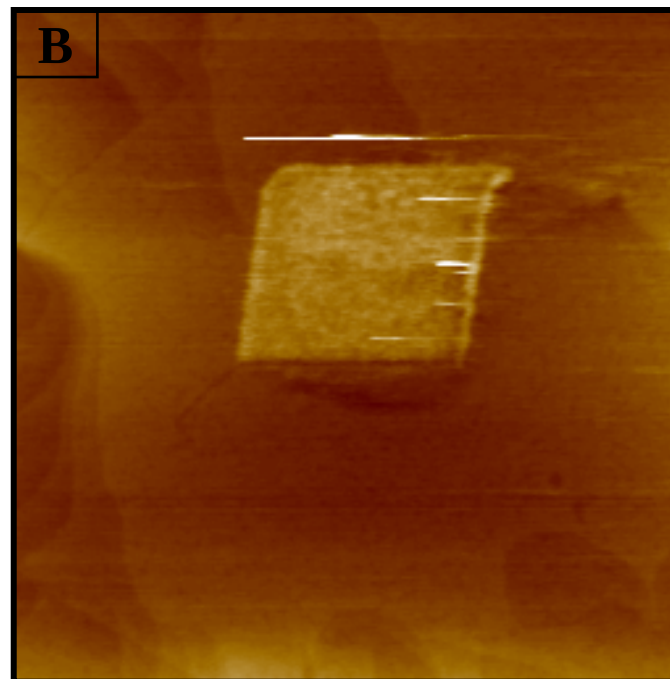
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Robustness Test of Nanografting with Longer n-Alkanedithiols



scan size: 1000 nm × 1000 nm



scan size: 800 nm × 800 nm

[A] Topographic image of a C10 SAM matrix before fabrication. [B] *In situ* topographic image showing the fabricated pattern of C16DT layer is taller than the surrounding C10 SAM.

Yu et al. *Langmuir* 2008, 24, 11661-11668.

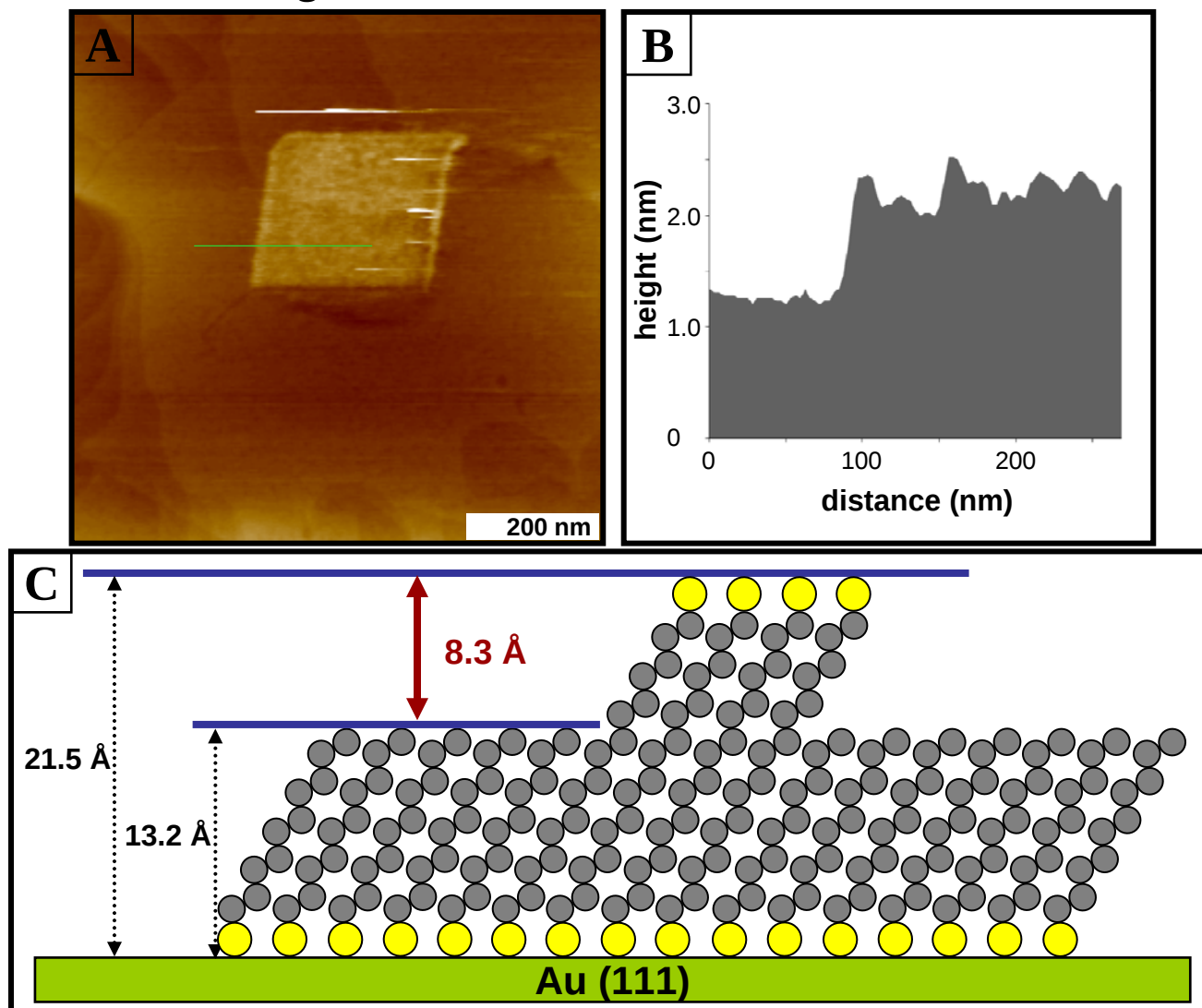


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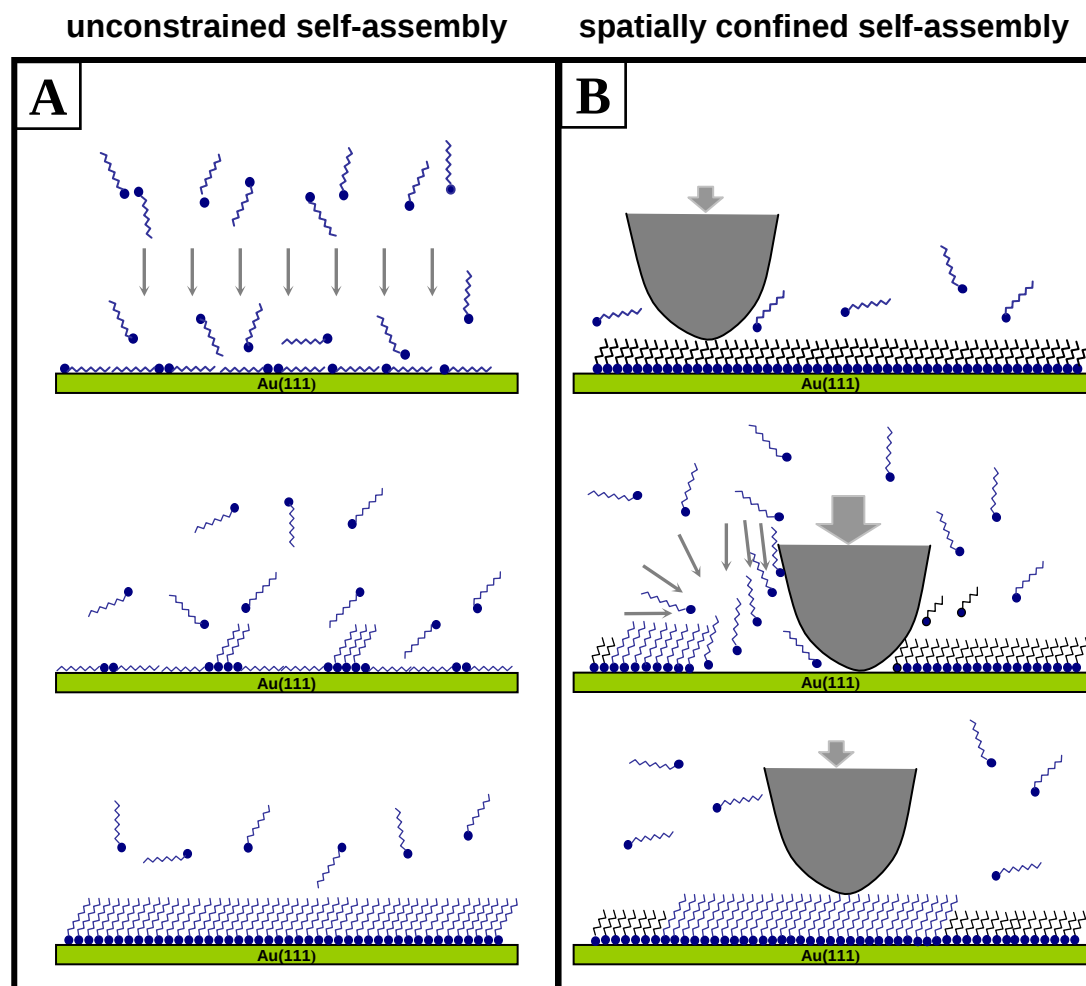
Quantitative Height Measurement of Fabricated C16DT SAM



[A] A high-resolution topographic image showing that dithiol molecules are densely packed in the pattern. [B] Cursor profile corresponding to the line drawn in [A]. [C] A model showing the theoretical height difference between a standing-up C16DT monolayer and a standing-up C10 SAM.



Different Thiol Self-Assembly Reaction Pathway during Nanografting



Schematic diagram of two different surface reaction pathways of thiol self-assembly on gold. [A] Unconstrained thiol adsorption occurs during natural self-assembly. [B] Spatially confined self-assembly occurs in nanografting.

Xu et al., J. Am. Chem. Soc. 1998, 120, 9356-9361.

Yu et al. J. Am. Chem. Soc. 2006, 128, 11574-11581.

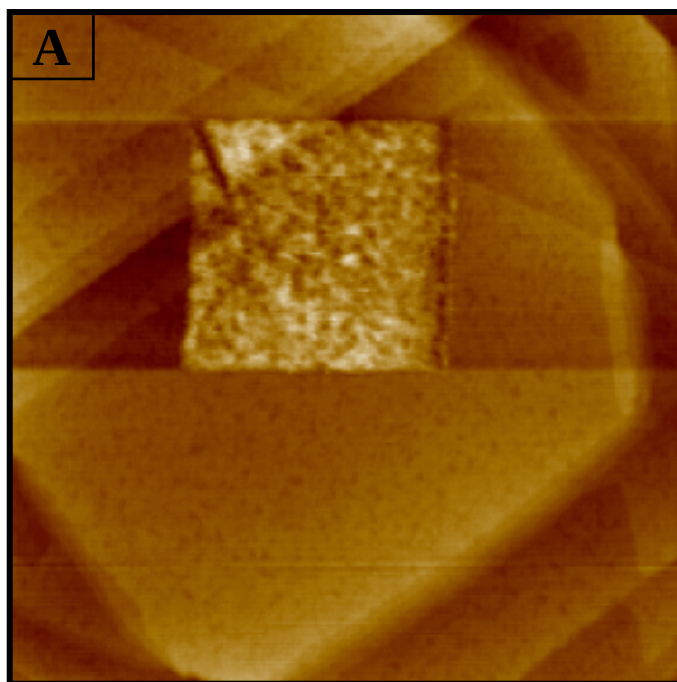


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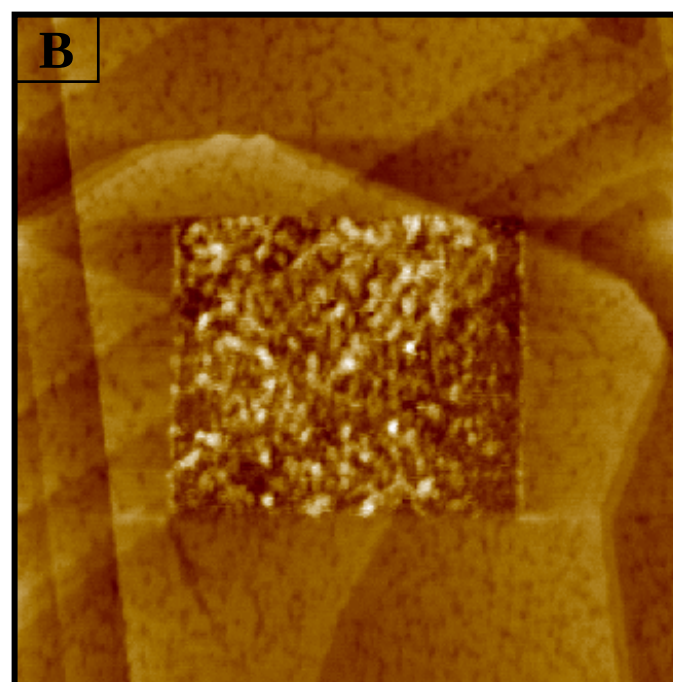
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Impact of Fabrication Speeds in our Approach (using a 0.02 mM C8DT solution)



scan size: 800 nm × 800 nm



scan size: 600 nm × 600 nm

Topographic images showing C8DT patterns were nanografted into a C6 matrix with a fabrication speed of [A] 1500 nm/s, and [B] 5000 nm/s, respectively.



Conclusions

1. AFM studies using both high-resolution imaging and height measurements allow the differentiation of molecular orientations and accurate determination of the layer thickness. Using C8DT as an example, alkanedithiol SAMs prepared from natural growth approach are characterized. Most dithiol molecules adopt a lying-down configuration in the resulting SAM.
2. We report and demonstrate a new approach, using AFM-based lithography method known as nanografting, to quickly fabricate high-quality thiol-terminated SAMs on gold. Dithiol molecules adopt a standing-up configuration and are densely packed within the SAMs.
3. The improved quality of C8DT SAMs from our new approach can be ascribed to a different self-assembly pathway in the nanografting, during which the spatial confinement effect may allow the dithiols to bypass the lying-down phase. Therefore, impact of fabrication speed in our approach is observed.

