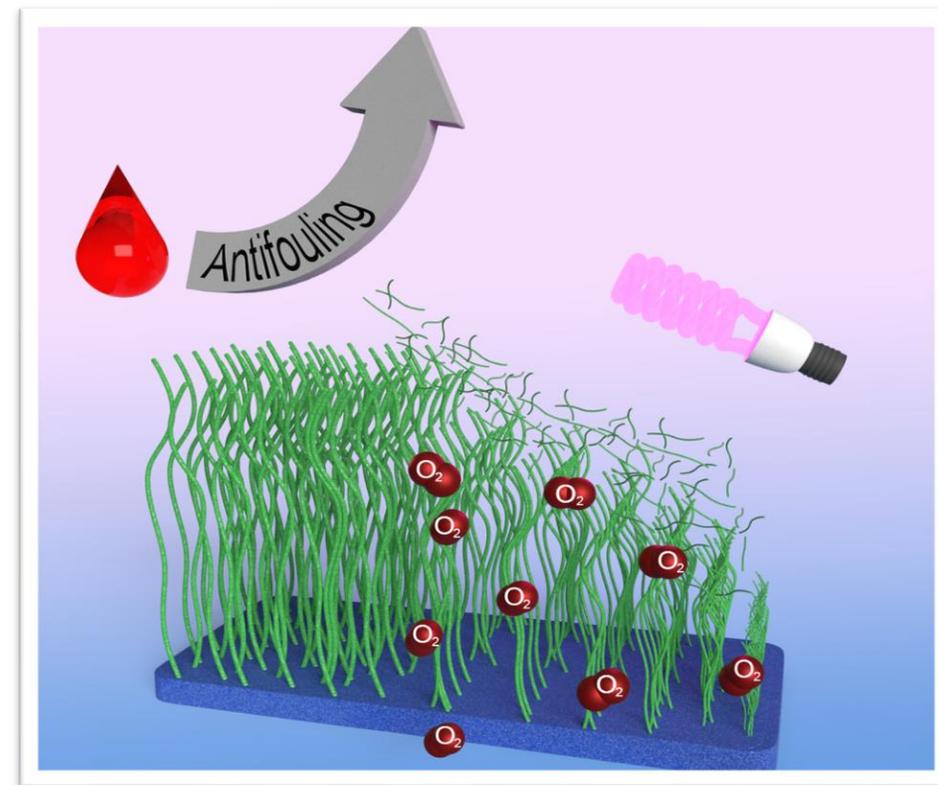
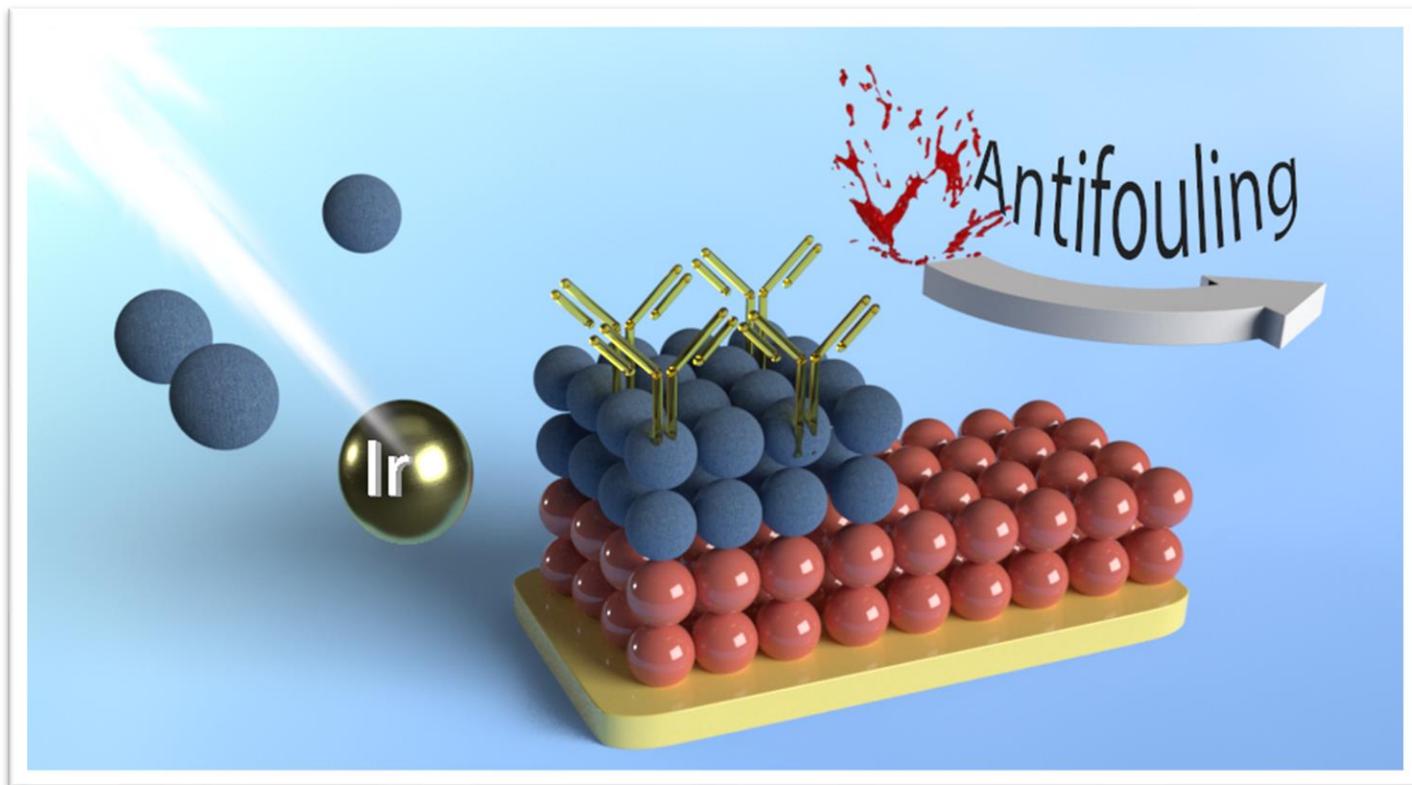


Visible Light-triggered Living Polymerization for Creating Antifouling and Bioactive Surfaces



Andriy Kuzmyn

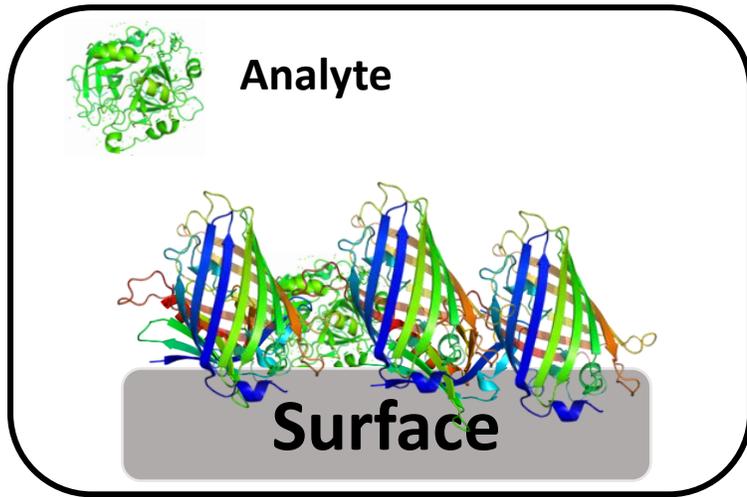
4TU.HTM

M2 materials
innovation
institute

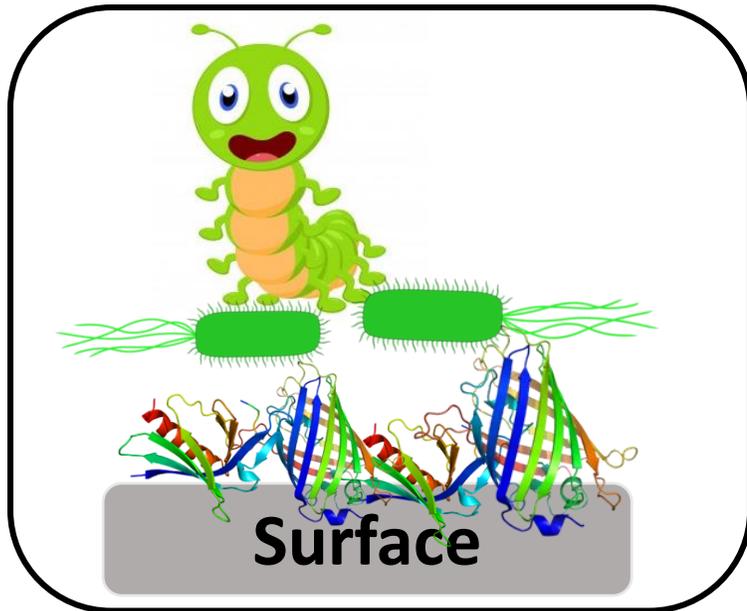


WAGENINGEN
UNIVERSITY & RESEARCH
ORGANIC CHEMISTRY

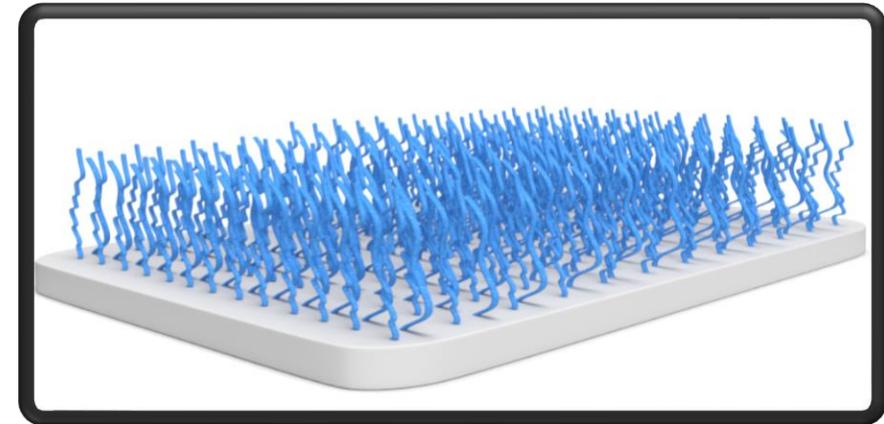
Fouling, and How to Deal with It ?



➔ Biosensors



➔ Tissue engineering
Membranes
Implants
Ships



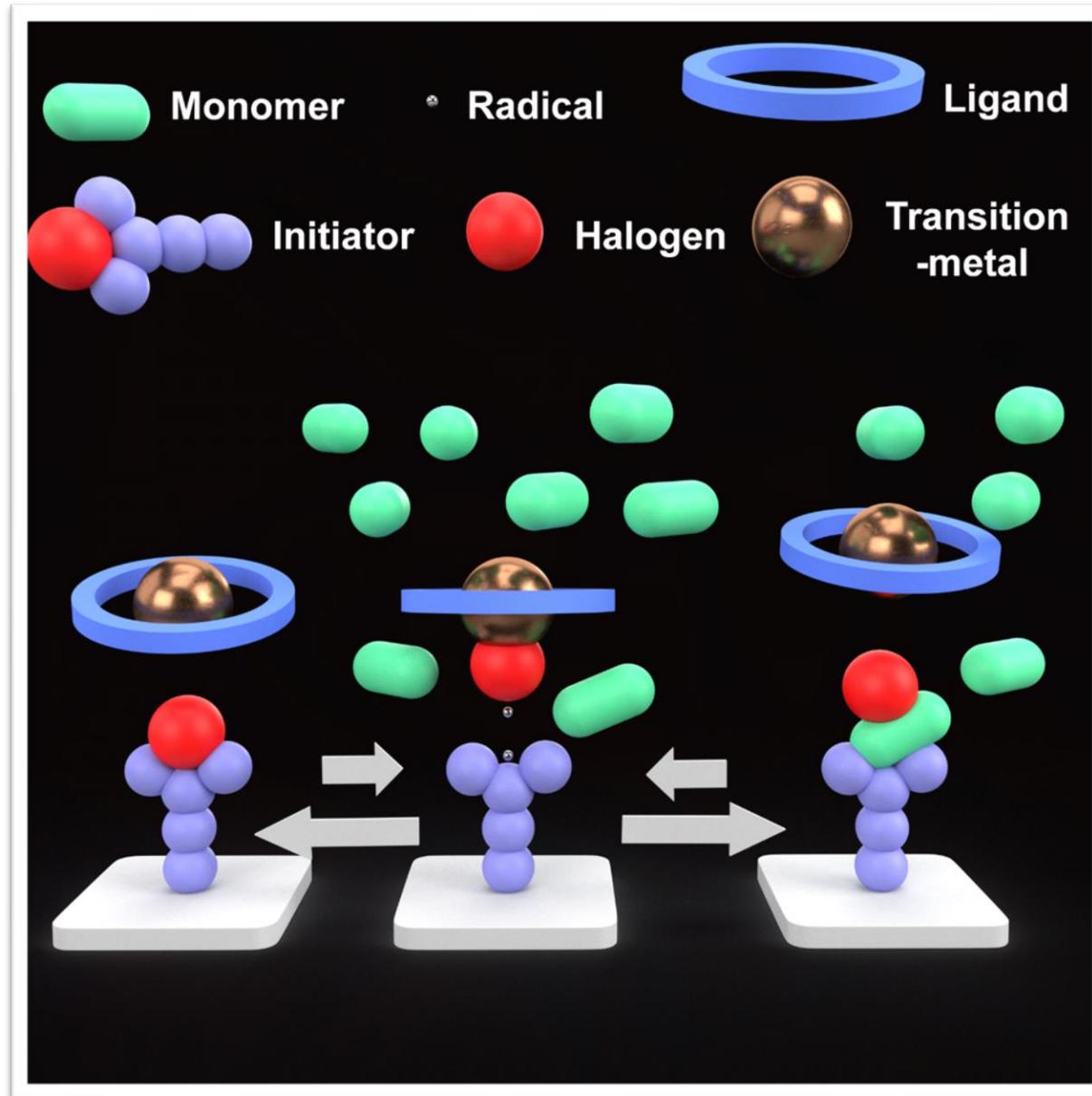
Best solution

Polymer brushes

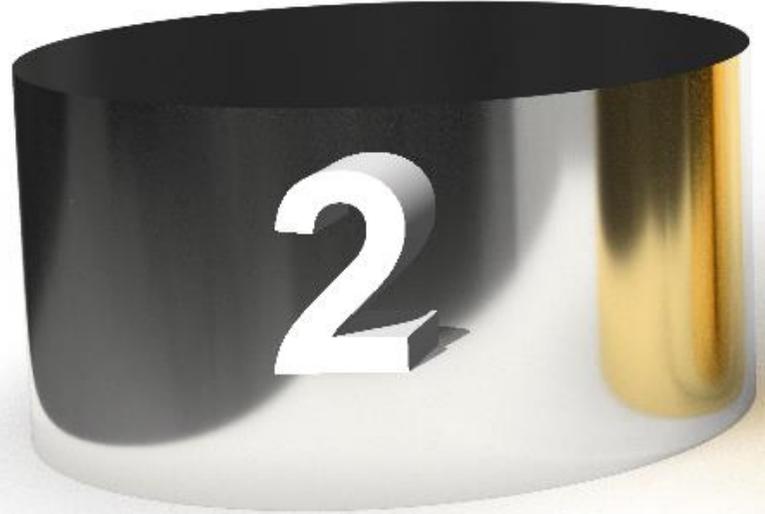
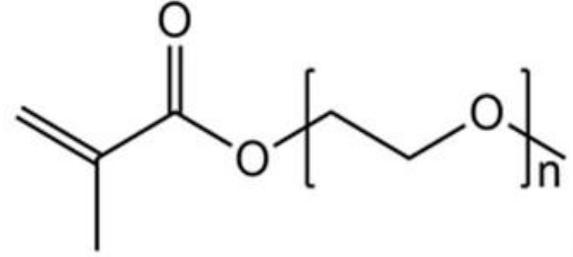
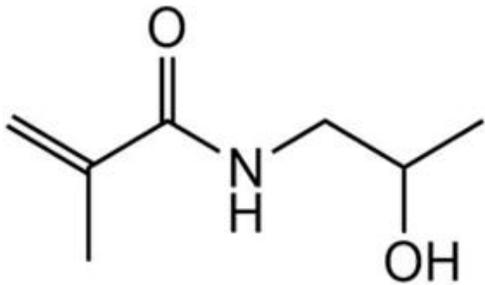
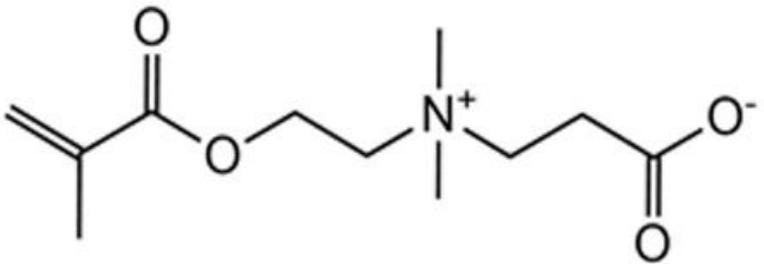


Surface

Atom Transfer Radical Polymerization (ATRP)

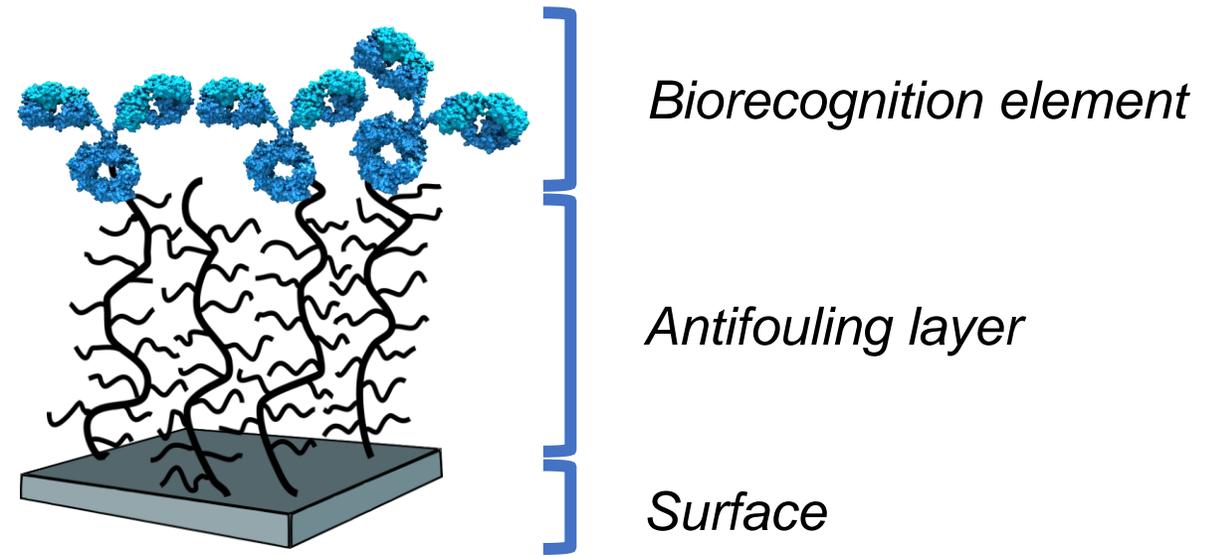
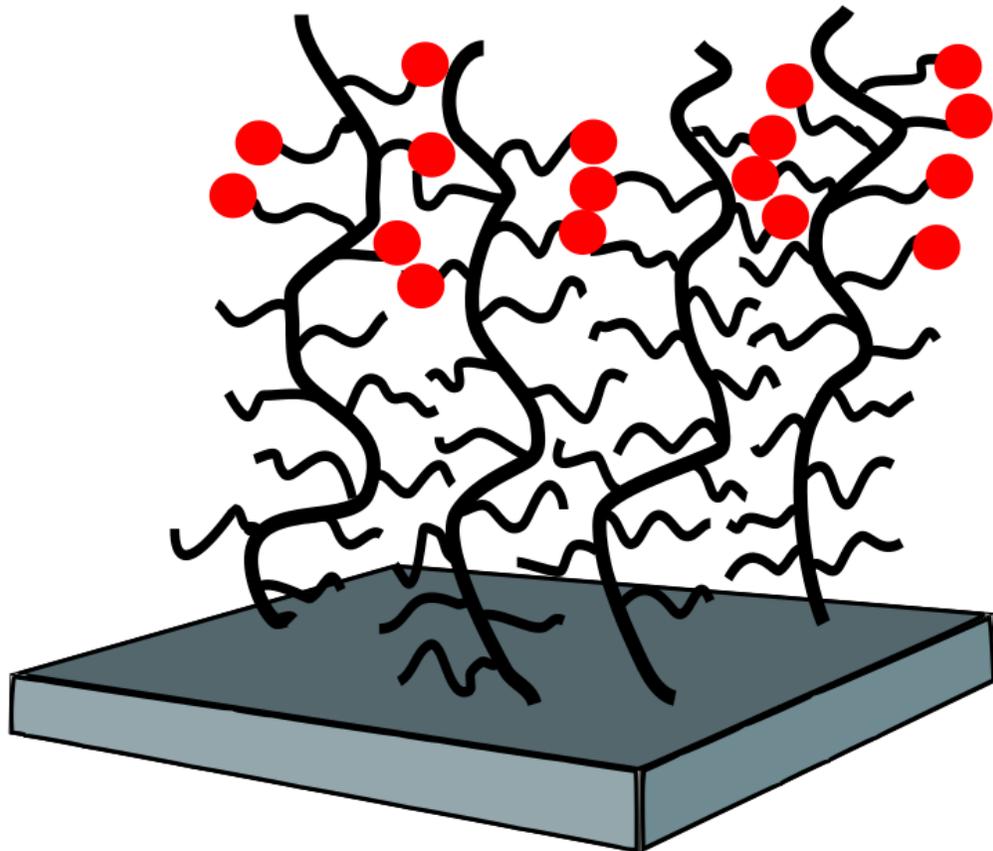


Best Performing Antifouling Polymer Brush Surfaces



van Andel, E., Lange, S. C., Pujari, S. P., Tijhaar, E. J., Smulders, M. M. J., Savelkoul, H. F. J., & Zuilhof, H. Systematic Comparison of Zwitterionic and Non-Zwitterionic Antifouling Polymer Brushes on a Bead-Based Platform. Langmuir (2019) 35, 5, 1181

Biofunctionalization of Antifouling Polymer Brushes

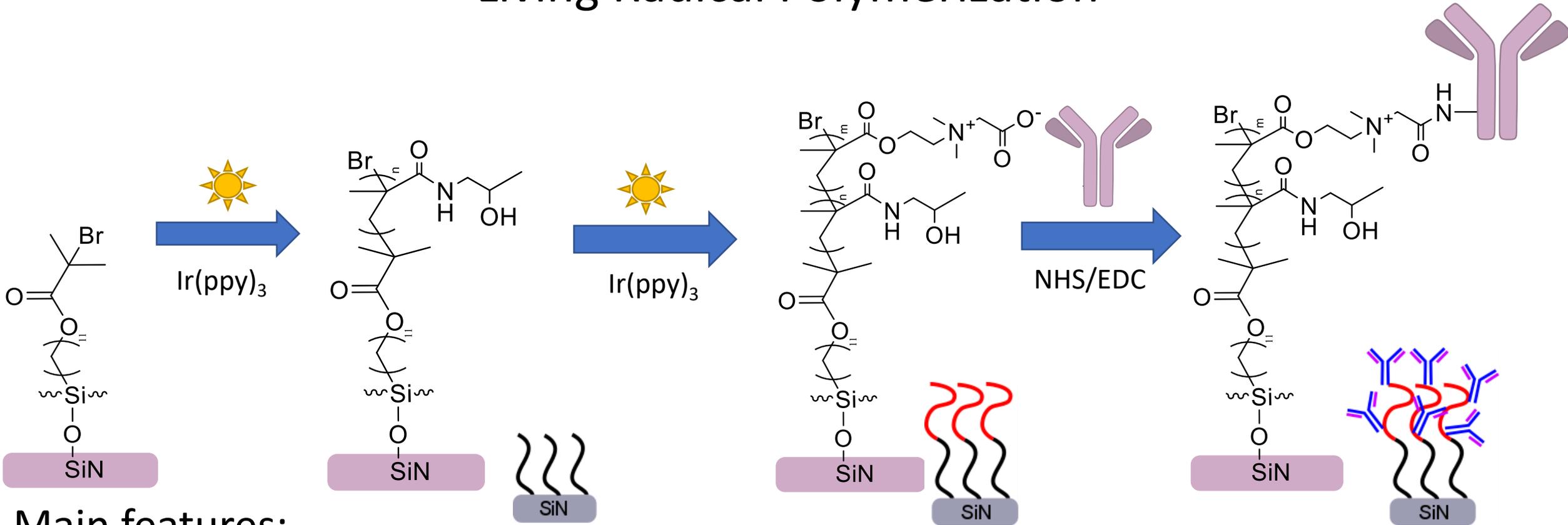


Chain-end modification

Side-chain functionalization

Block copolymer functionalization

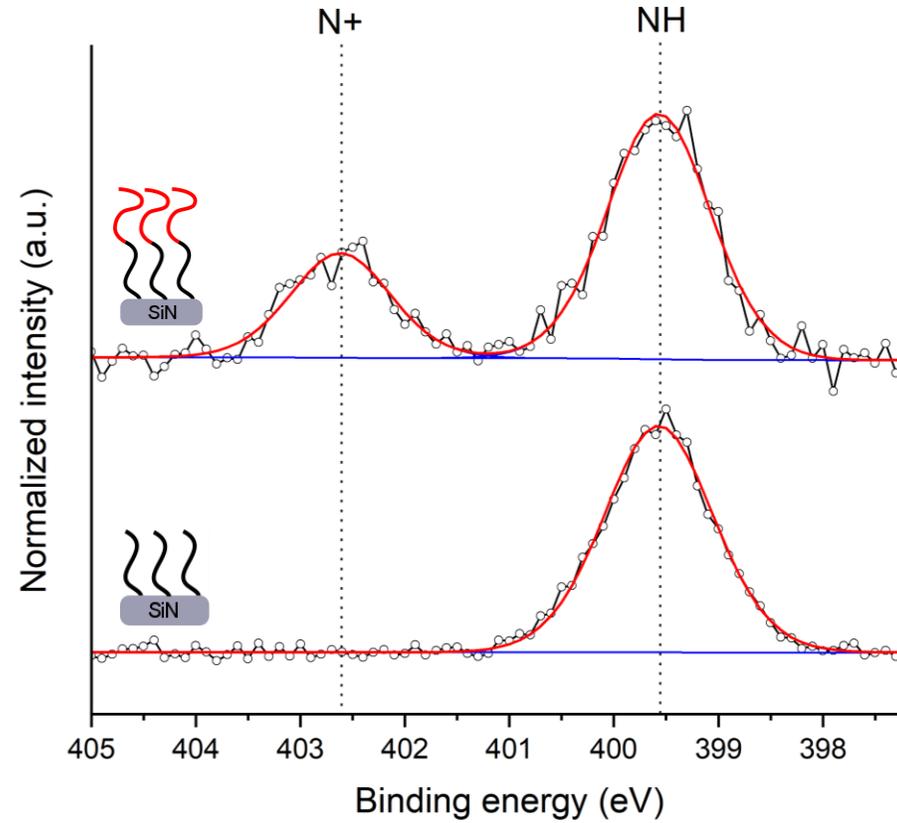
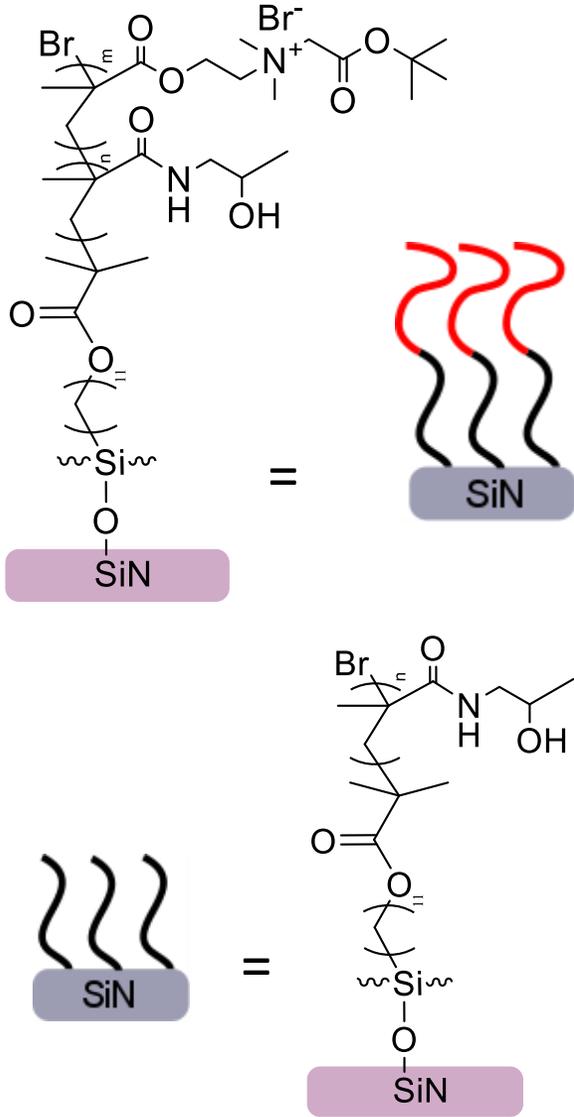
Surface-Initiated Visible Light-triggered Living Radical Polymerization



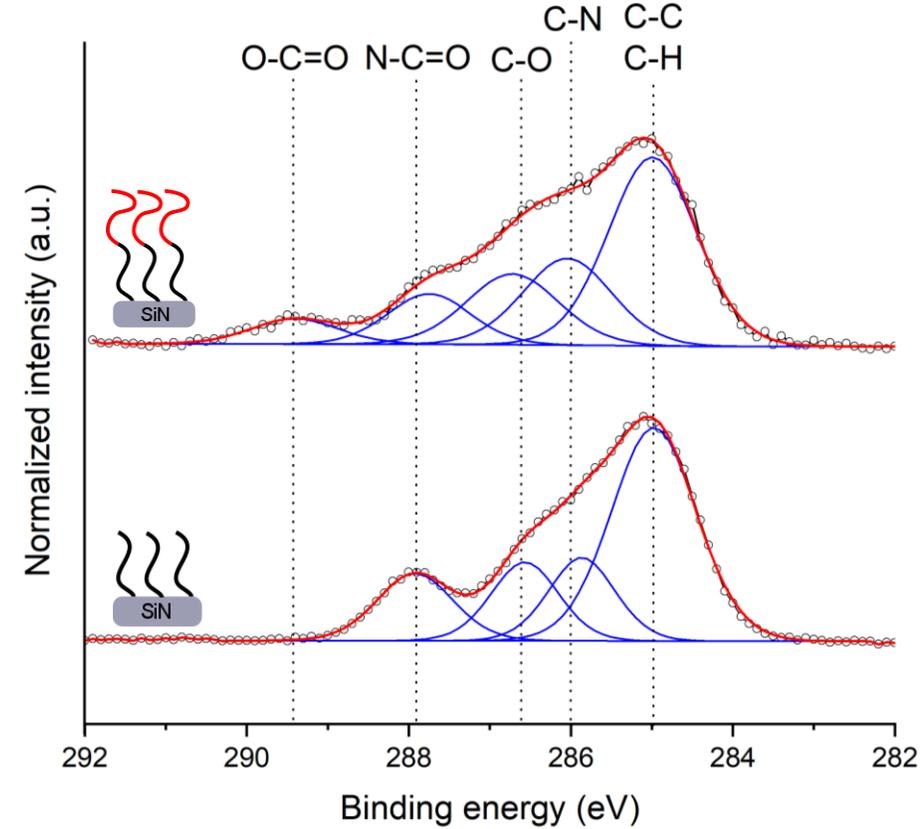
Main features:

- Well- controlled polymerization
- Patterning

XPS Characterization of Synthetized Polymer Brushes

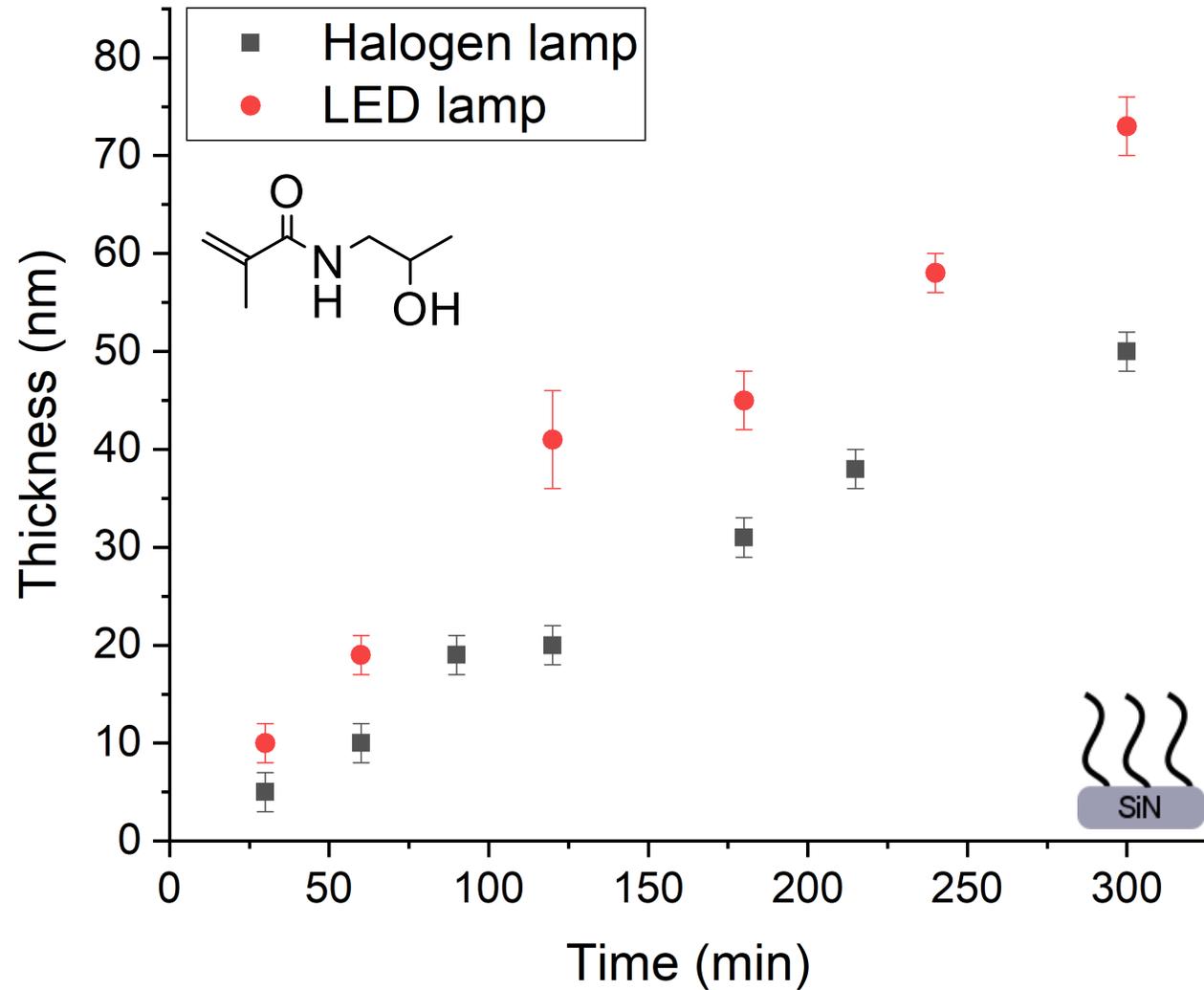


Narrow $C1s$ XPS spectra

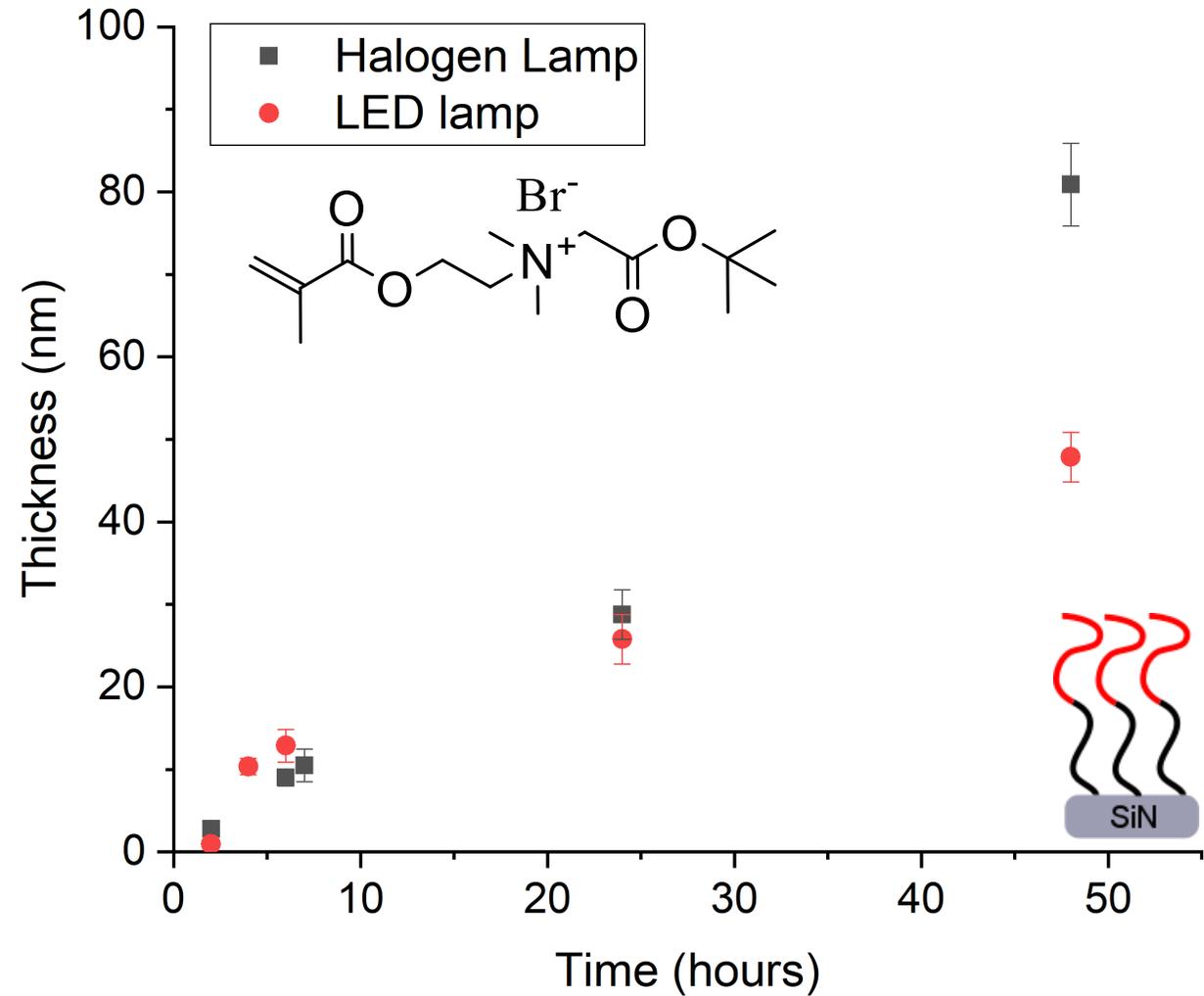


Narrow $N1s$ XPS spectra

Kinetics of Polymerization

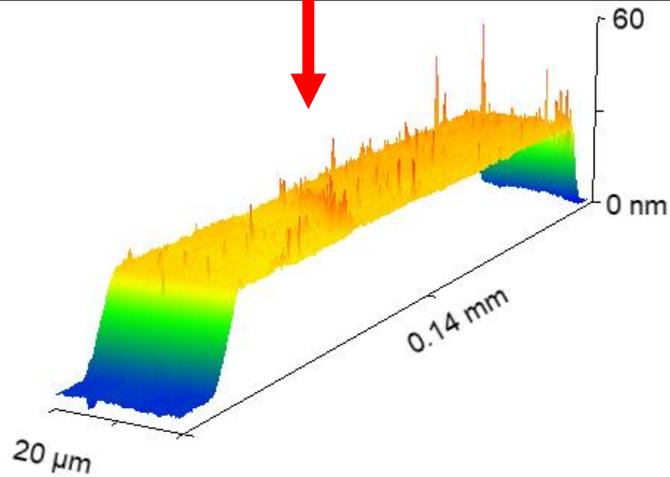
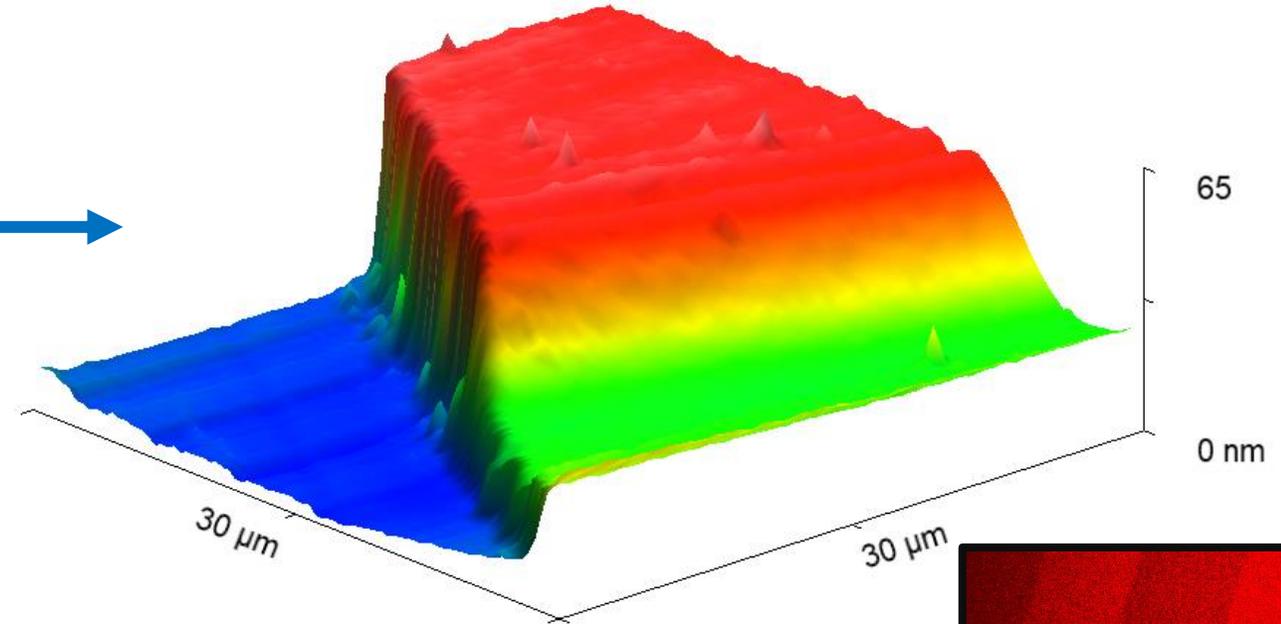
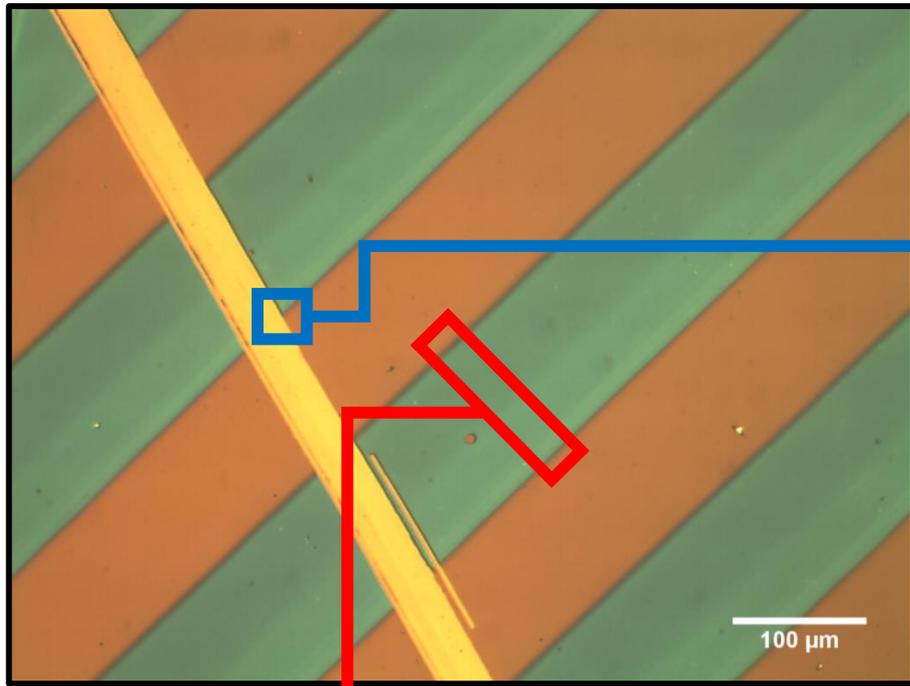


Growth of poly(HPMA) brushes vs polymerization time

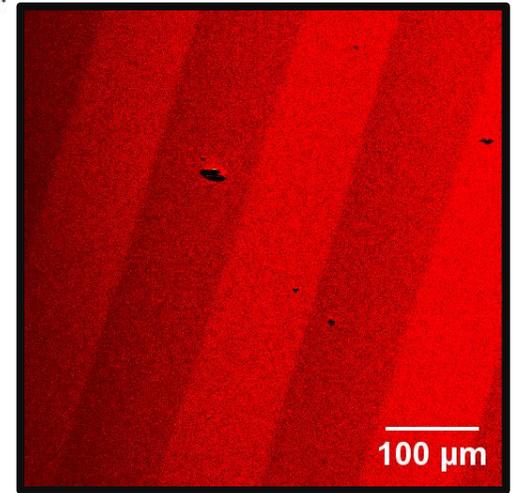


Growth of poly(CBMA-tBu) brush from poly(HPMA) brush of 20 nm

Patterned Antifouling Polymer Brush Surfaces

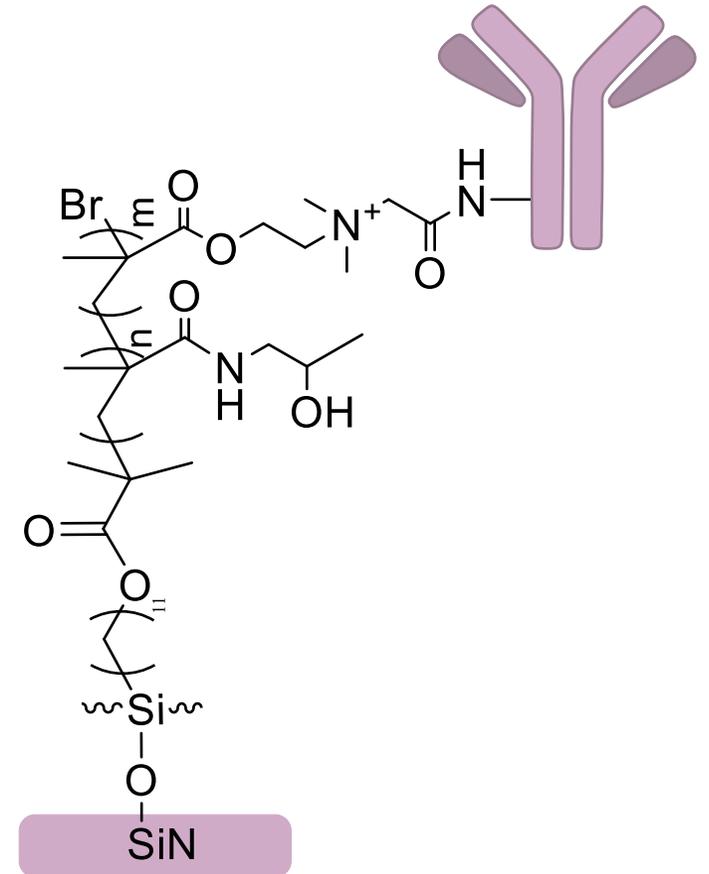
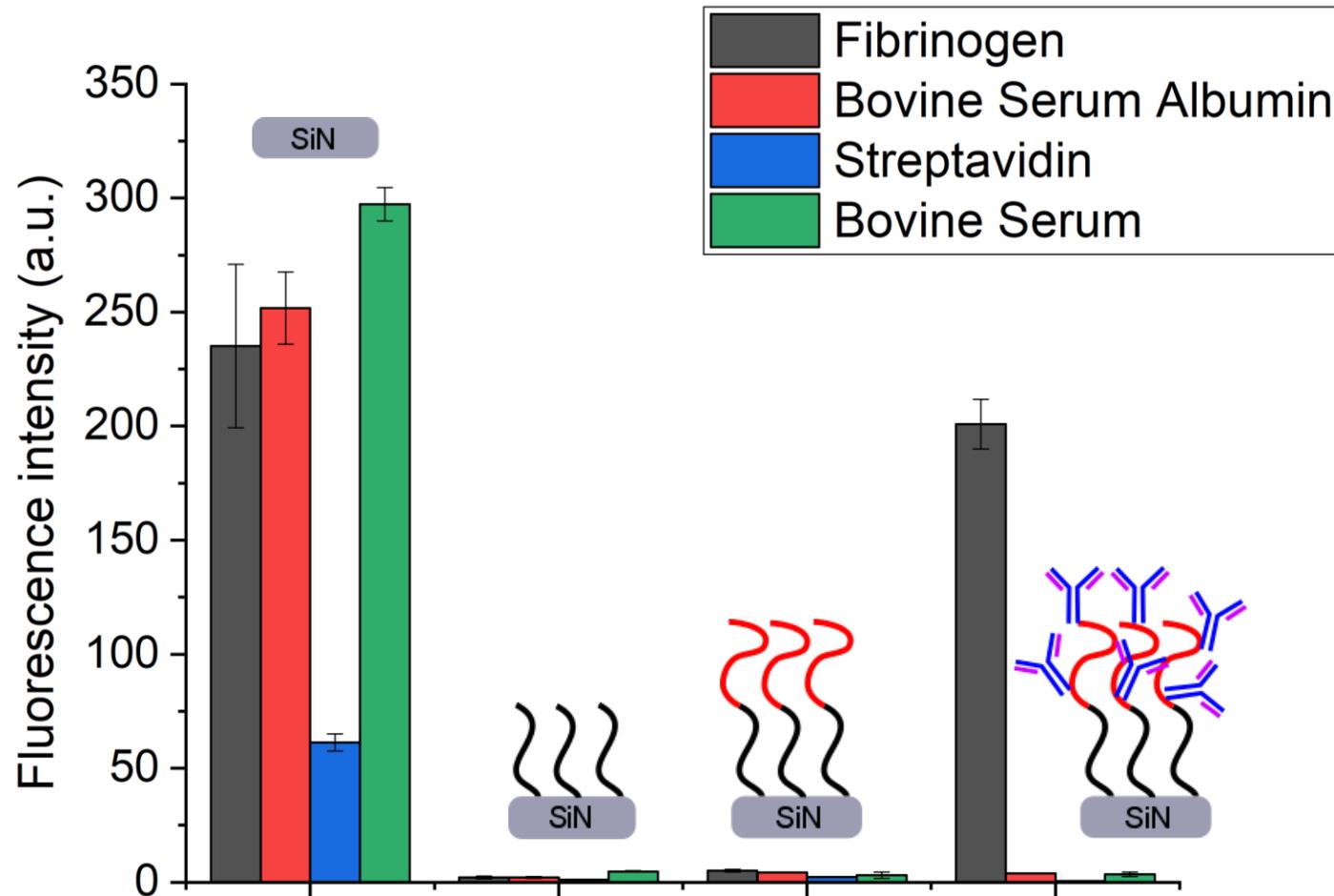


⇒ Potential for
multiplex biosensors



Auger mapping of Nitrogen(NH)

Antifouling & Bioactive Properties of Hierarchical Brushes



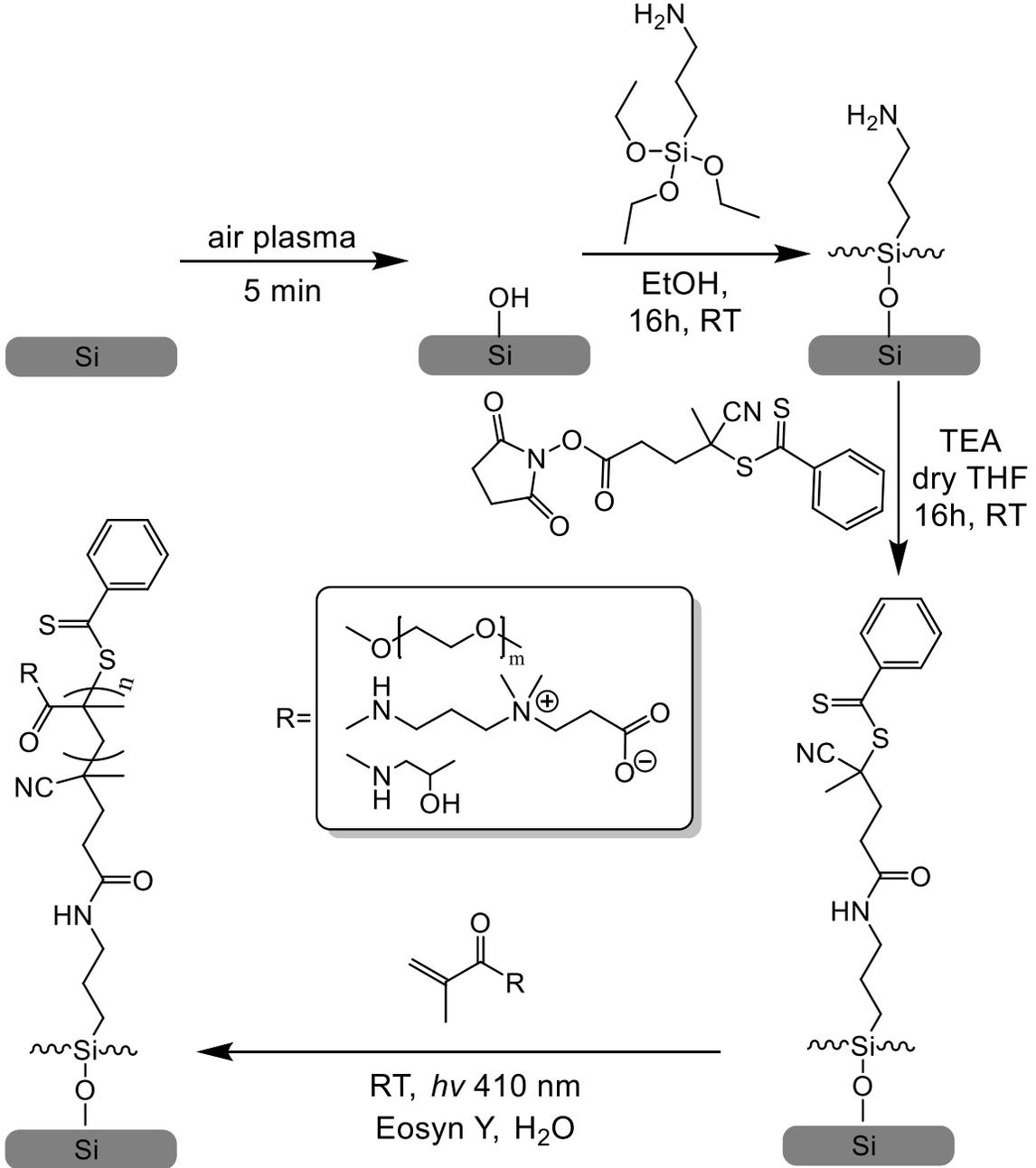
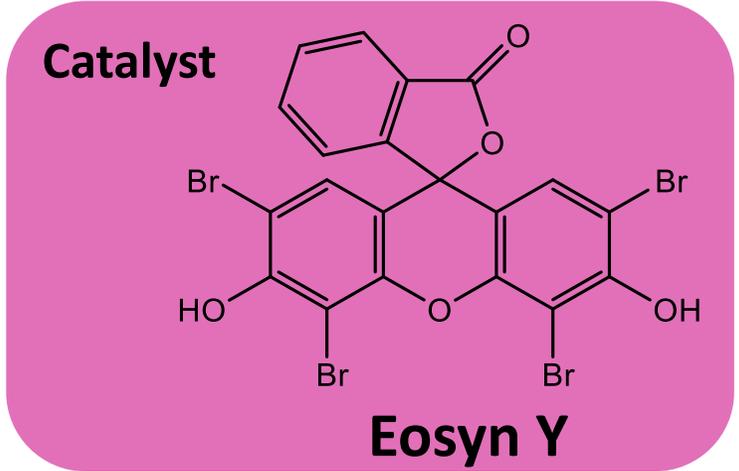
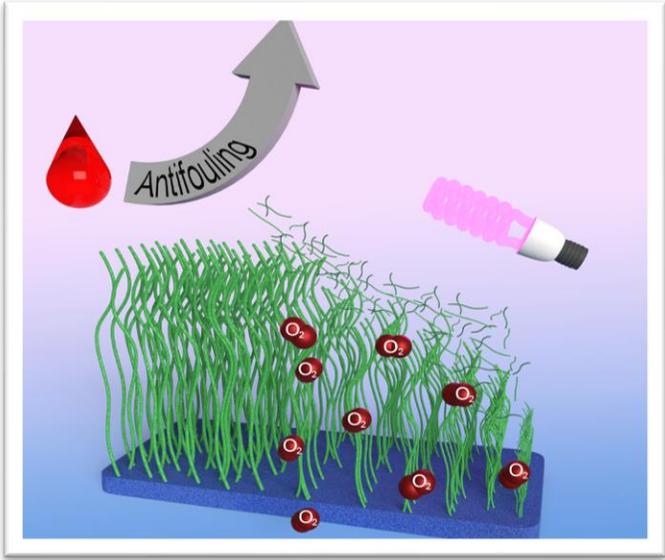
⇒ Efficient & selective antifouling

Drawbacks of Traditional Synthesis of Polymer Brushes

Heavy metals

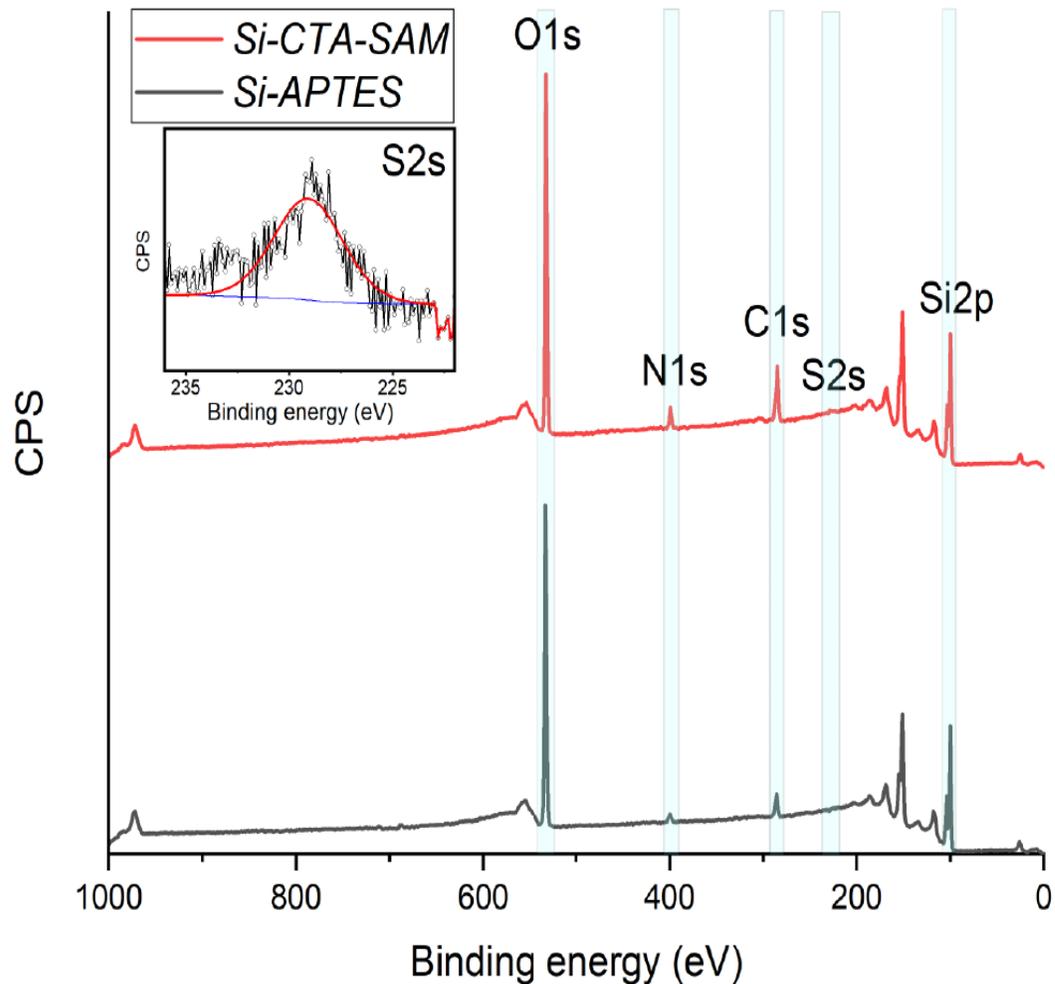
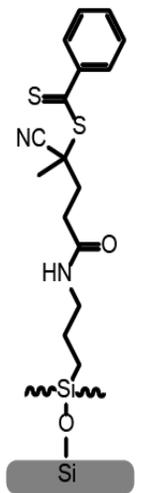


PET-RAFT



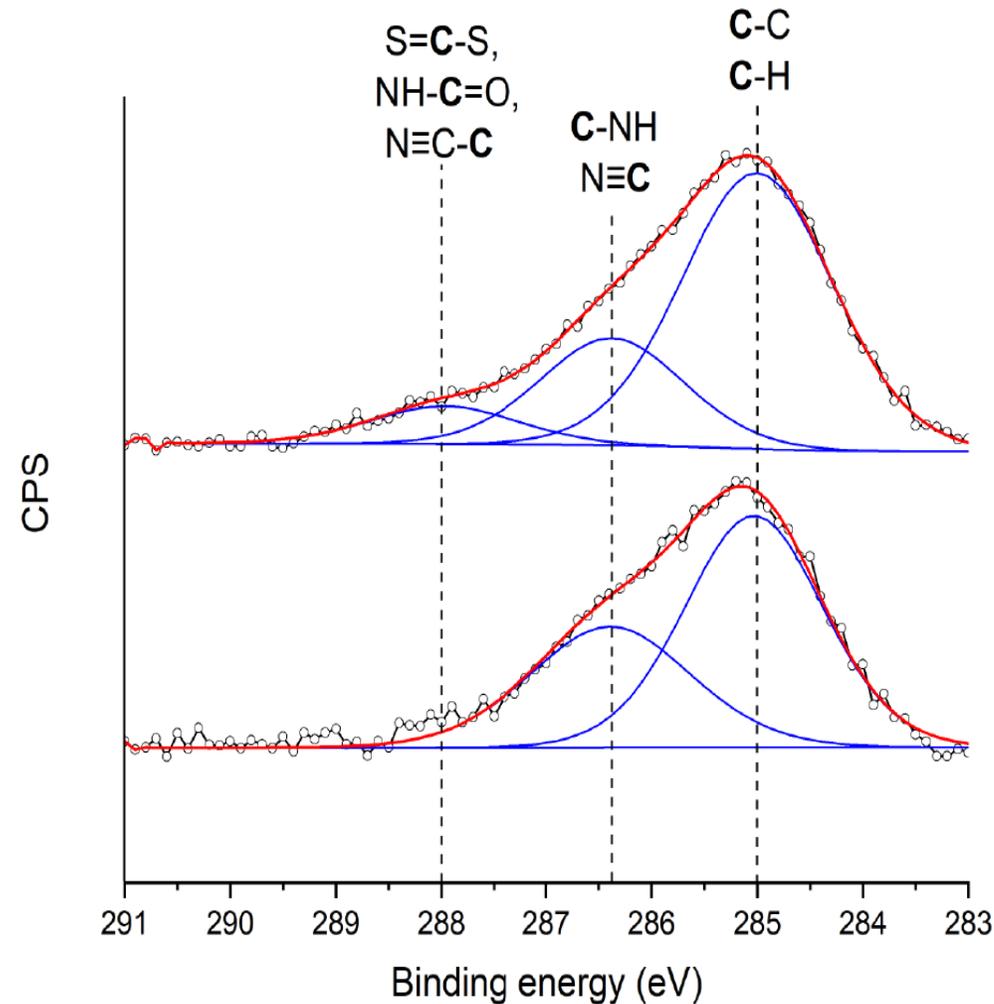
Kuzmyn, A. R., Nguyen, A. T., Teunissen, L. W., Zuilhof, H., & Baggerman, J. Antifouling Polymer Brushes via Oxygen-Tolerant Surface-Initiated PET-RAFT. Langmuir, (2020), 36(16), 4439

Immobilization of RAFT-agent



Conversion 29%

Wide XPS spectra



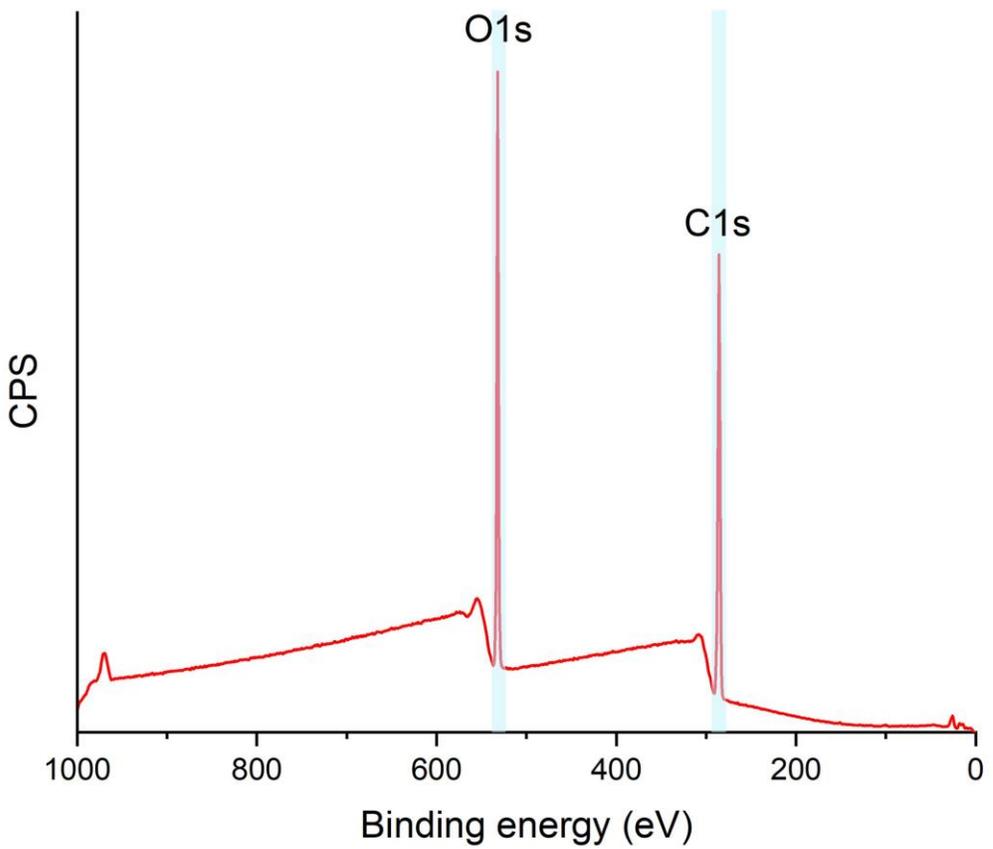
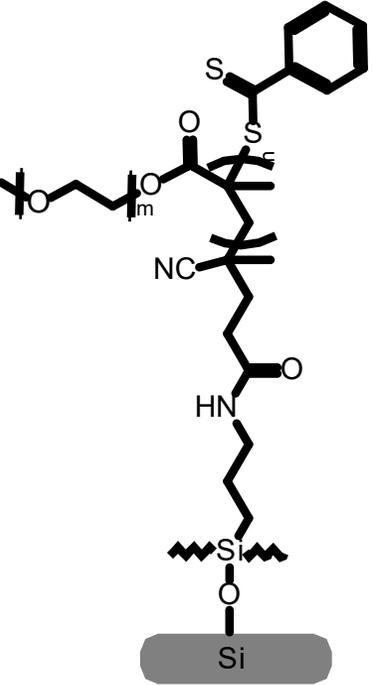
Narrow C1s region XPS spectra

Thickness by XPS

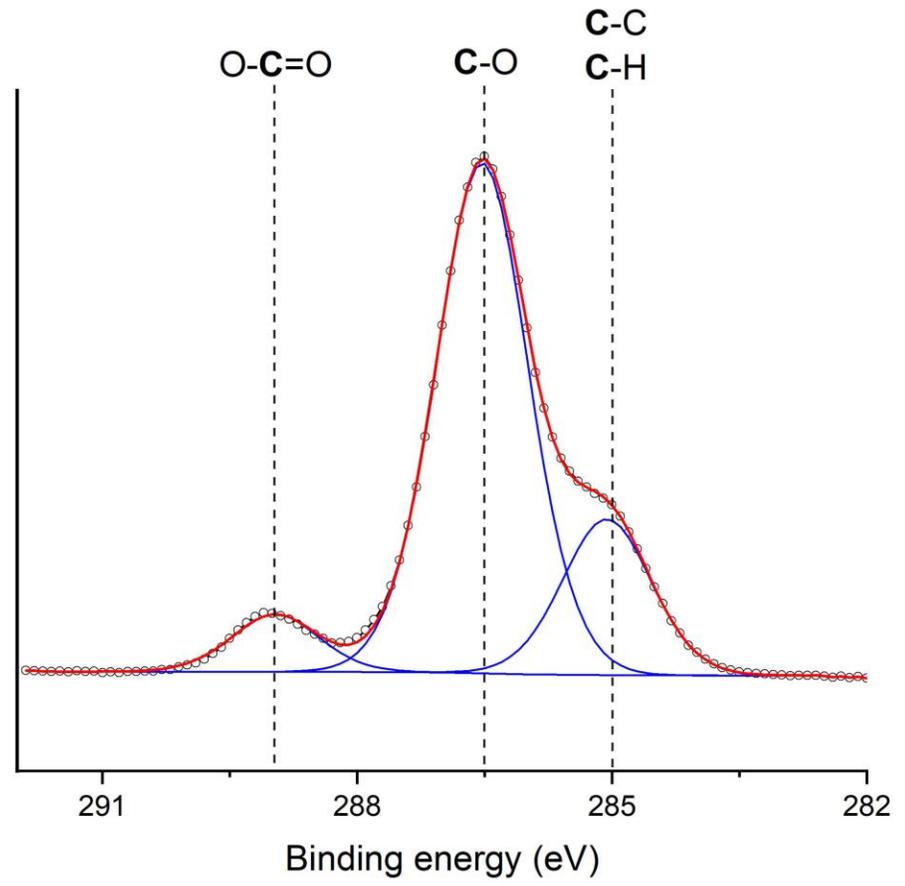
1.1 nm

0.5 nm

Chemical Characterization of Poly(MeOEGMA) Brushes



Wide XPS spectra

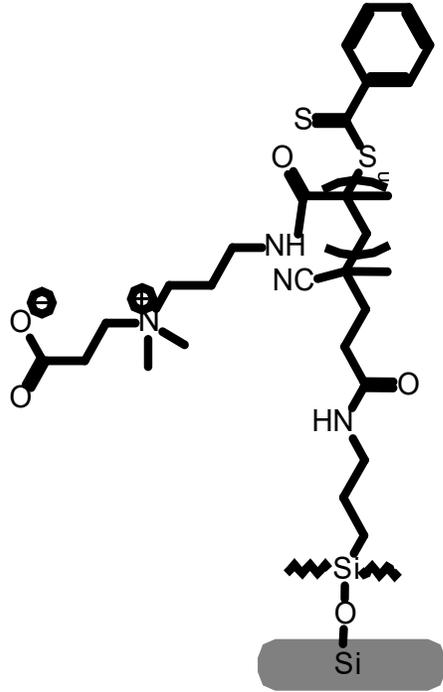


Narrow C1s region XPS spectra

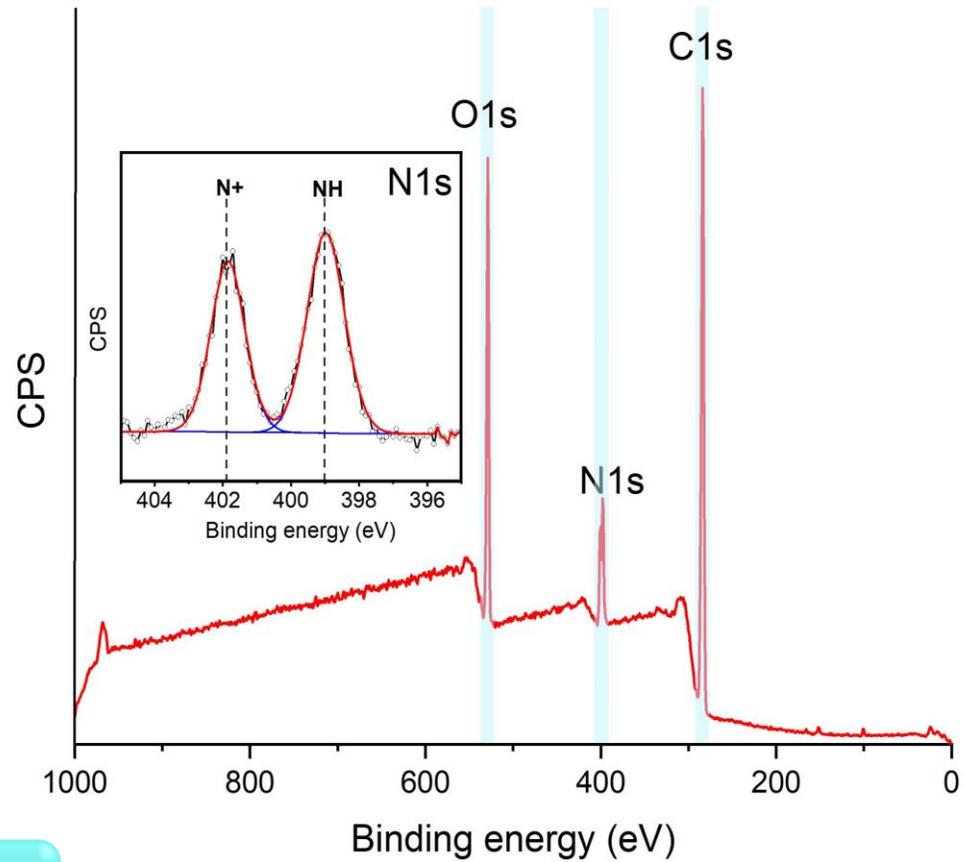
Thickness by ellipsometry : 26 nm

Kuzmyn, A. R., Nguyen, A. T., Teunissen, L. W., Zuilhof, H., & Baggerman, J. Antifouling Polymer Brushes via Oxygen-Tolerant Surface-Initiated PET-RAFT. Langmuir, (2020), 36(16), 4439

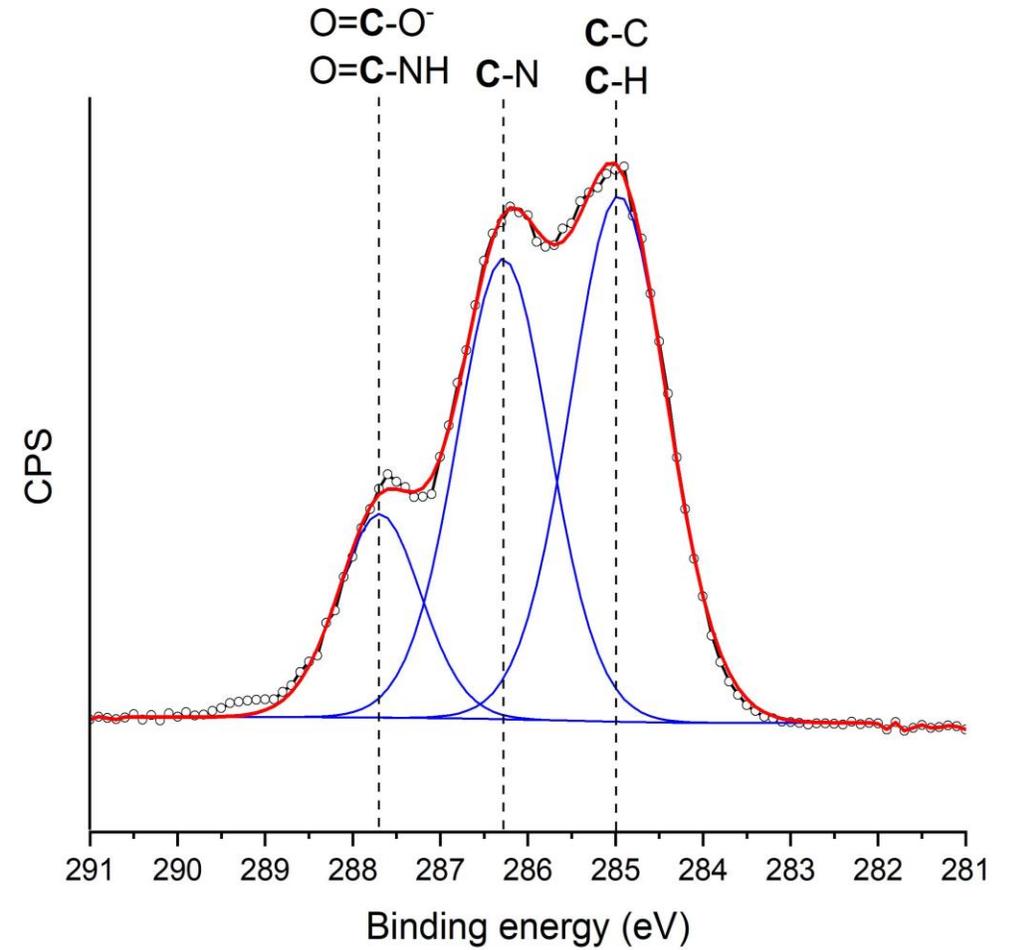
Chemical Characterization of Poly(CBMA) Brushes



Thickness by
ellipsometry : 29 nm

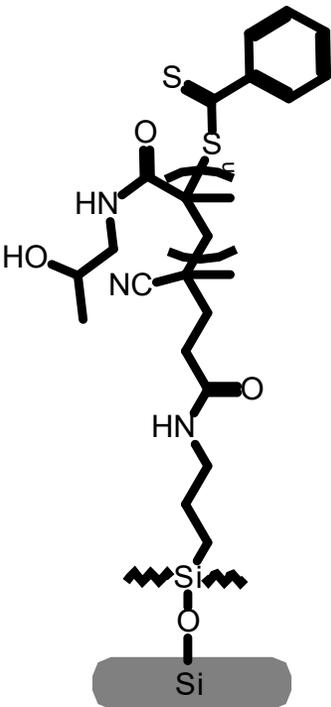


Wide XPS spectra

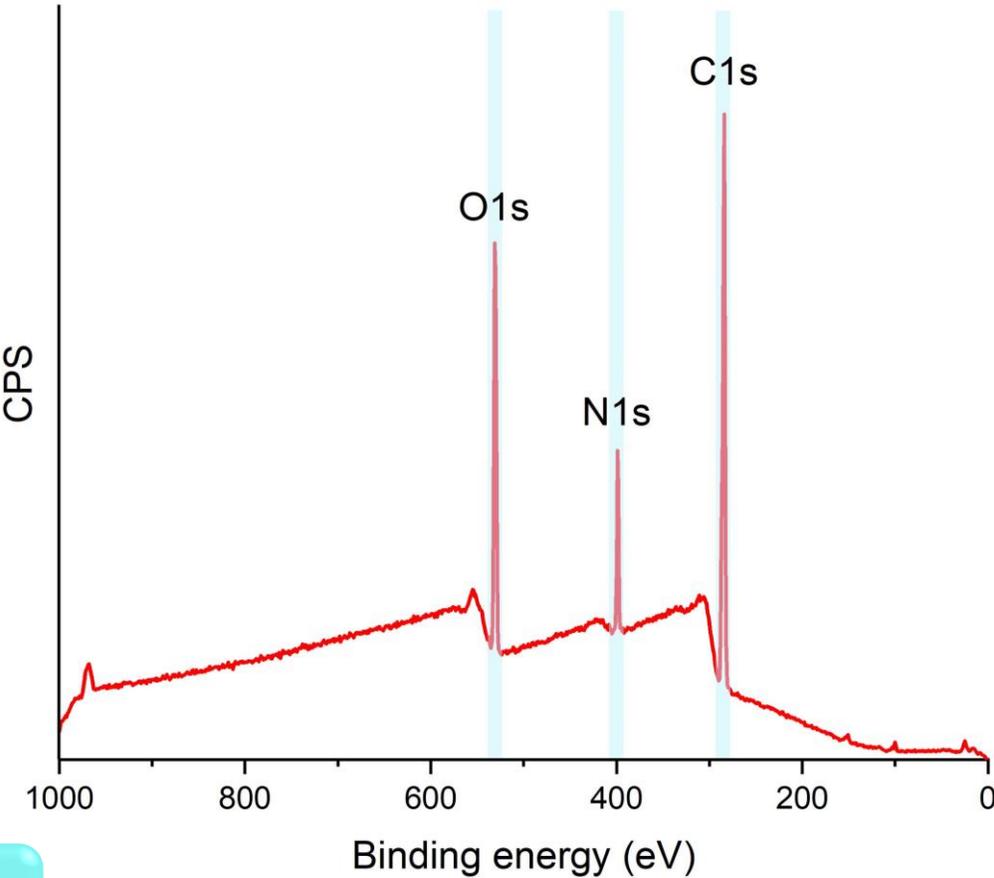


Narrow C1s region XPS spectra

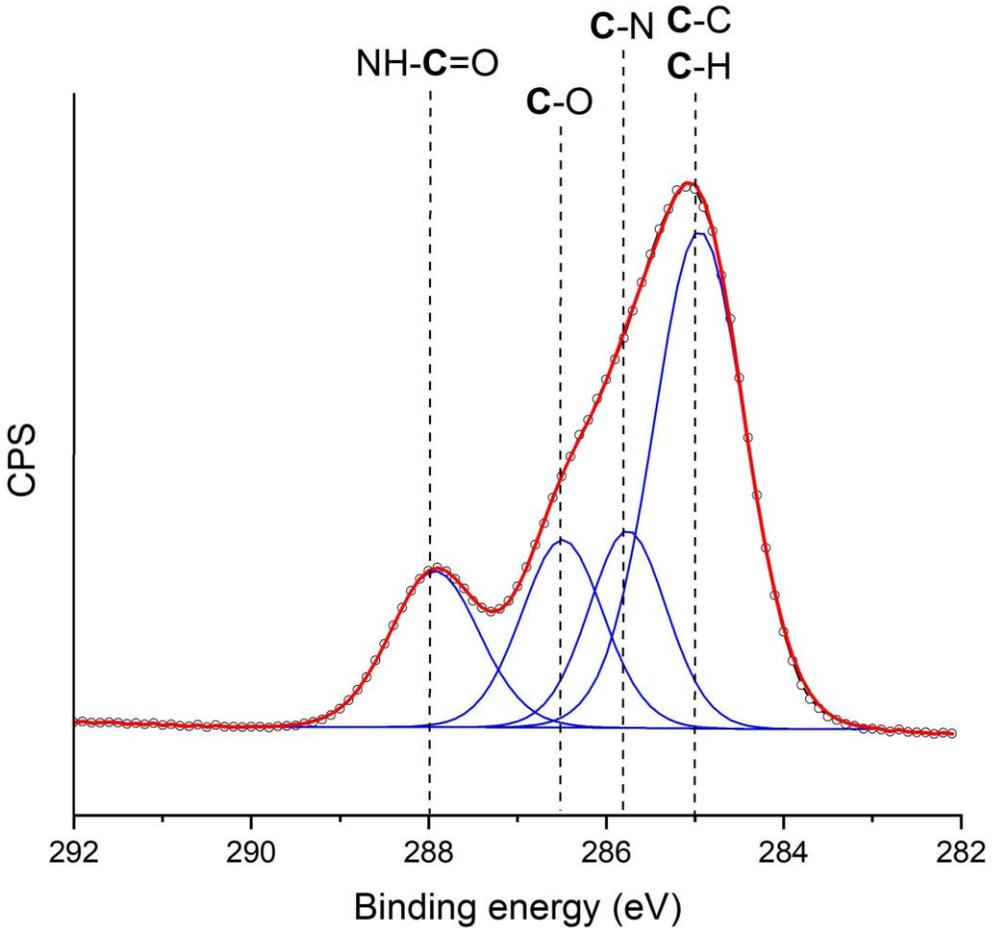
Chemical Characterization of Poly(HPMA) Brushes



Thickness by ellipsometry : 27 nm



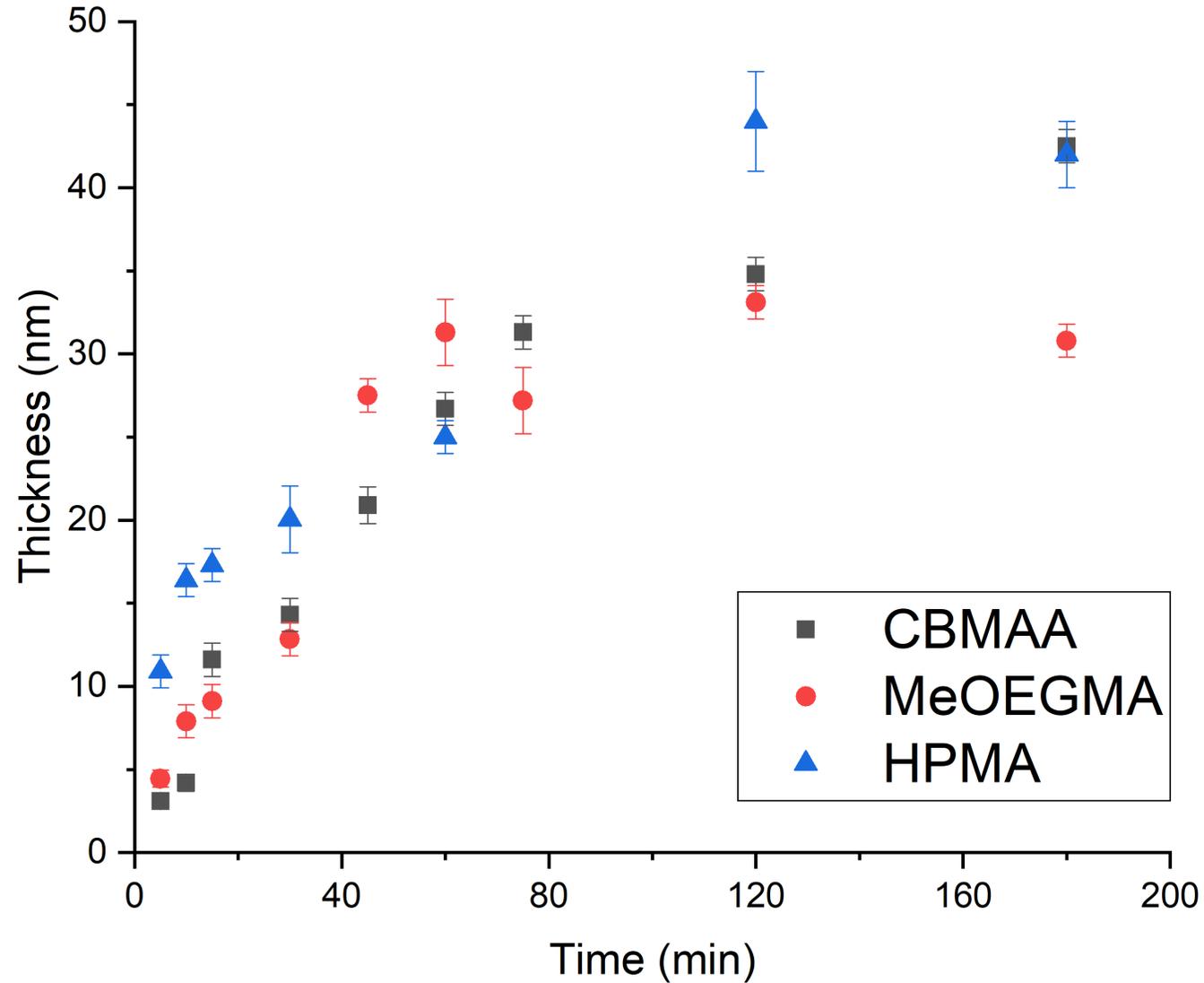
Wide XPS spectra



Narrow C1s region XPS spectra

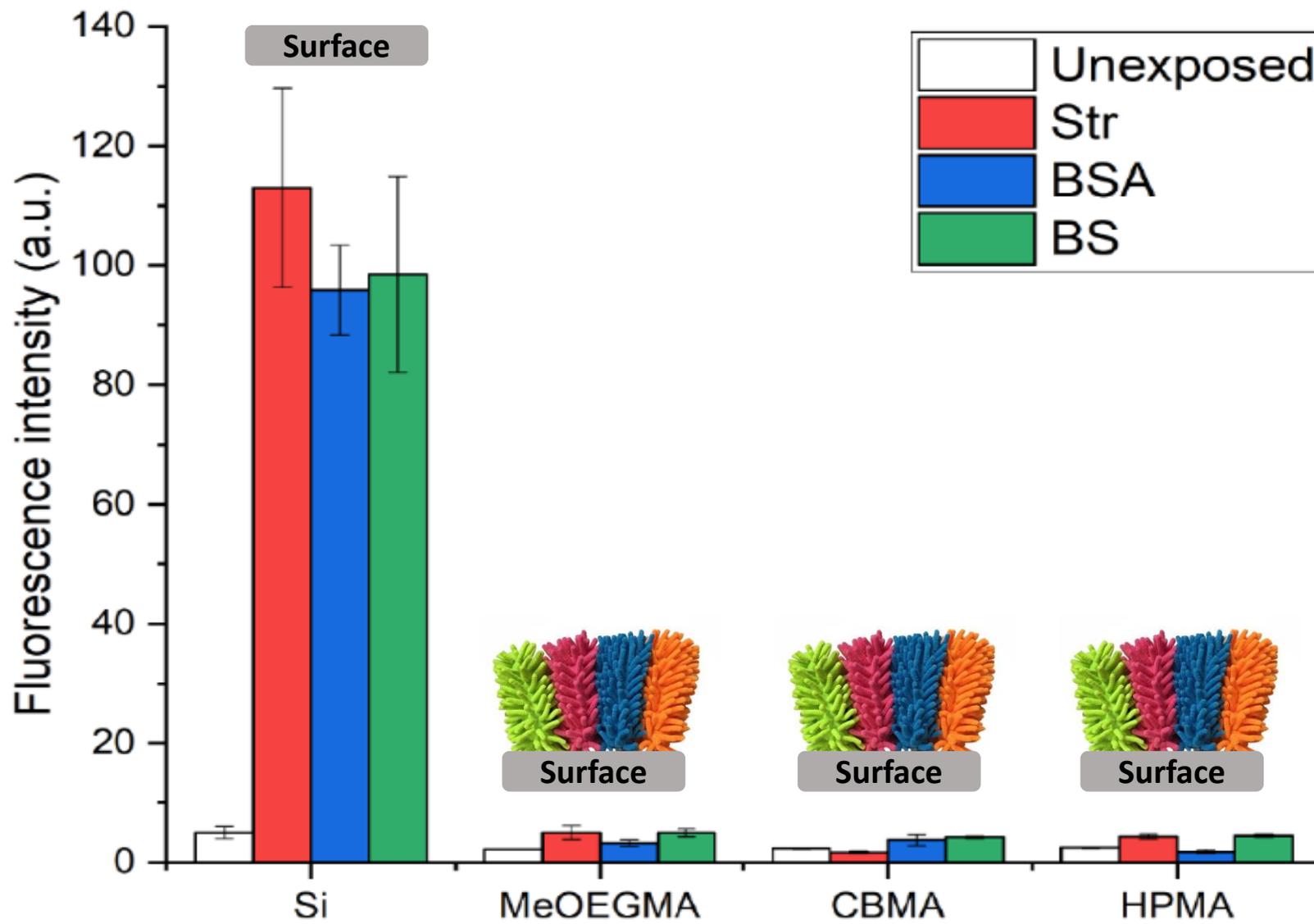
Kuzmyn, A. R., Nguyen, A. T., Teunissen, L. W., Zuilhof, H., & Baggerman, J. Antifouling Polymer Brushes via Oxygen-Tolerant Surface-Initiated PET-RAFT. Langmuir, (2020), 36(16), 4439

Kinetics of Polymerization



*Controlled nature
of polymerization*

Antifouling Properties



Good antifouling properties

Summary

Hierarchical diblock polymer brushes using living radical polymerization and iridium-based catalyst:

- antifouling, bioactive & patternable

Simple technique for creation antifouling coating using PET-RAFT:

- Oxygen tolerant
- Does NOT require heavy metals
- Scalable
- Visible light-triggered

Thank you for you attention ! Questions ?

Acknowledgments

Han Zuilhof



Lucas Teunissen

Esther van Andel

Jacob Baggerman

Sidharam Pujari

Barend van Lagen

Jan Willem Borst



WAGENINGEN
UNIVERSITY & RESEARCH
ORGANIC CHEMISTRY



@AndriyKuzmyn andrii.kuzmyn@wur.nl