École polytechnique fédérale de Lausanne

Laboratory of Chemical Nanotechnology

Surface Patterning and Polymer Chemistry
Lesson 9

MSE 304

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Plan of the Course: Fundamentals, Characterization, and Applications

1: Intro to Surfaces & Interfaces

2: Surfaces in the Real World - Adsorption

3: Surface Energetics & Interfacial Phenomena

4: Atomic Structure of Real Surfaces

5: Solid-Solid Interfaces

6: From Ideal Planes to Real Materials (Recap)

7: Characterization of Surfaces & Interfaces

8: Surface Chemistry

9: Surface Patterning and Polymer Chemistry

10: Characterization of Molecular Assembly

11: Electronic Properties of Surfaces

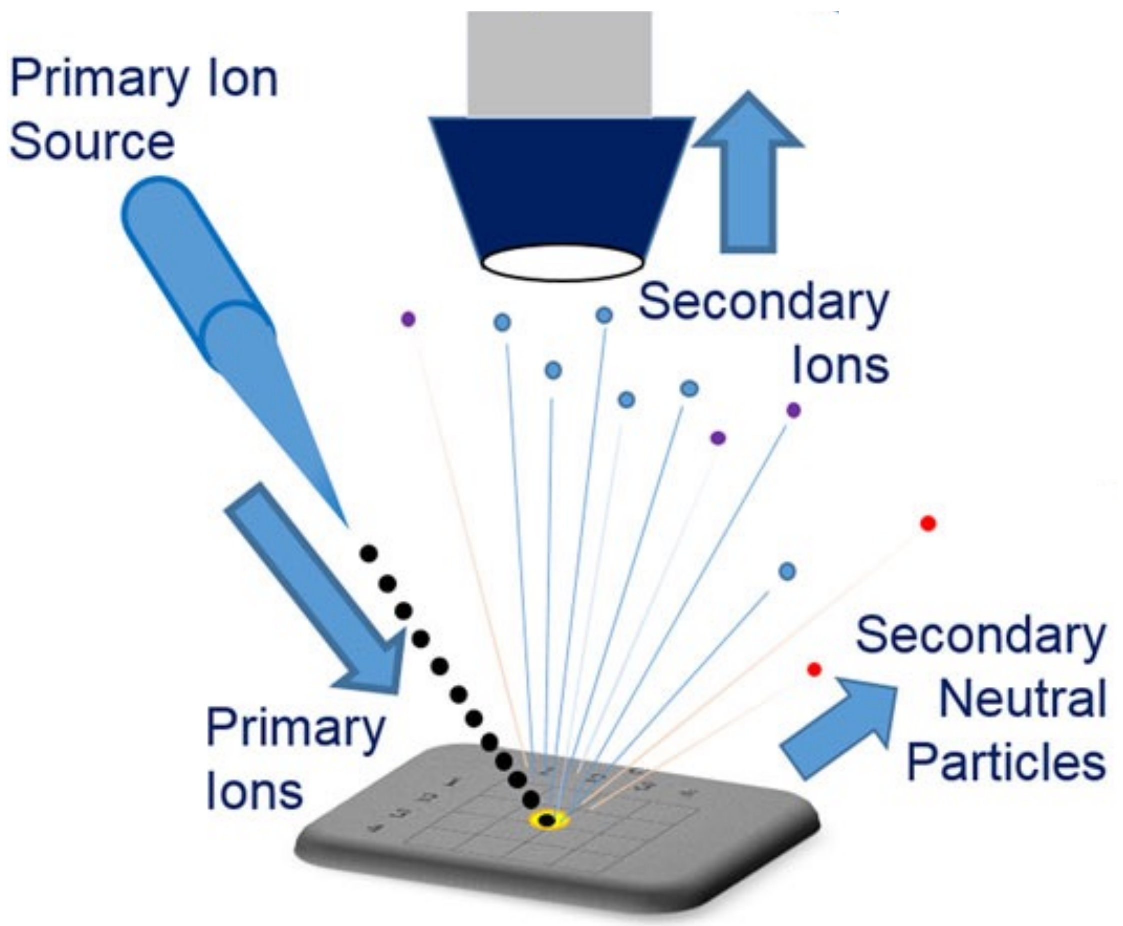
12: Biosensor Fundamentals

13: Biosensing applications

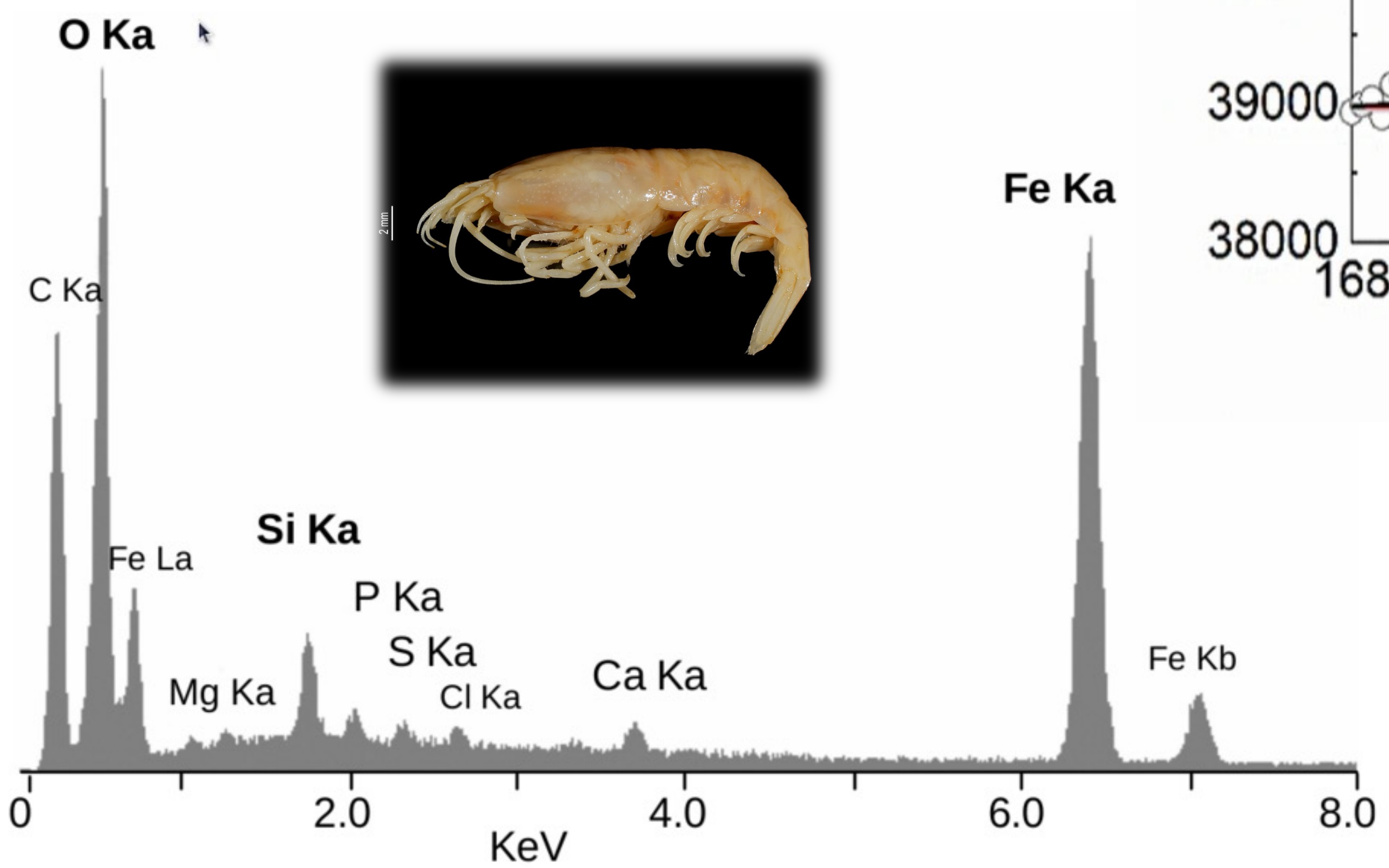
14: Chemistry of Semiconductor Surfaces and Beyond

Recap from Lesson 6/7: Surface Chemistry Characterization

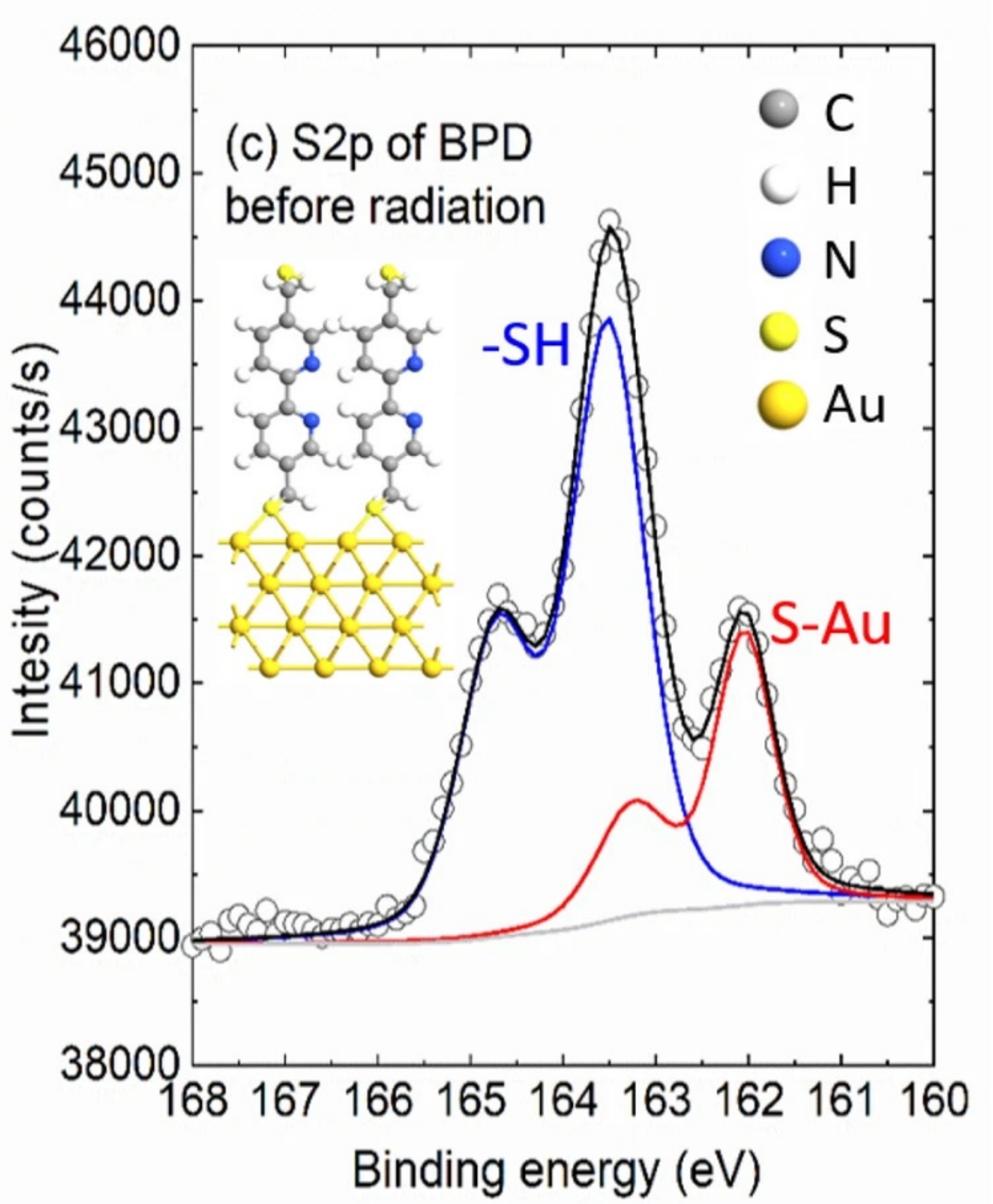
SIMS



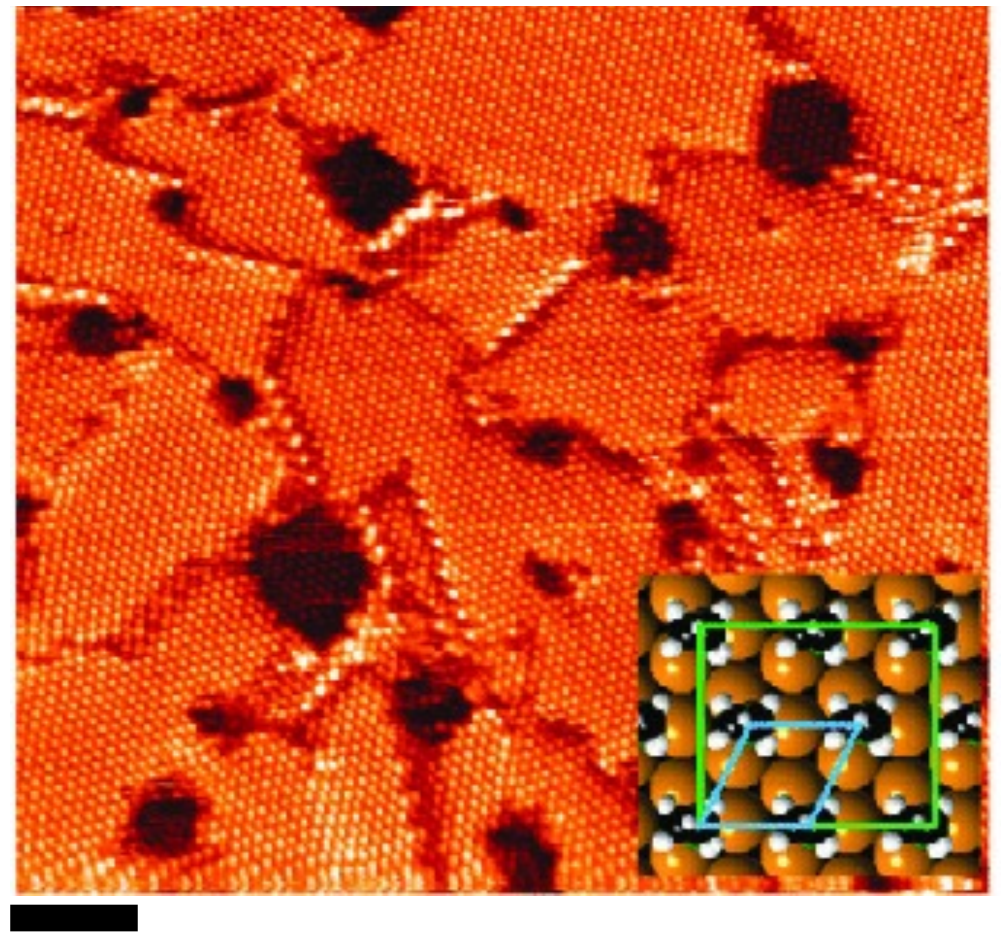
EDX



XPS

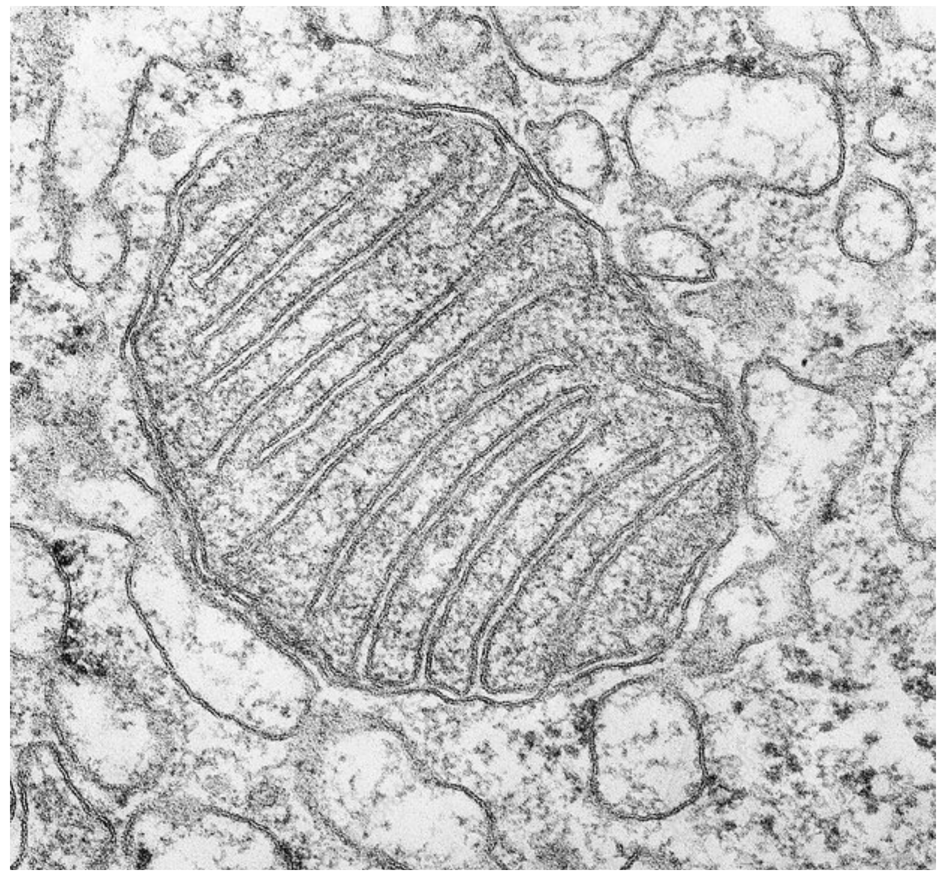


STM

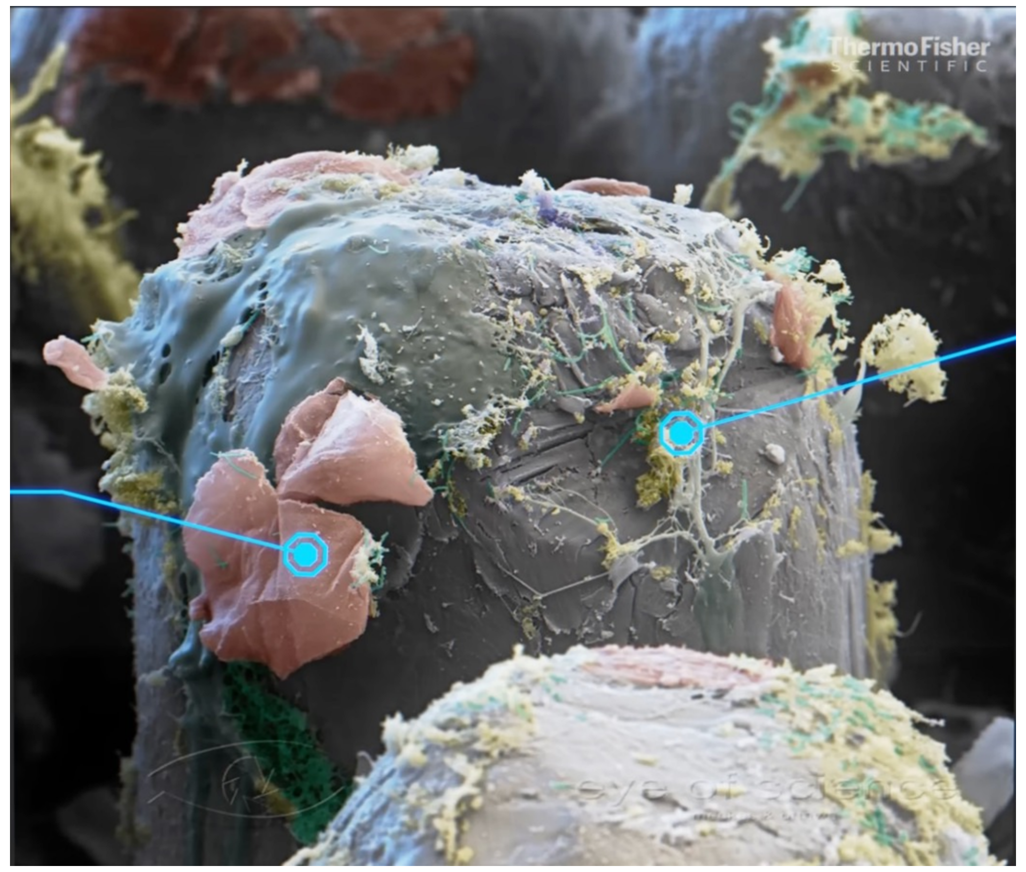


5 nm

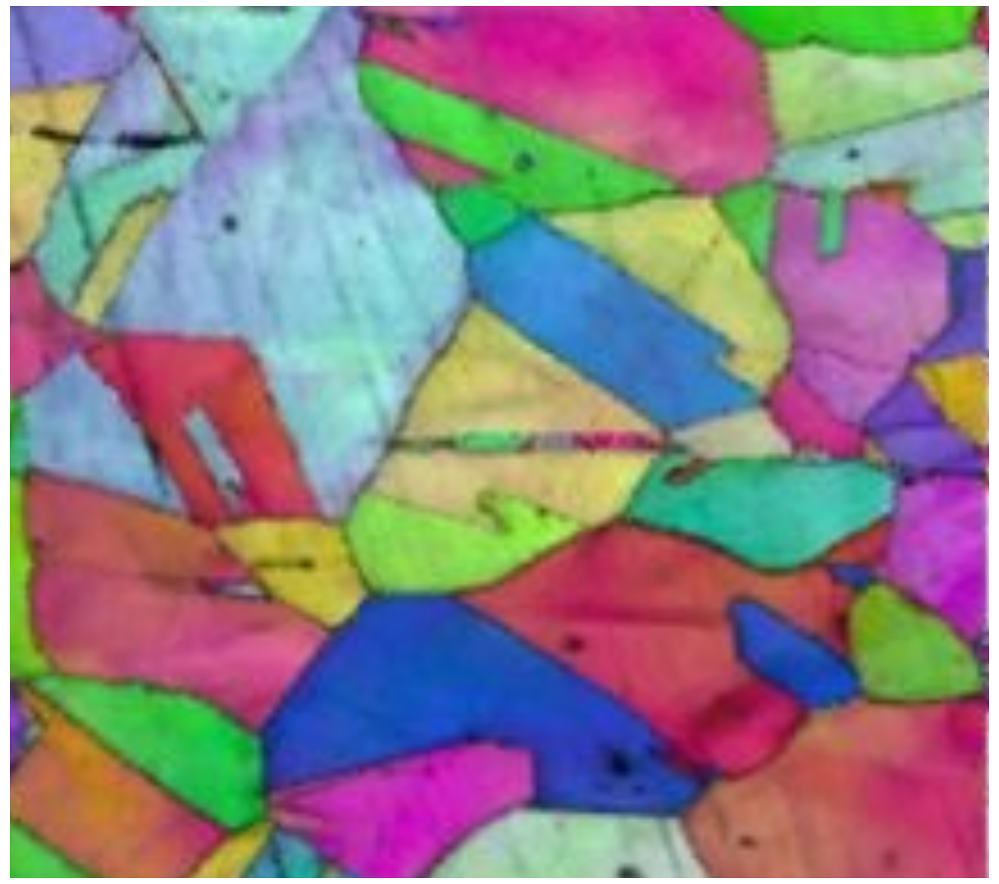
TEM



SEM



EBSD



Recap from Lesson 6: Surface Characterization Techniques

What techniques enable **quantitative analysis of elements?**

Quantitative analysis is the determination of how much of a substance is present

It gives numerical results (%, concentrations, thickness, counts), not just identification

Category	Techniques	What They Provide
Quantitative / Semi-Quantitative	XPS, EDX, SIMS (with caveats)	Elemental or molecular amounts, sometimes depth
Qualitative (Structural / Imaging)	STM, TEM, SEM, EBSD	Shape, structure, lattice, atomic arrangement — but not how much

Elemental Quantification Reliability Ranking

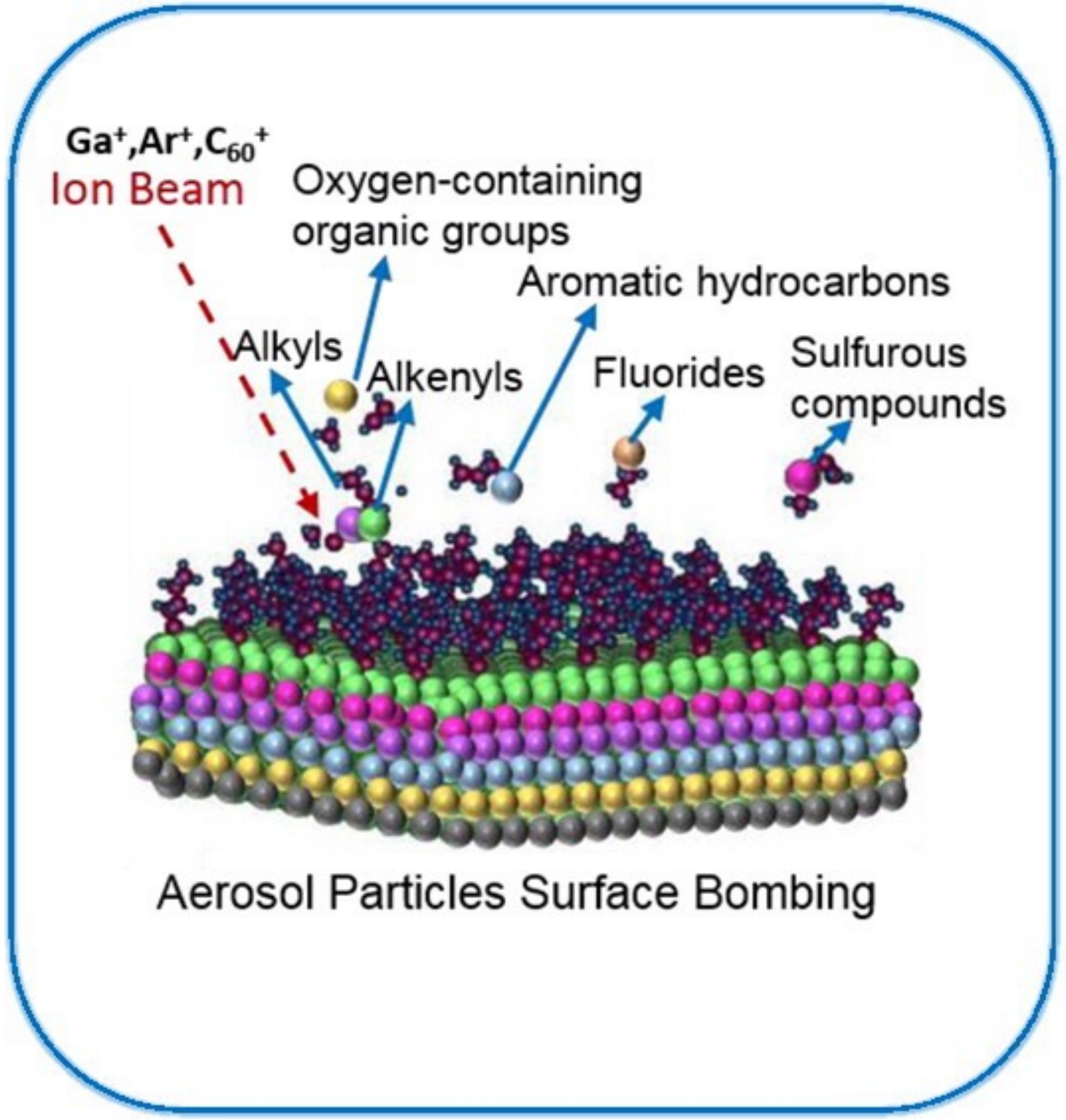
XPS = quantitative surface chemistry

EDX = rough elemental composition

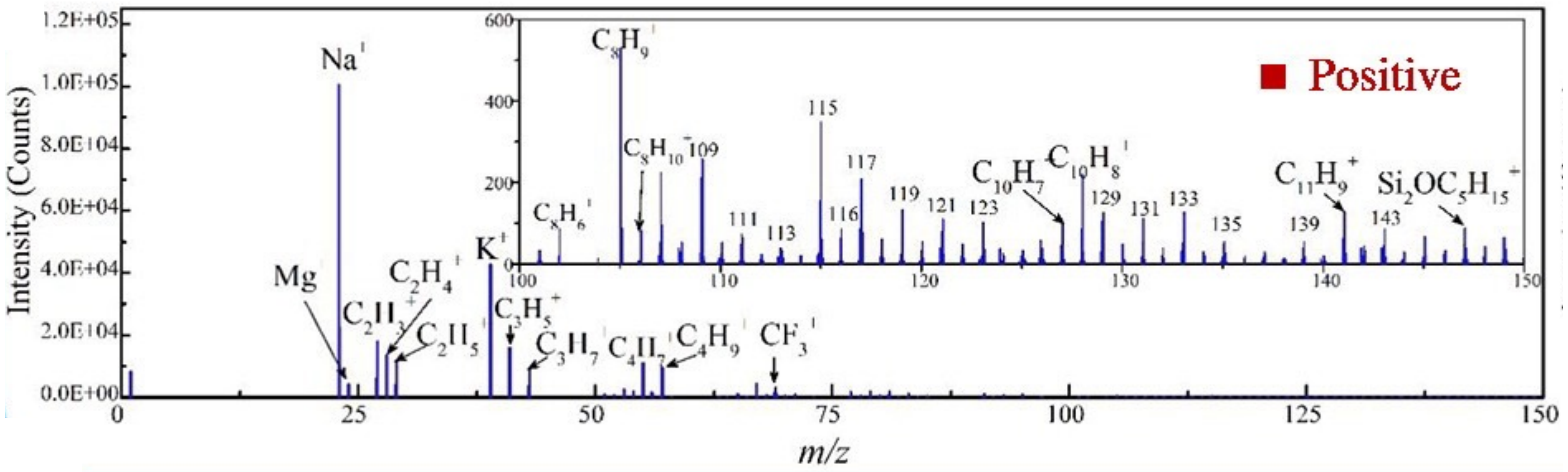
SIMS = relative composition and depth trends

Technique	Quality	Strength	Limitation	Best Use
XPS	Most reliable for surface atomic %	Chemical states + surface composition (~5–10 nm)	Needs flat, uniform samples	SAMs, oxides, thin coatings
EDX (in SEM/TEM)	Semi-quantitative (~±5–10%)	Fast, easy elemental survey	Poor for light elements; sees deeper (~0.5–2 µm)	Rough composition of bulk
SIMS	Relative quantification only	Extremely sensitive to trace organics	Need standards for absolute amounts	Surface contamination, polymer chemistry

SIMS Requires a "Standard" for Quantification



Li *et al.* | J. Environ. Sci. | 2018



SIMS measures intensity of ion fragments, not actual amount of material

The intensity depends on:

- How easily that element/fragment ionizes
- Surrounding chemical environment
- Instrument settings

So **raw SIMS signal ≠ concentration** ➔ need a reference sample (**standard**)

- Known composition
- Same environment

Quantitative Analysis of Height

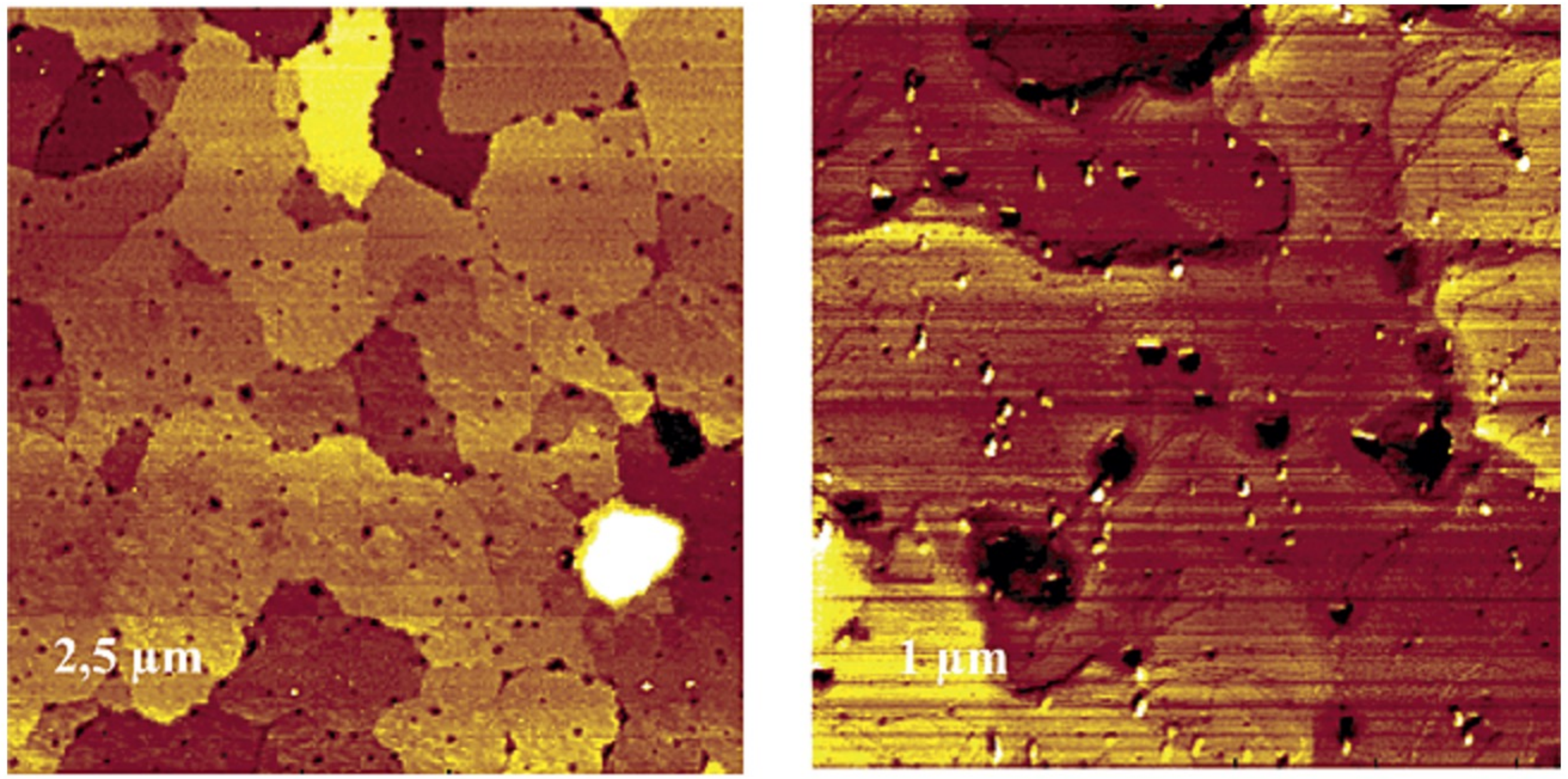
What techniques enable **quantitative analysis of height/thickness?**

Technique	Quality of height measure	How it works	Typical thickness range
STM	Direct, very accurate	Measures tunneling current change as tip follows surface	Sub-nanometer to a few nm (atomic steps)
TEM (cross-section)	Direct in thin sample	Image sliced cross-section and measure	1–200 nm layer thickness very precisely
SEM (cross-section)	Indirect, from image	Tilt sample + measure thickness from magnified image	~50 nm to many microns

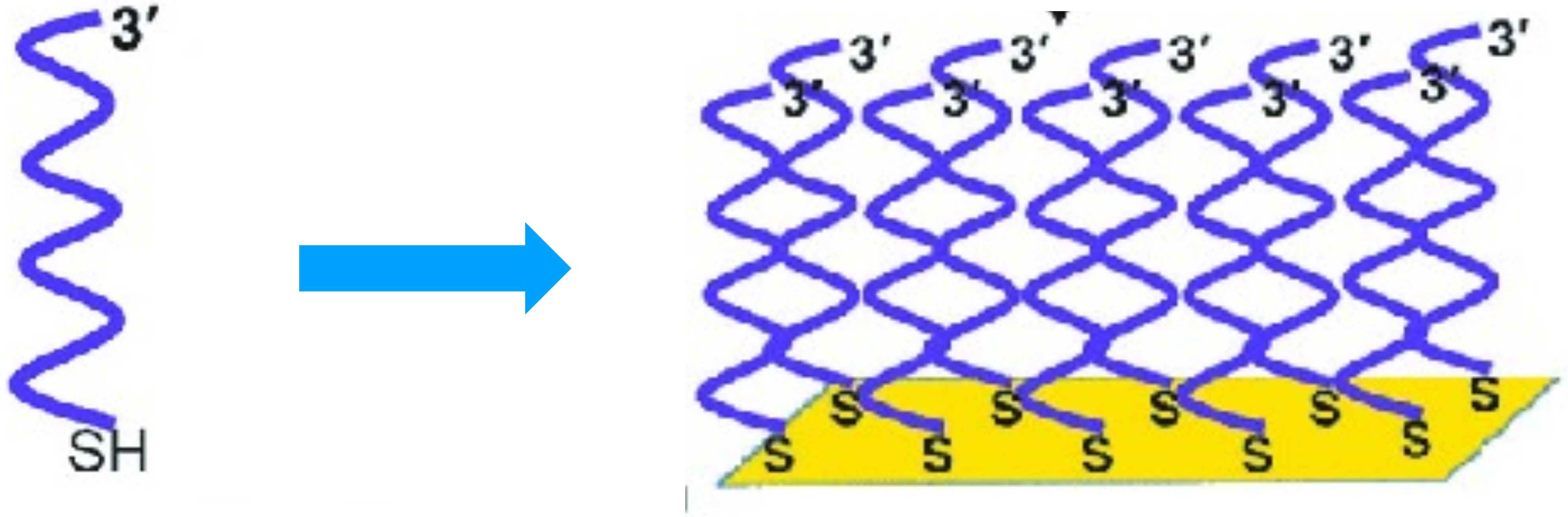
XPS and SIMS can only estimate thickness based on models/calibration

We will cover **atomic force microscopy (AFM)** later – go-to method for measuring nanoscale height

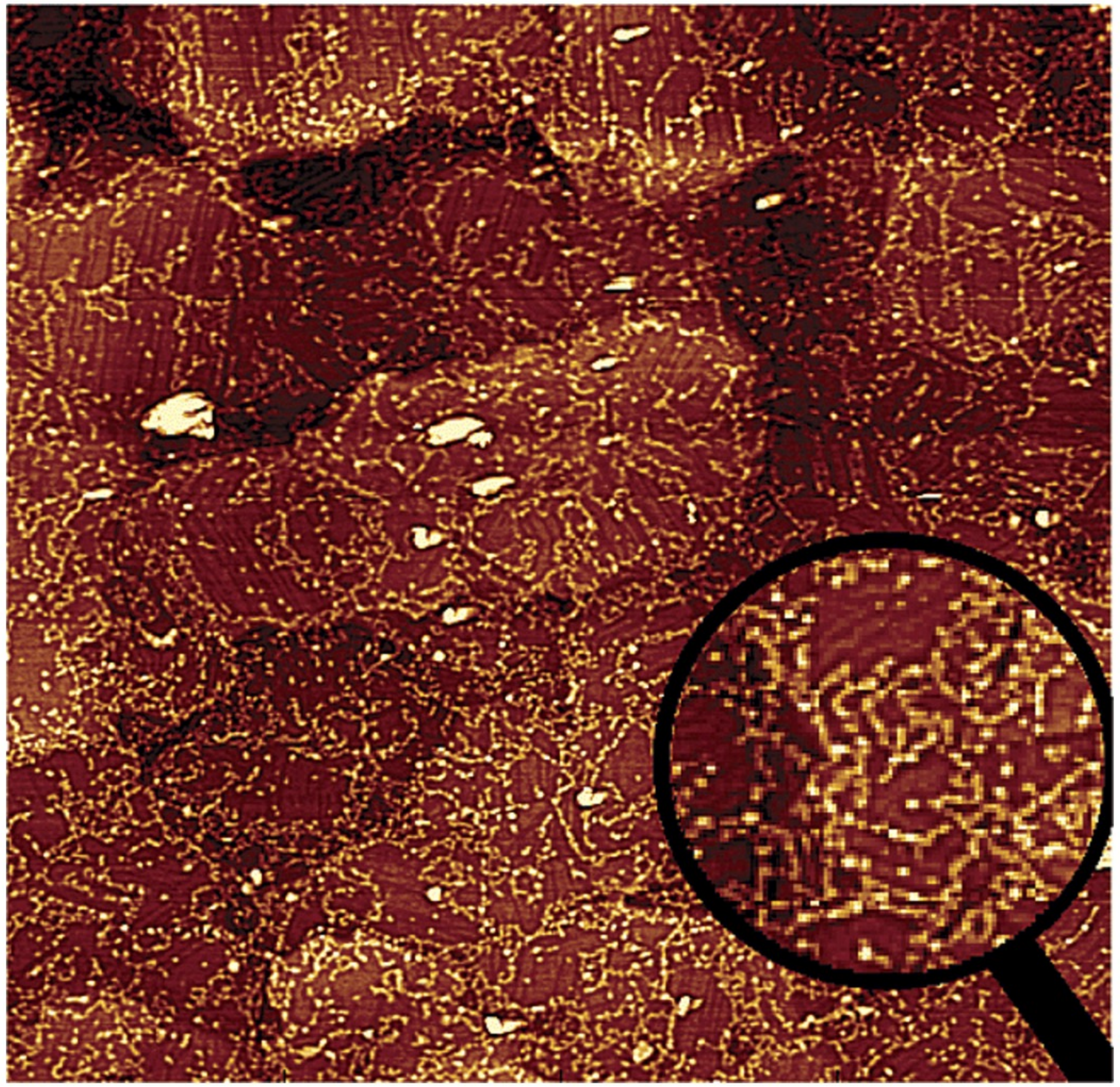
Upcoming Tool Next Week: Atomic Force Microscopy



AFM image of Au (111) surface (terraces observed)



Surface exposed to a solution of oligonucleotides
(25-base thiolated DNA)



Mourougou-Candoni, *et al.* | *Langmuir* | 2003

Recap from Lesson 8: Factors Governing Self Assembly

Preparation conditions

Stability

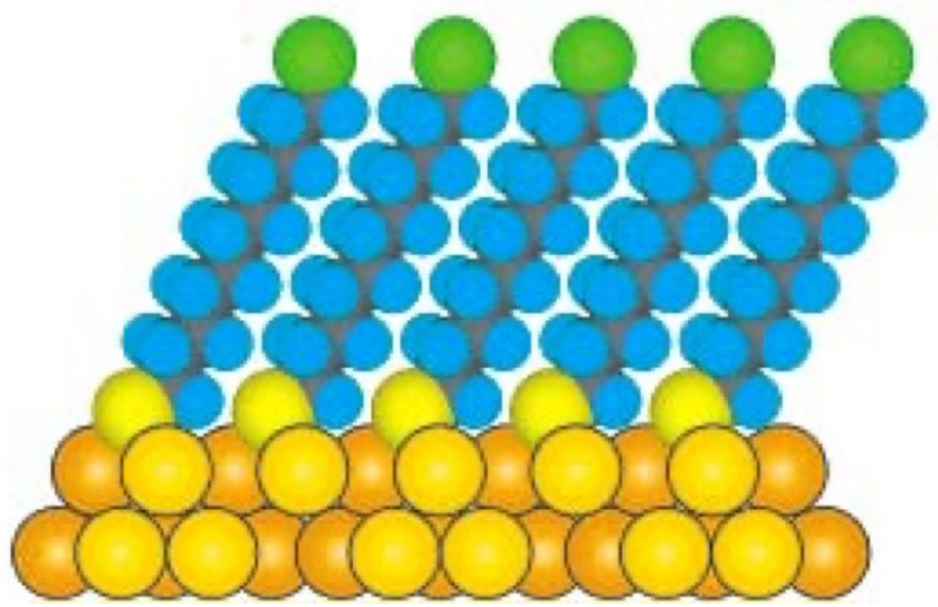
Crystallinity

Substrate

Curvature

Roughness

SAM Properties



Anchoring group

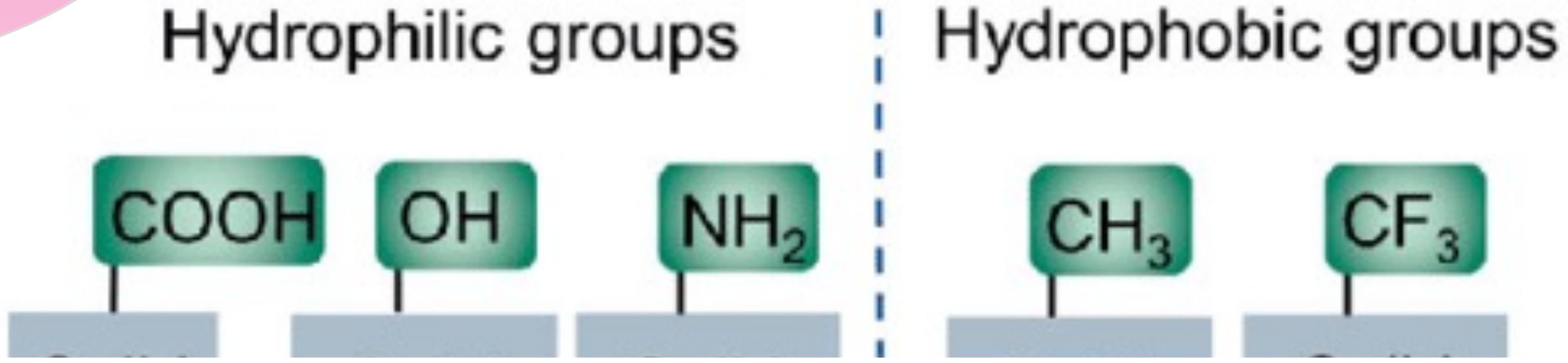
Micelle formation

Spacer

Adsorbate

Solvent

Purity



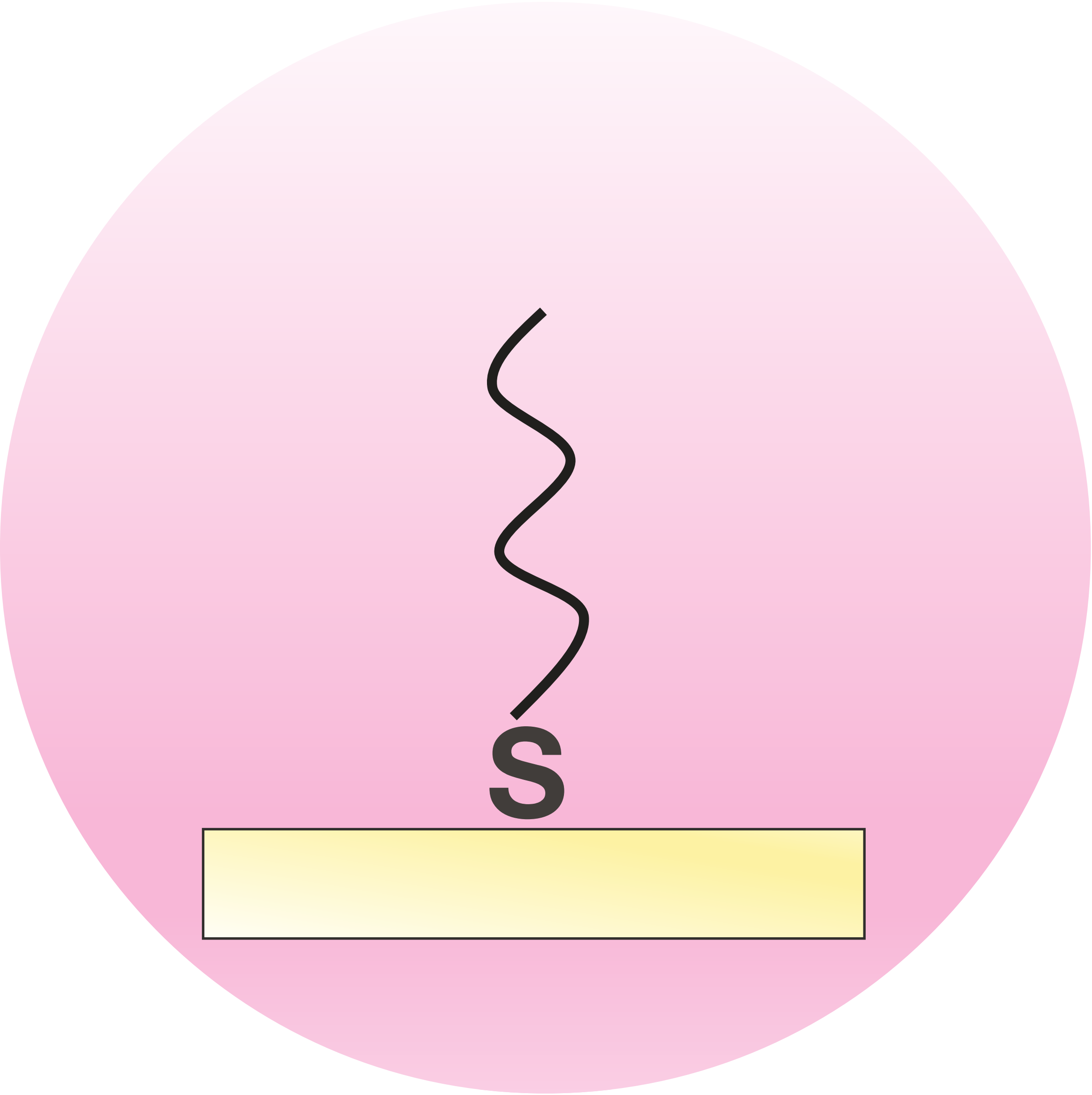
Solubility

Compatibility

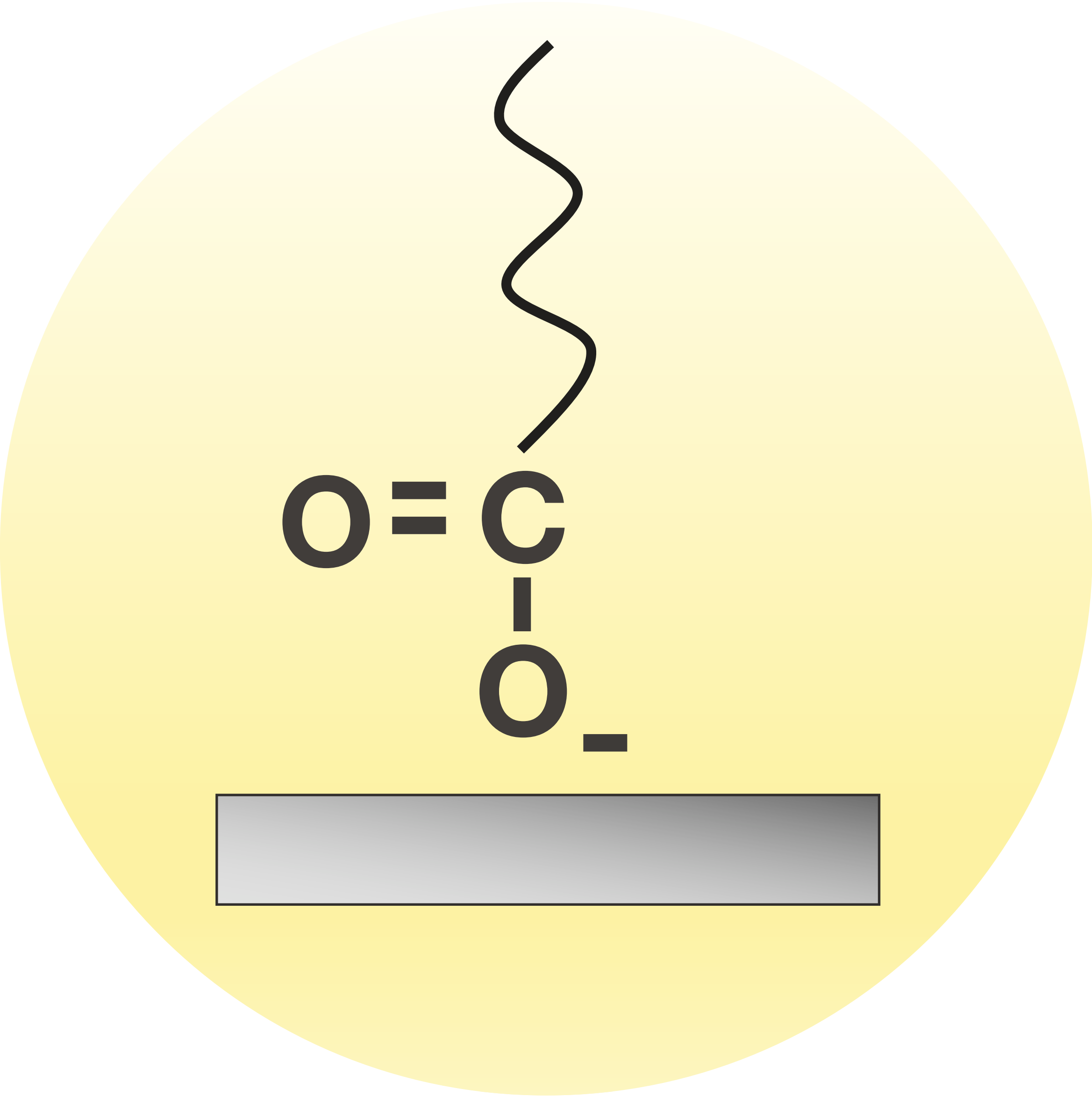
Functional group

Recap from Lesson 8: Surface Chemistry Strategies

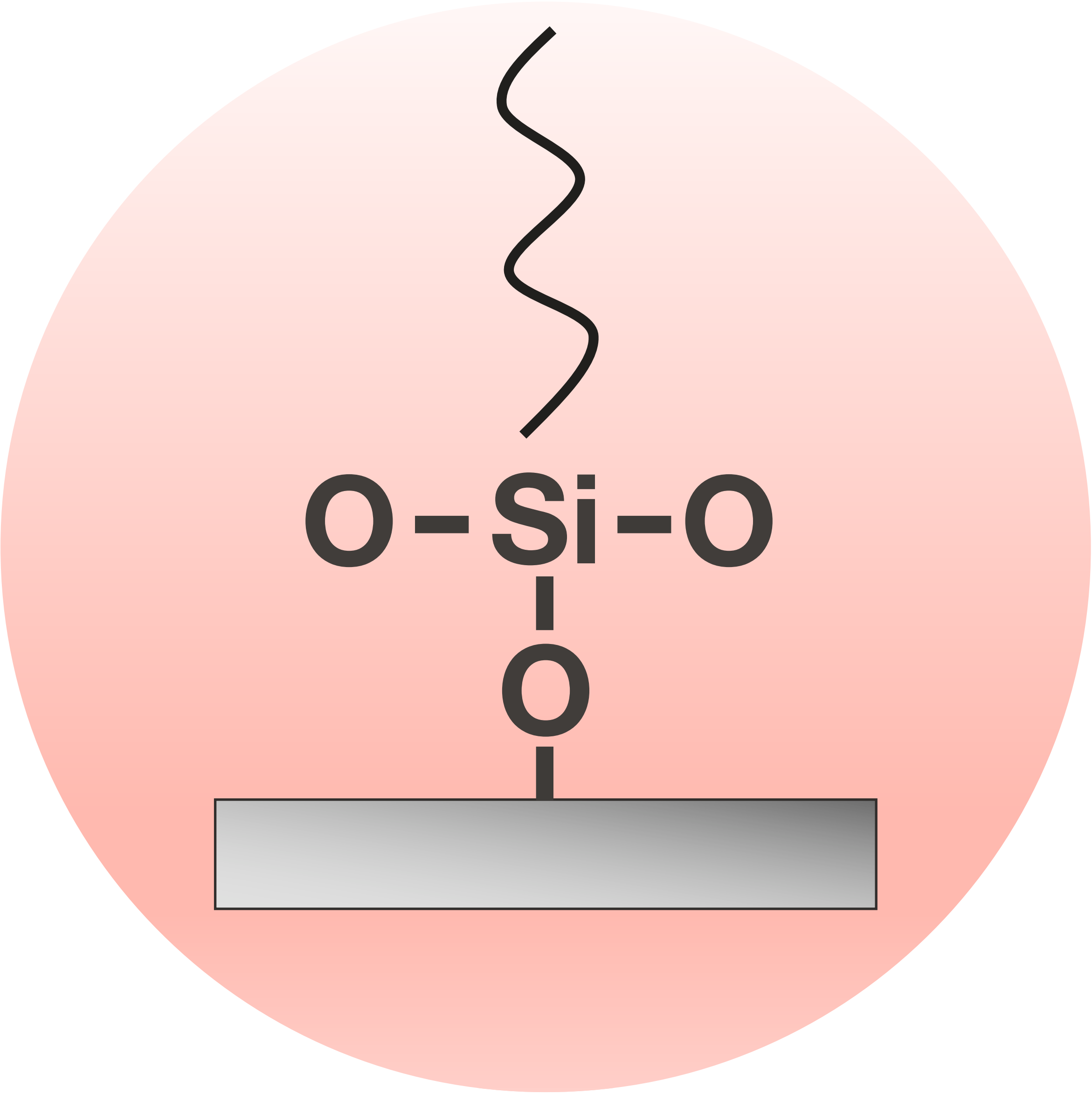
Surface chemistry



Thiol-based chemistry
Metallic surfaces



Carboxylic acids
Metal oxide surfaces

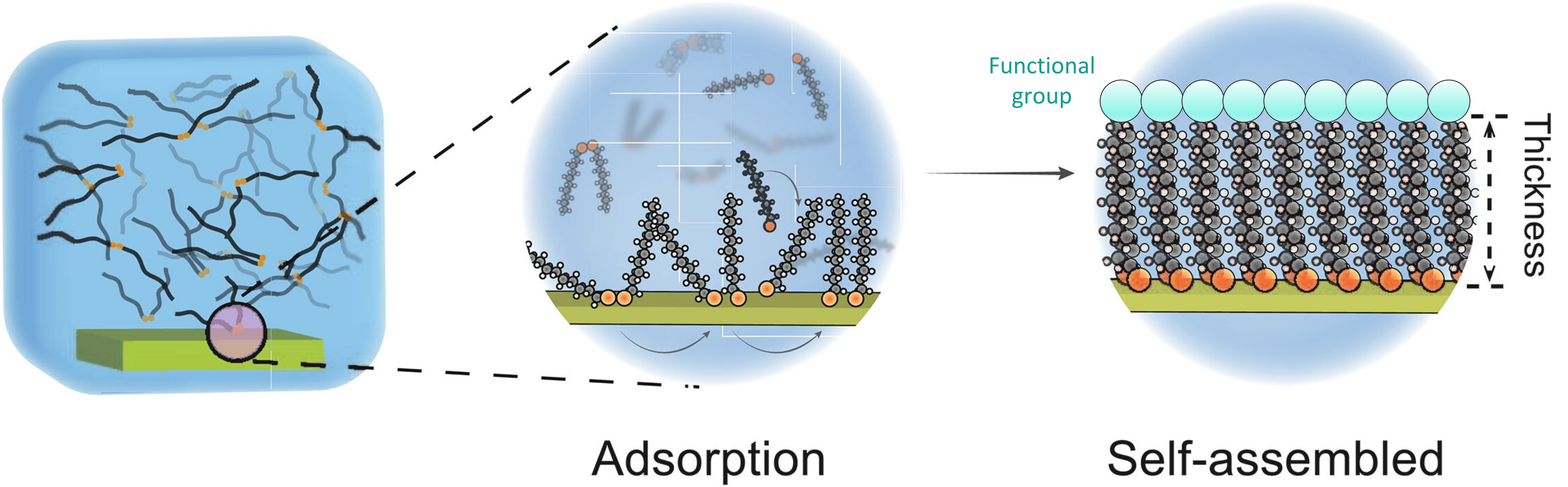


Silane, Phosphonates
Metal oxide surfaces

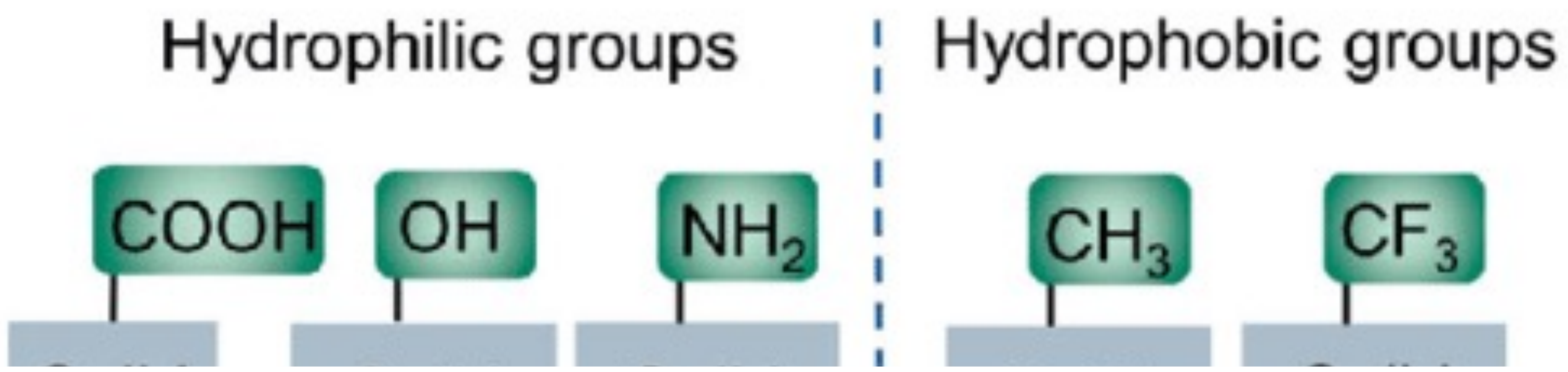
Outline of Lesson 9

- Coupling chemistries to surface functional groups
- Why *where* we immobilize matters – the need for patterning
- Four patterning methods for microscale – nanoscale patterning of surfaces
- Motivate the need for polymer-based surface chemistries – protein fouling on surfaces
- How do proteins stick to surfaces of different properties – thermodynamics
- Polymer grafting to tackle nonspecific binding

Assembled SAMs Serve As Interface for Molecular Immobilization

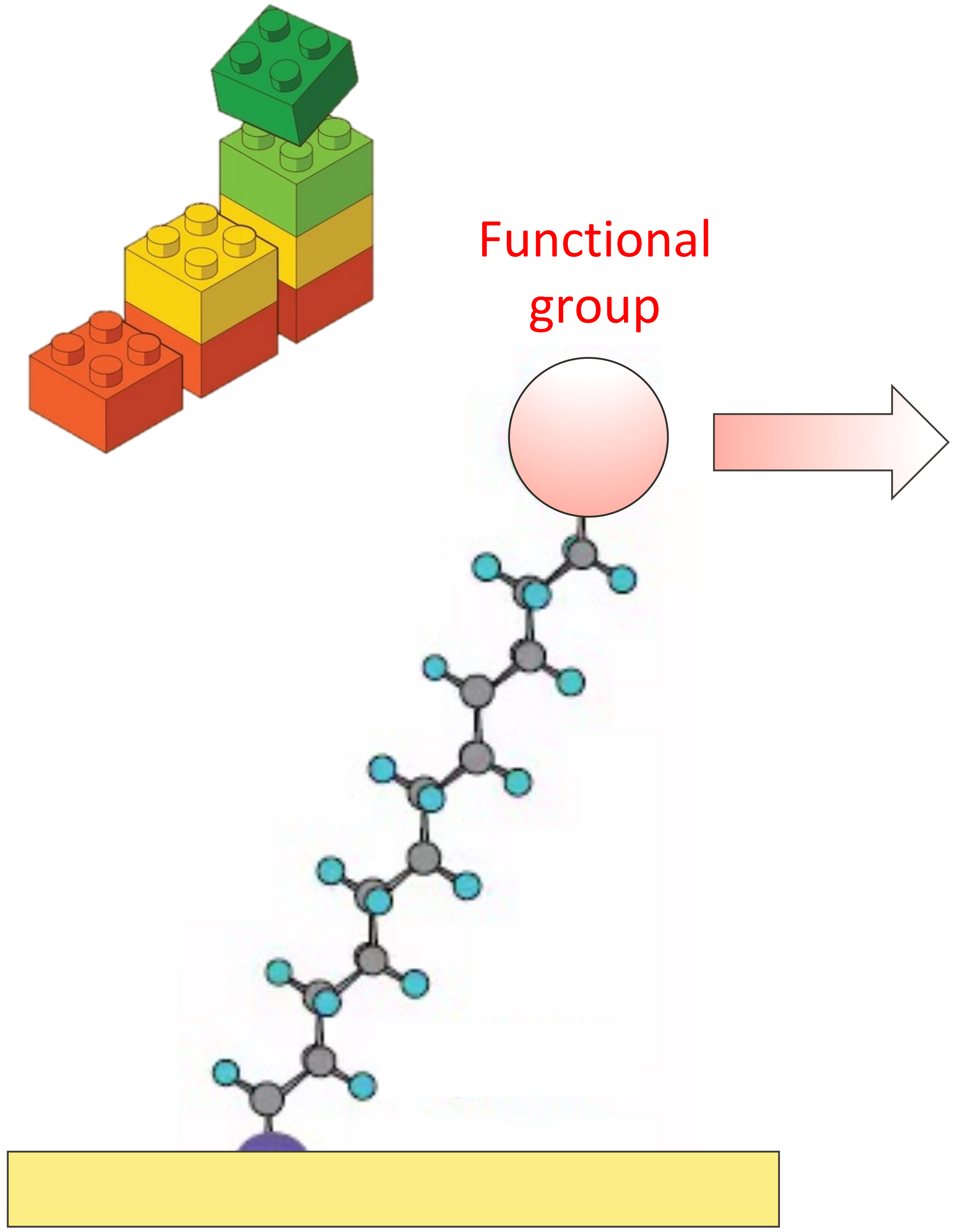


Functional groups can tune surface properties:

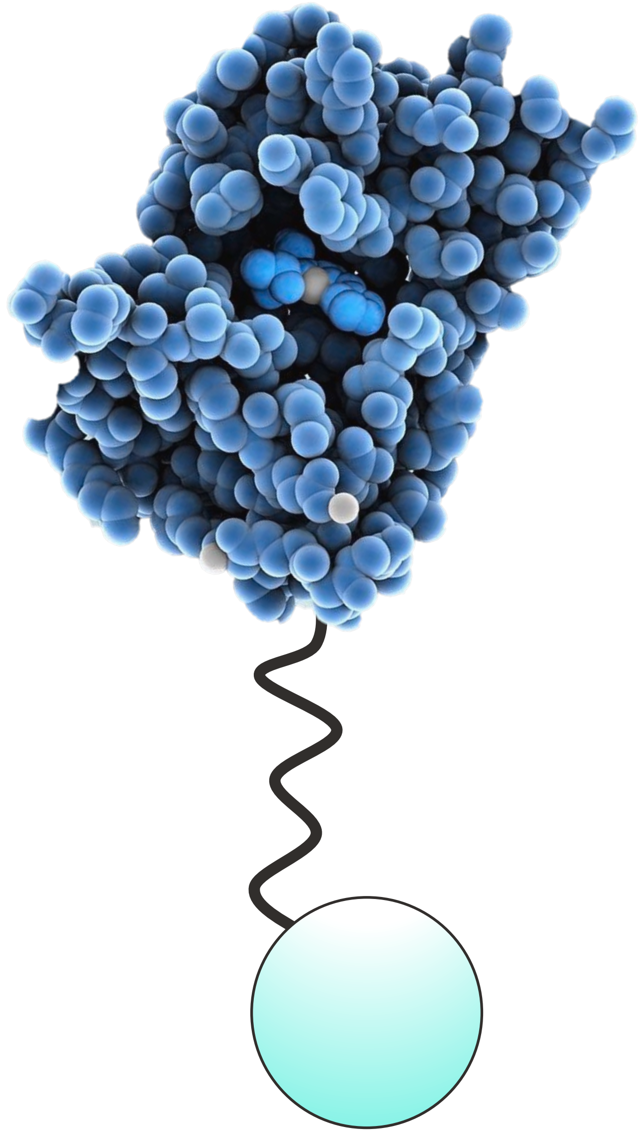


In addition, they enable coupling of molecules to surfaces

Assembled SAMs Serve As Interface for Molecular Immobilization



Functional group of surface molecule	Coupling chemistry	Functional group of tether molecule
Amine **$-NH_2$**	**Maleimide** →	**Thiol** **$-SH$**
Carboxyl **$-COOH$**	**NHS/EDC** →	**Amine** **$-NH_2$**
Azide **$-N_3$**	**Click chemistry** →	**Alkyne** **$-C\equiv C$**



When We Tether Biomolecules, *Where* We Immobilize Matters

1^0 antibody

2^0 antibody

Test line

Antibody specific
to the target

Control line

Antibody that binds to
1^0 antibody (no target)

Molecules Stick Everywhere – Patterning for Spatial Control

Inkjet printing

~ 50 – 100 µm

Microfluidic patterning

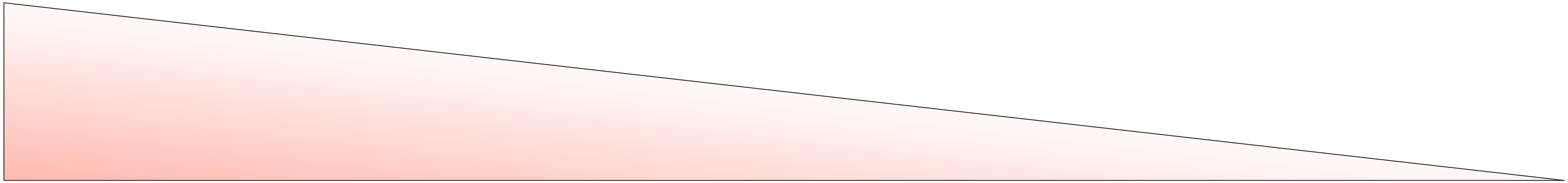
~10 – 100 µm

Microcontact printing

~1 – 10 µm

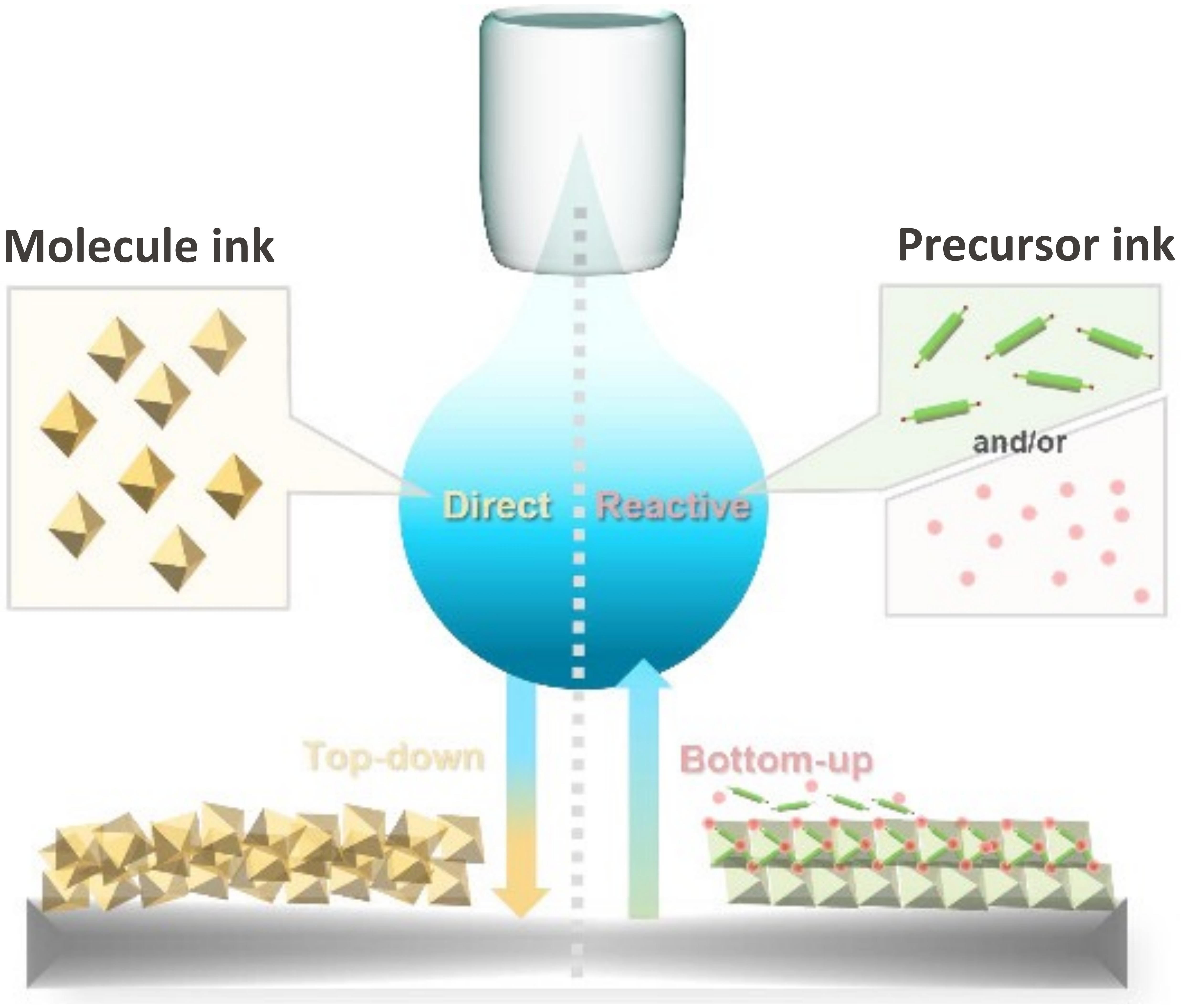
Chemical lift-off lithography

~10 – 50 nm



Spatial limit

Inkjet Printing Large Areas with Controlled Volume Droplets



- Nozzle size
- Droplet velocity

- Viscosity
- Surface tension
- Particle size
- Density

- Wetting ability
- Adhesion

Najafabadi *et al.* | *ACS Appl. Mater. Interf.* | 2025

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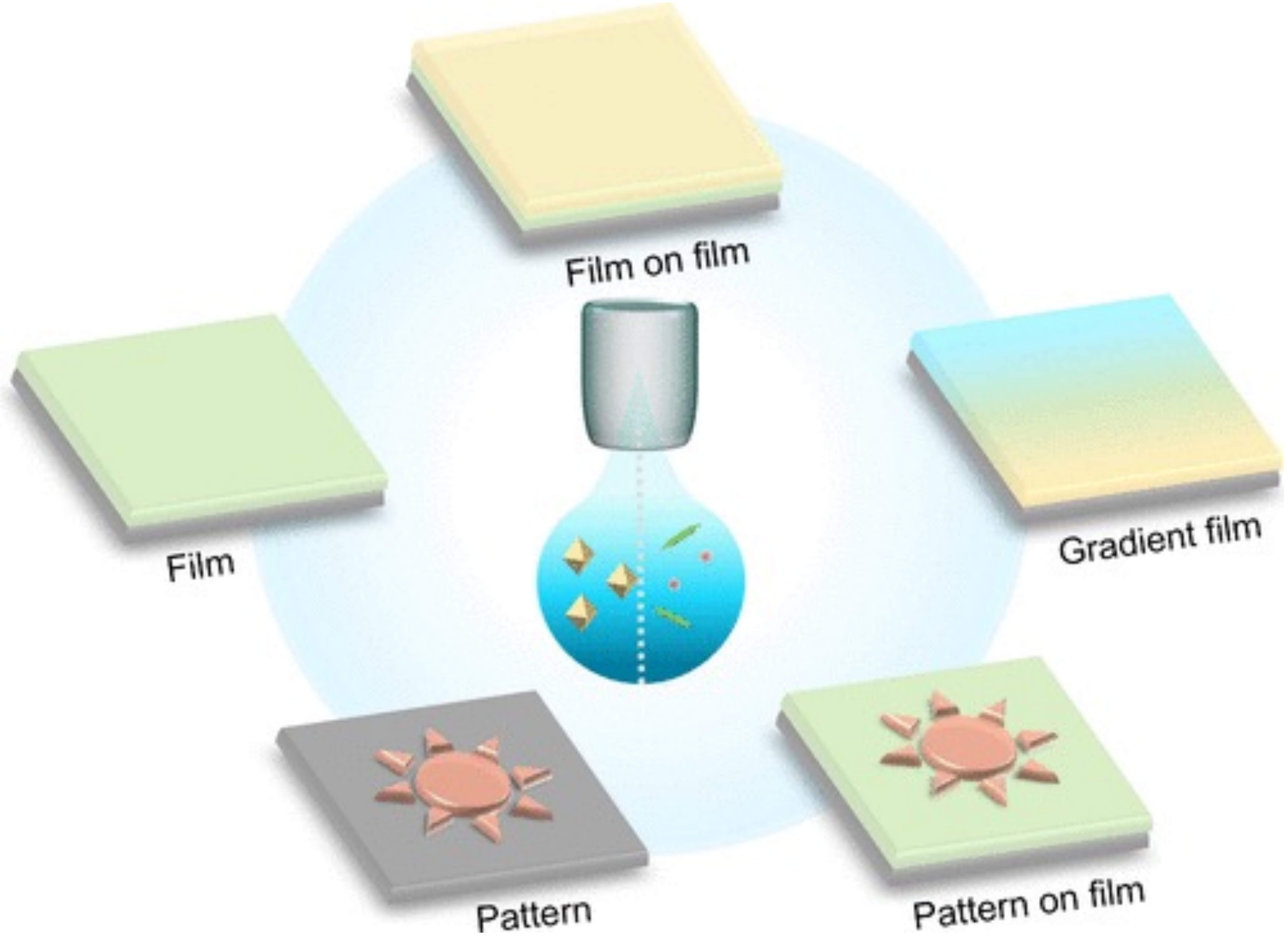
Diversity of Inkjet Patterning on Surfaces



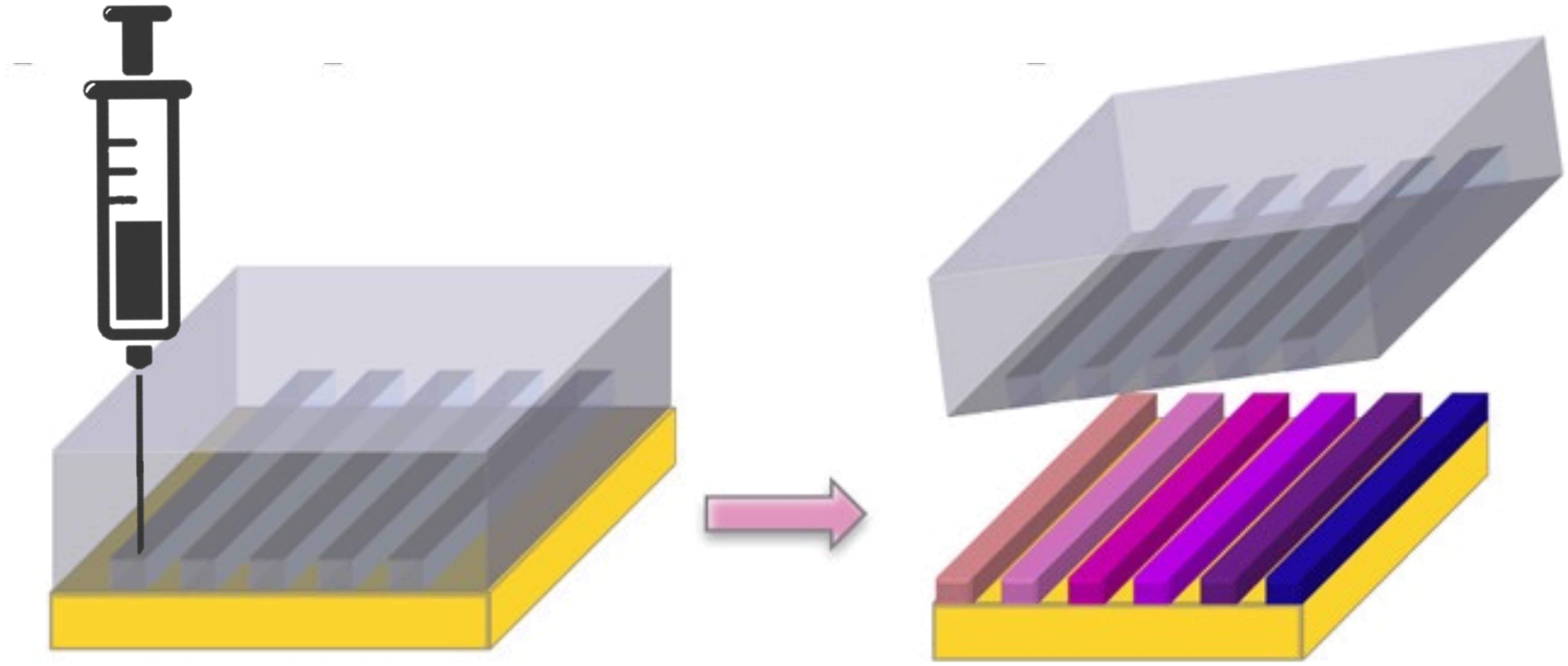
Multiple chemistries can be printed

High-throughput, flexible, and computer controlled

Appropriate for larger patterns (~50 – 100 µm for alkanethiols)

Najafabadi *et al.* | *ACS Appl. Mater. Interf.* | 2025

Microfluidic Patterning (Polymer Channels)



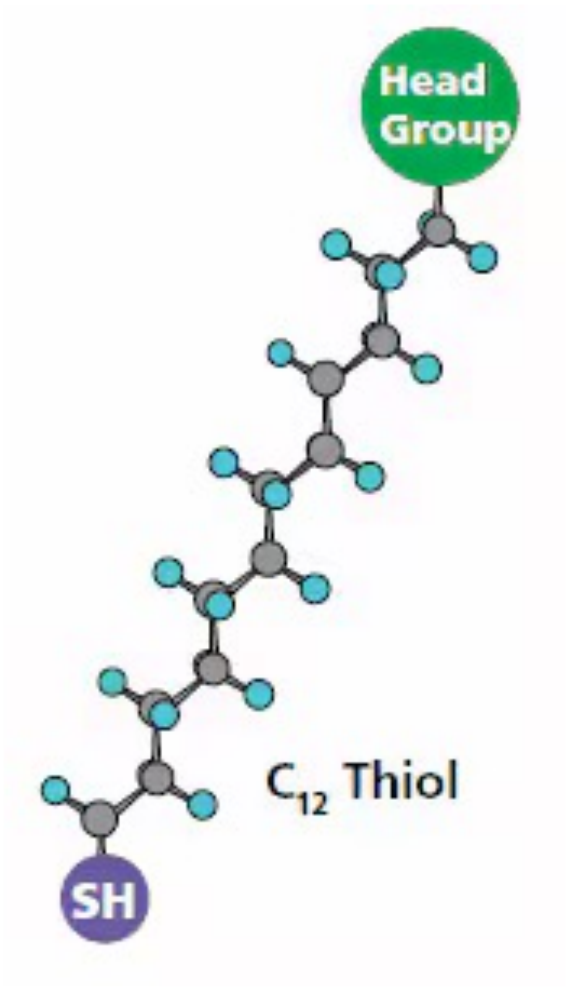
Inject different molecules in each channel

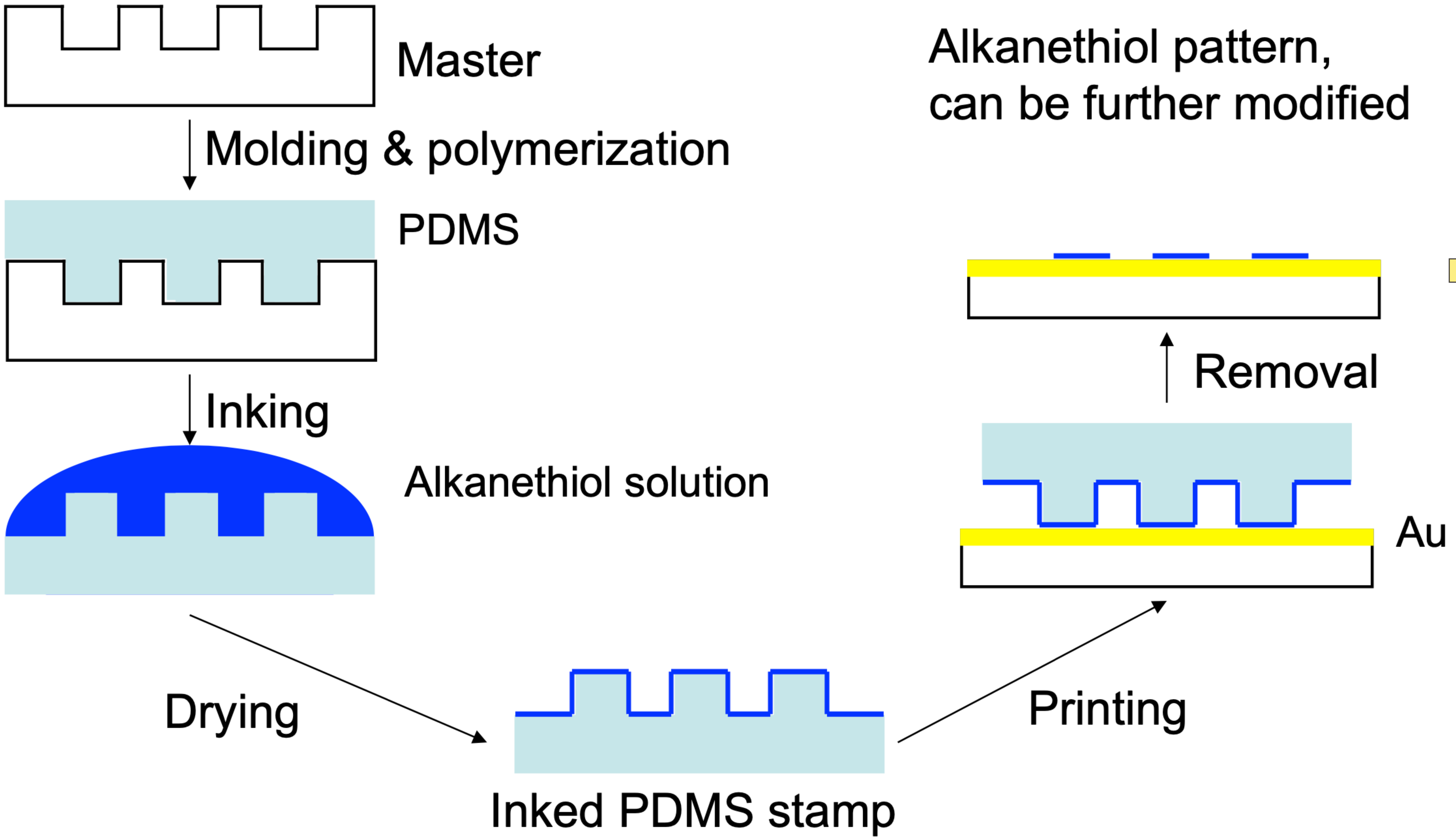
Pattern different molecules

Spatial resolution: ~10–100 µm, limited by channel width and molecular diffusion

Nakatsuka *et al.* | *ACS Appl. Mater. Interf.* | 2018

Microcontact Printing – Transferring Molecules to Surfaces





Master

Molding & polymerization

PDMS

Inking

Alkanethiol solution

Drying

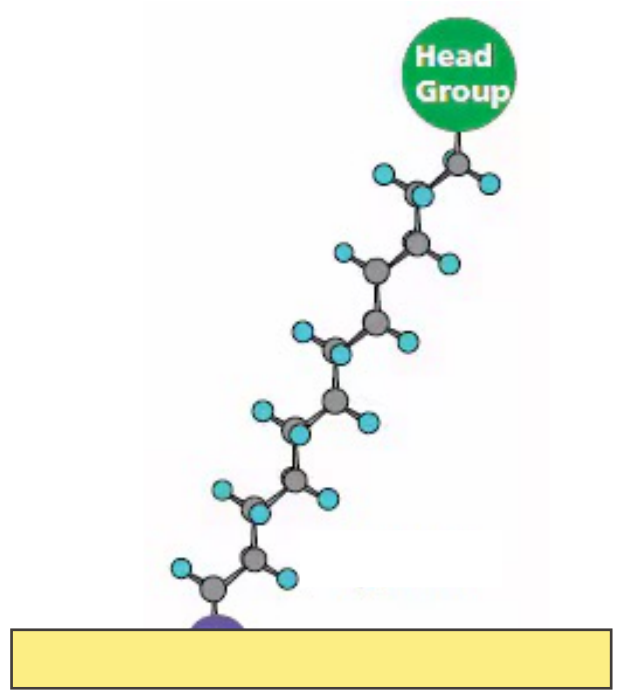
Inked PDMS stamp

Printing

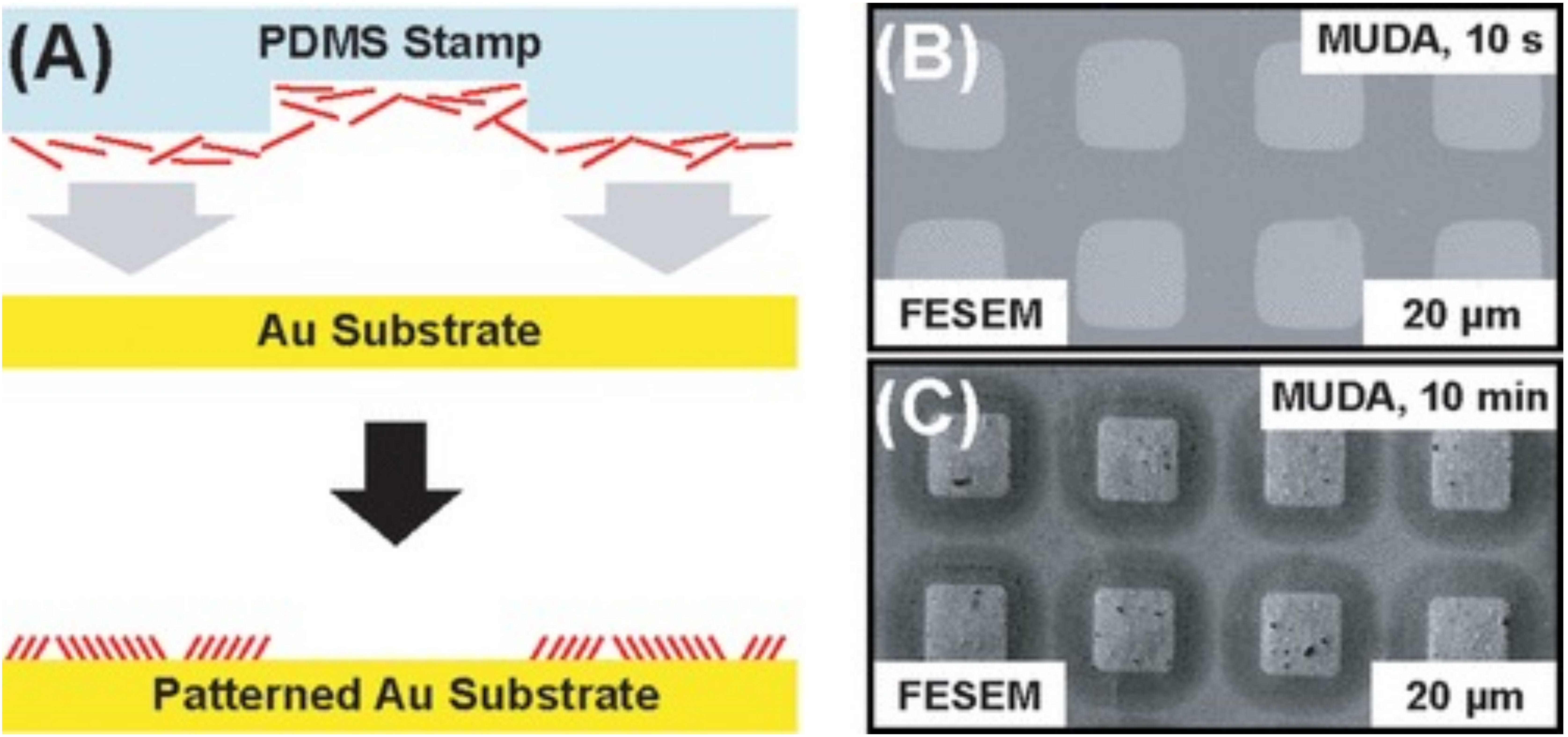
Au

Removal

Alkanethiol pattern,
can be further modified



Microcontact Printing – Resolution Limit of ~100 nm



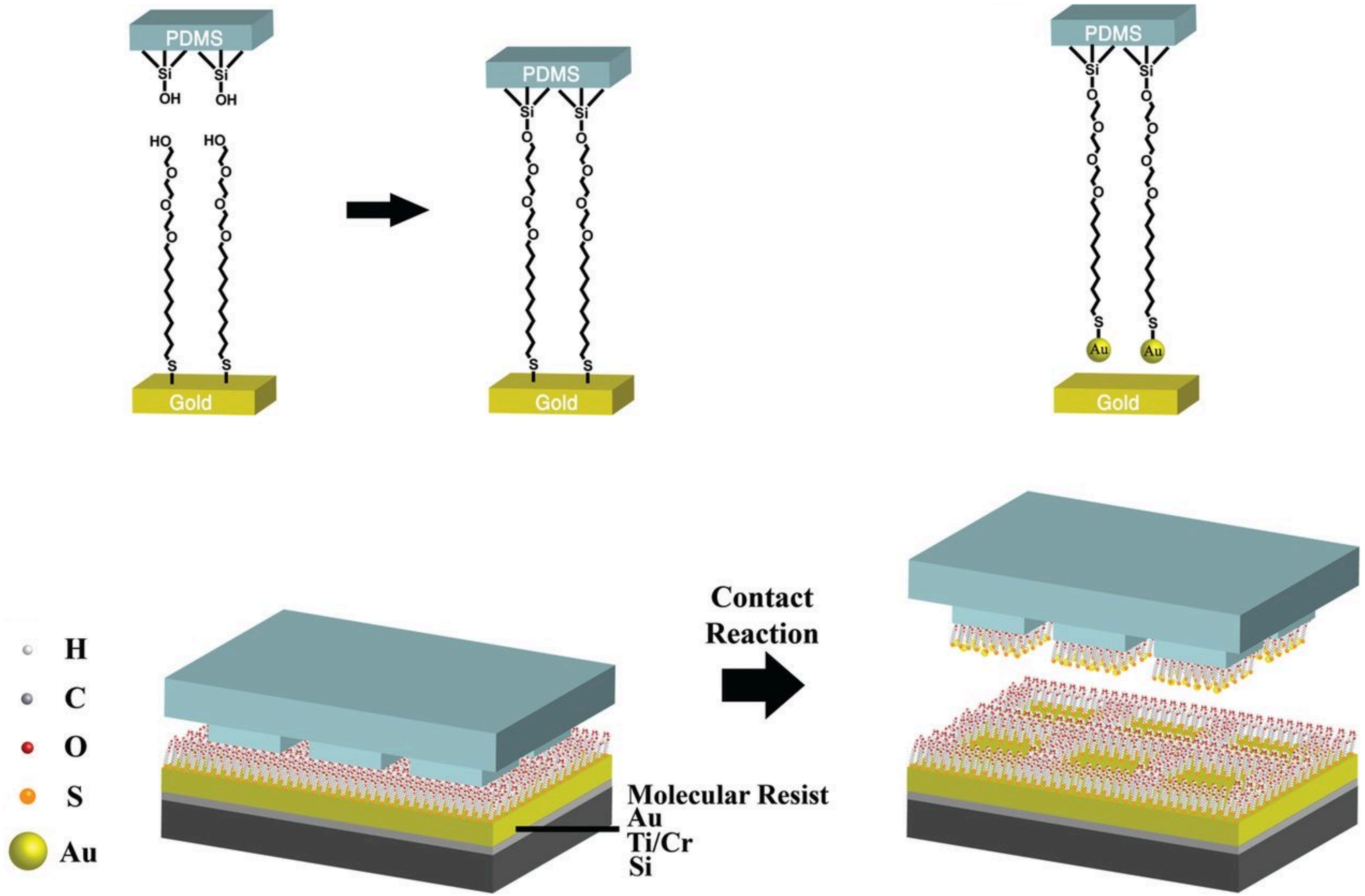
Success of printing limited by chemistries and compatibilities of inks, stamps, and substrates

Lateral diffusion of inked molecules reduce pattern fidelity (sharpness of pattern without blurring)

Realistic resolution ~1–10 µm

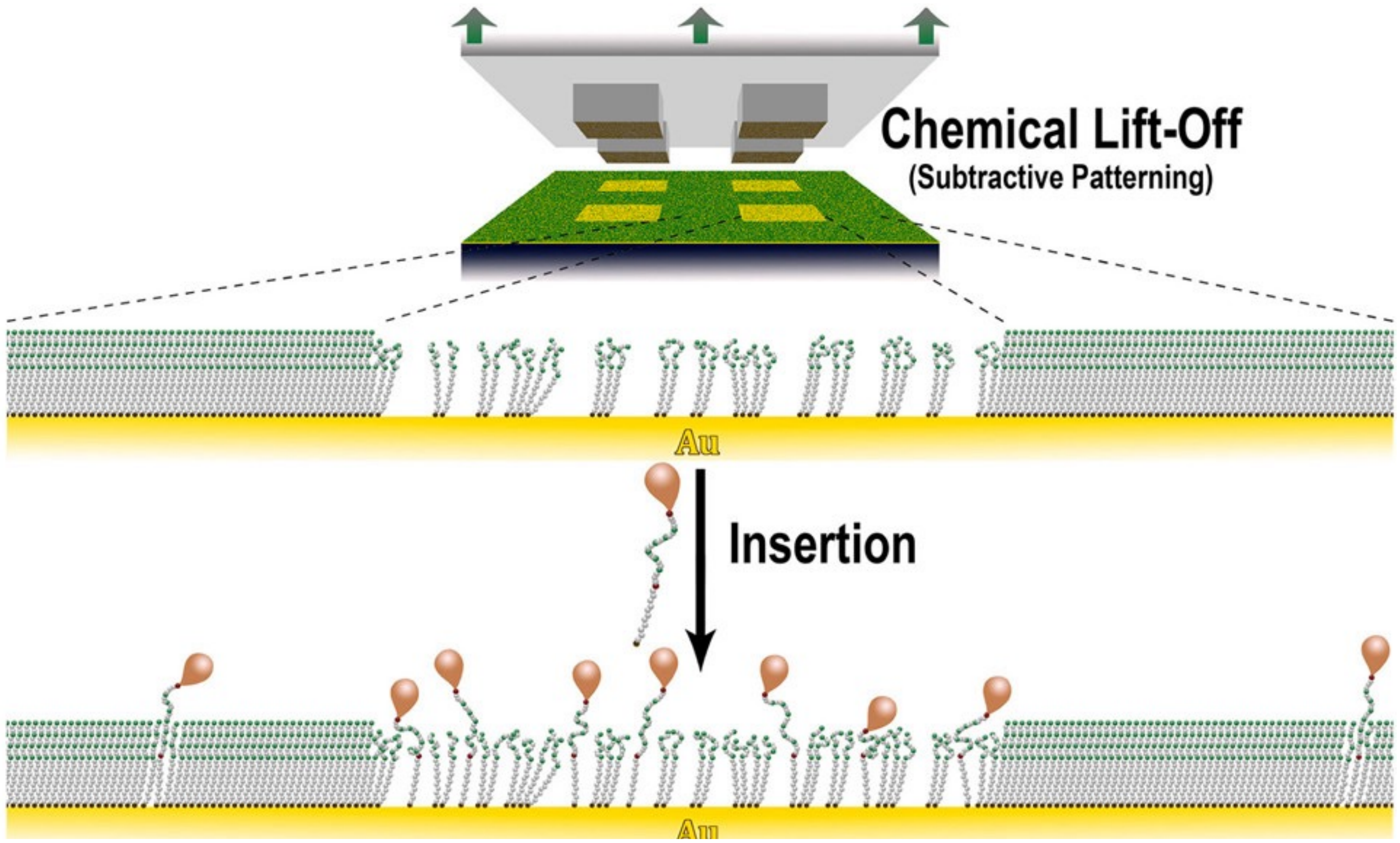
Srinivasan *et al.* | *ACS Nano* | 2007

Chemical Lift-Off Lithography (CLL) – Patterning Smaller Features



Liao *et al.* | *Science* | 2012

Chemical Lift-Off Lithography (CLL) – Patterning Smaller Features



In the gaps formed from lifting off molecules, new molecules can be inserted patterning

Realistic resolution: ~ 50-200 nm

Best possible limit: ~ 10–20 nm

PDMS stamp with “UCLA” characters as positive features and “CNSI” as negative features

Fluorescent molecule inserted into patterned regions

250 µm

Liao *et al.* | *Science* | 2012

Key Takeaways

- Typically, multiple characterization techniques are used for surface analysis
- Once assembled, the functional groups of SAMs can be coupled to molecules
- Especially for biosensors, *where* we pattern molecules, matters
- There are various techniques to pattern SAMs from the microscale to nanoscale (we covered four examples)

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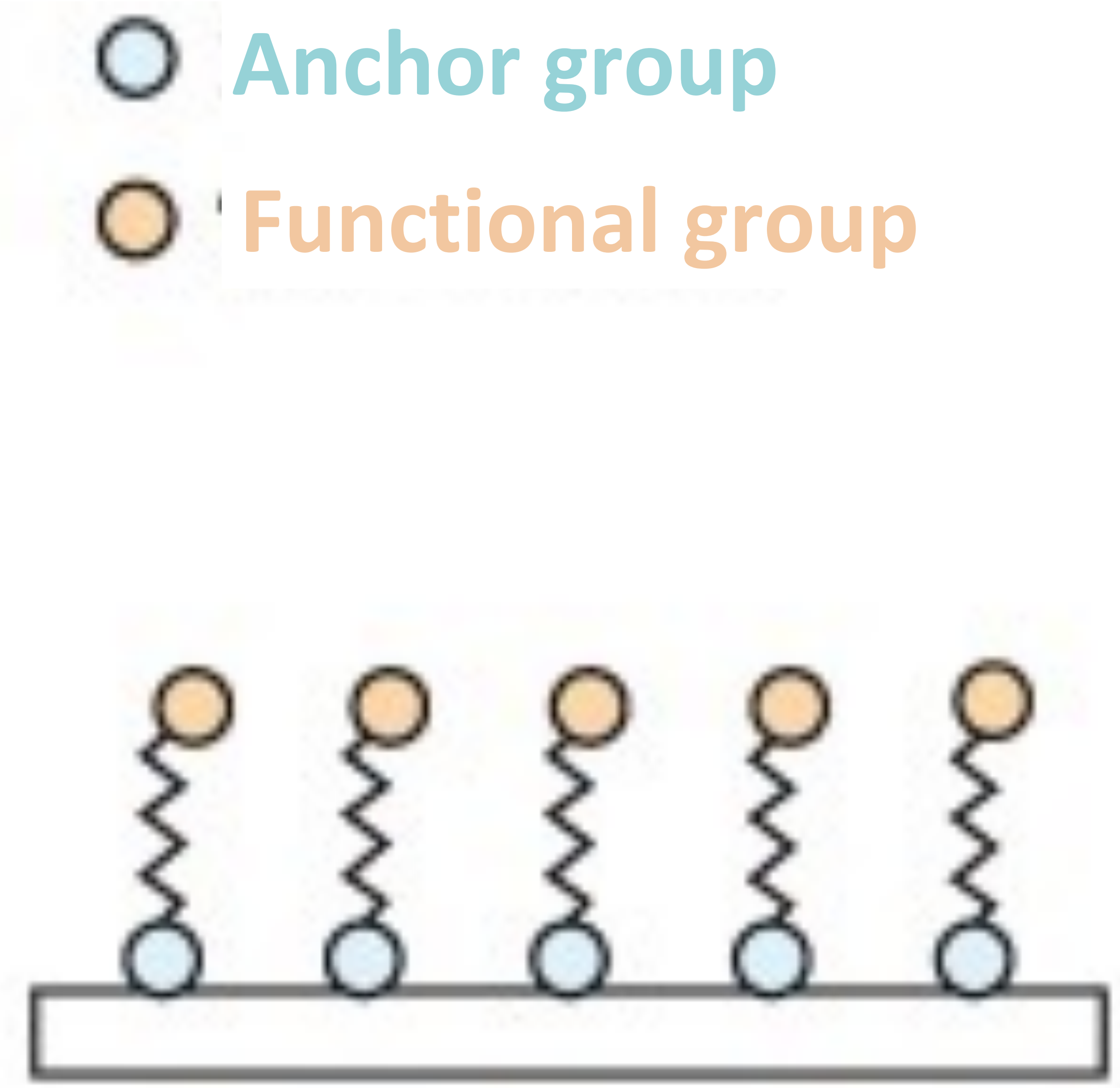
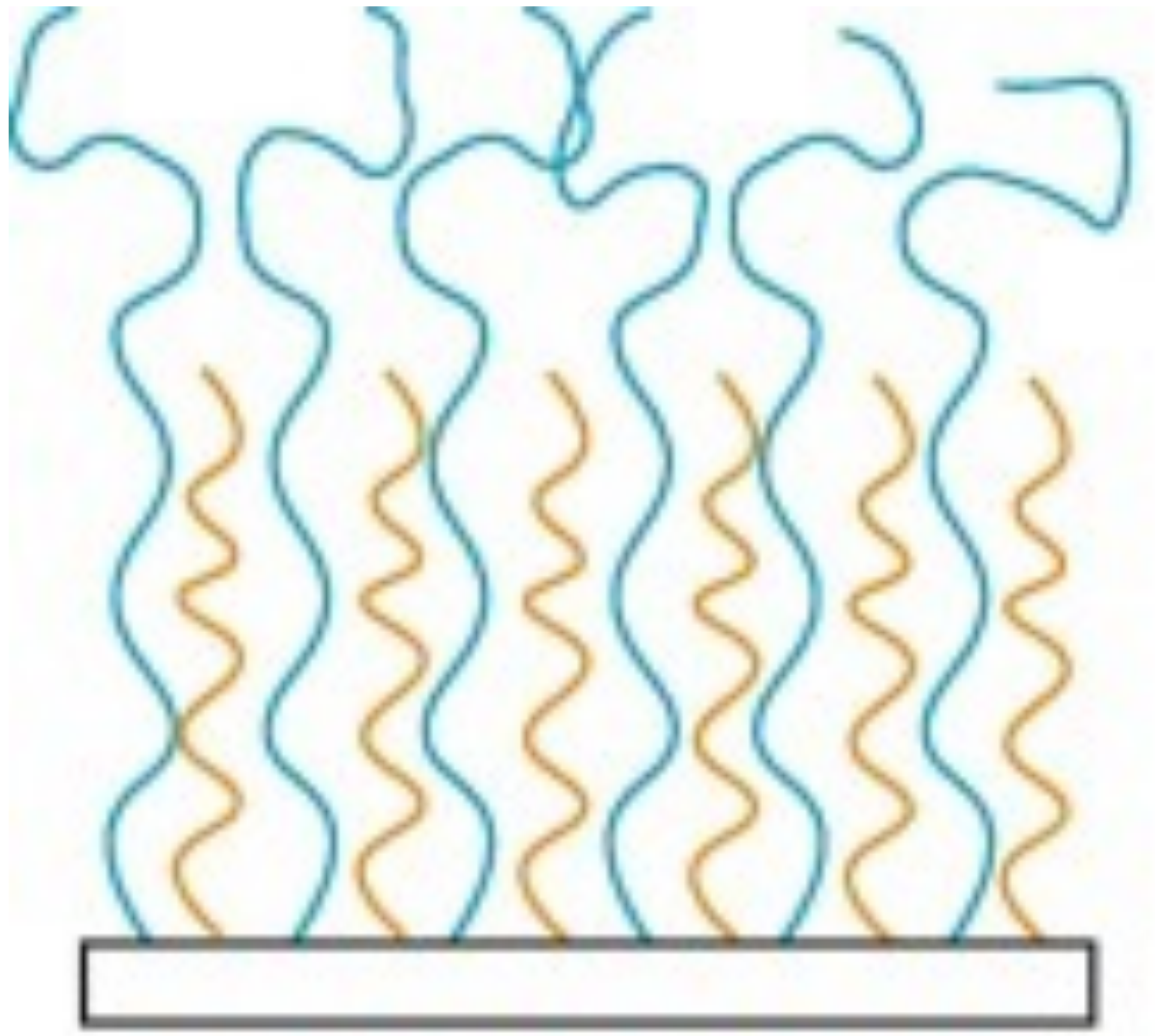
Why Move Beyond SAMs?

SAMs are thin + ordered, but limited – stability issues, limited thickness/hydration

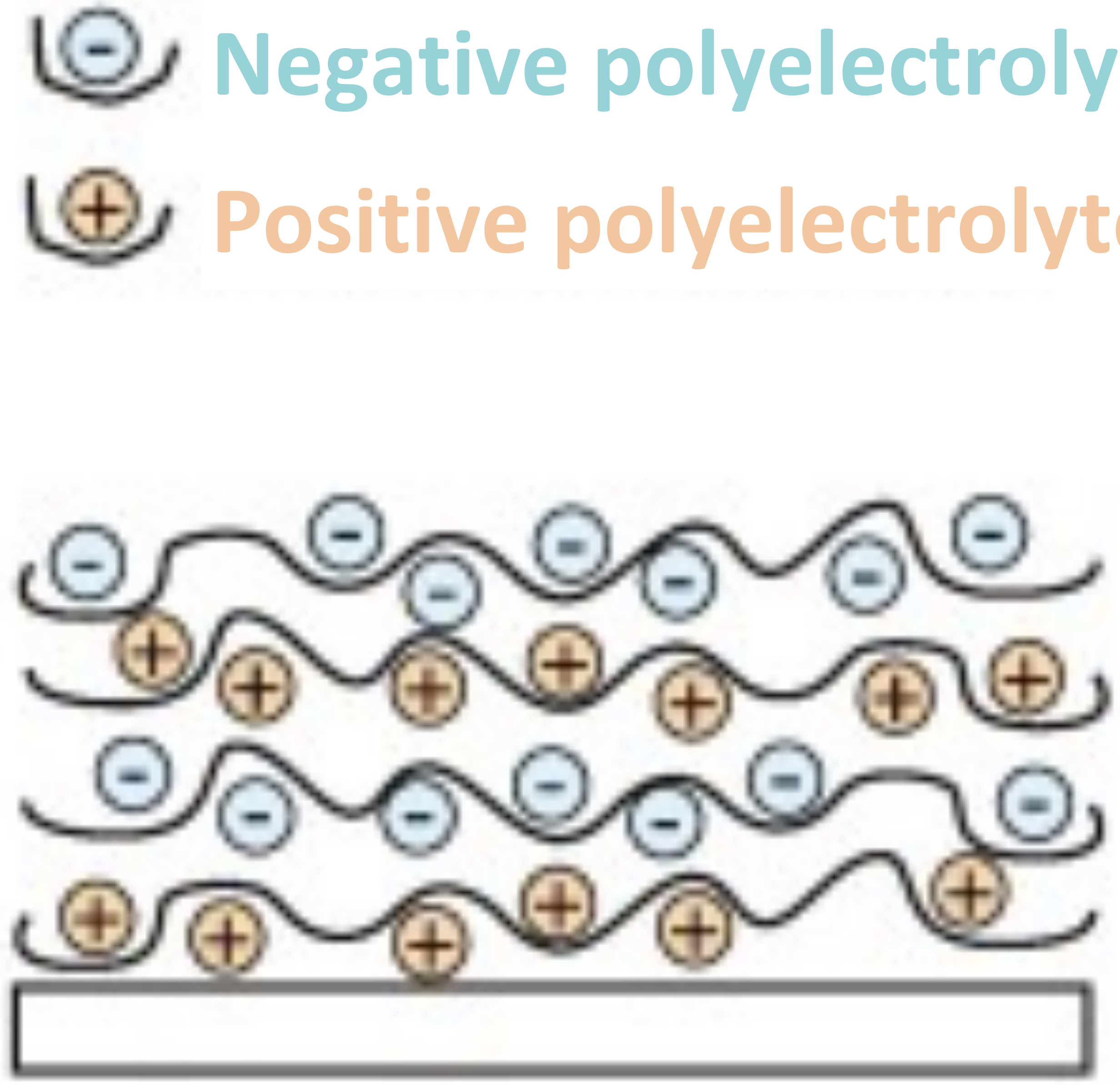
Need for thicker, tunable, hydrated surfaces especially at biological interfaces



SAM



Polymer brush (binary)



Polyelectrolyte multilayer

De Boer & Schroën | Sep. Purif. Tech.| 2024

Applications Driving Polymer-Coated Surfaces

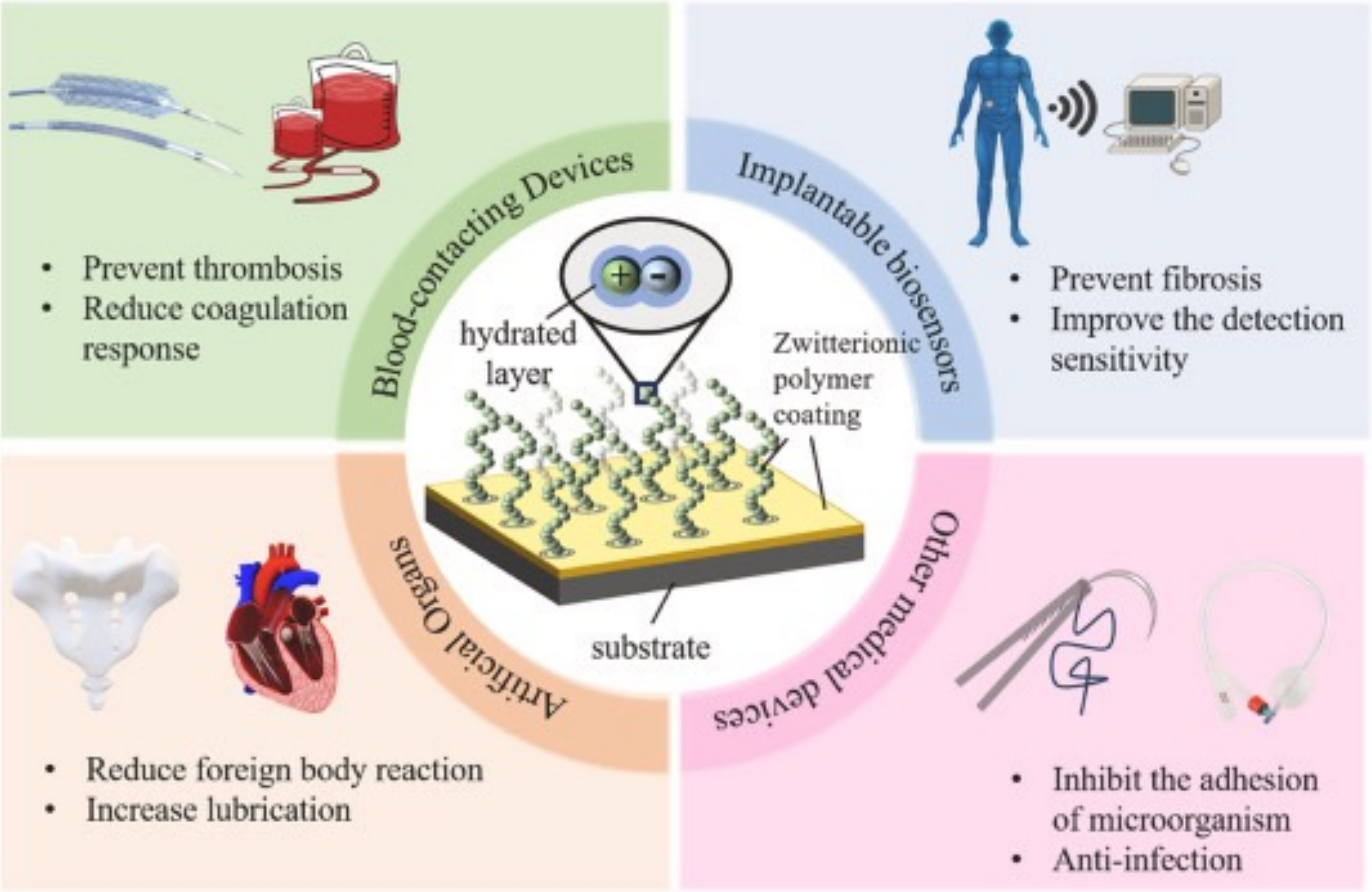
Biosensors

Medical implants

Microfluidics

Lab-on-chip

Antifouling coatings



Wen et al. | Mater. Today Chemistry | 2024

Where are Polymer-Coated Layers Most Useful in Surface Science?

Nonspecific protein adsorption in complex environments/biofluids

What are proteins and why do they stick everywhere?

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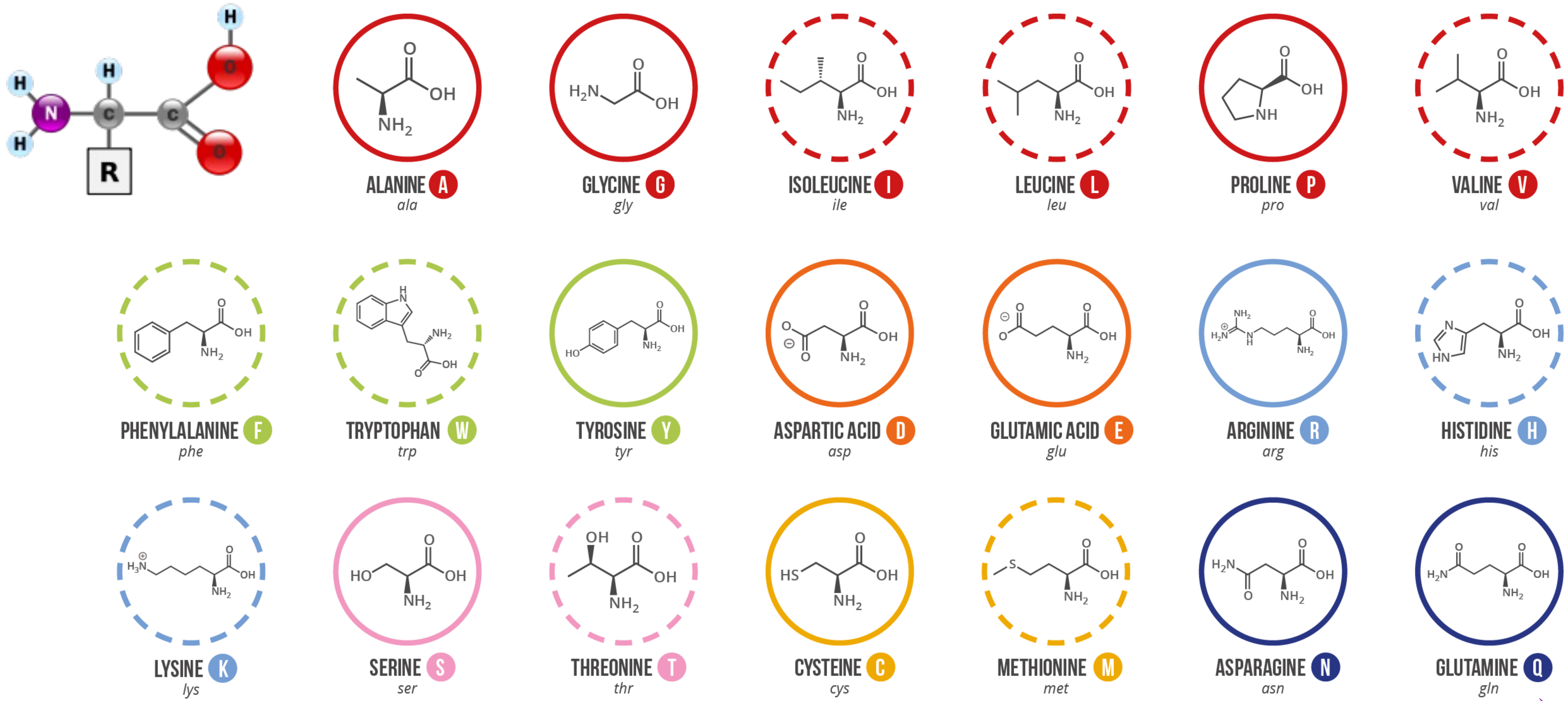
Amino Acids are the Monomer of Proteins

Chart Key: ● ALIPHATIC ● AROMATIC ● ACIDIC ● BASIC ● HYDROXYLIC ● SULFUR-CONTAINING ● AMIDIC ○ NON-ESSENTIAL ◌ ESSENTIAL



ALANINE A *ala*
GLYCINE G *gly*
ISOLEUCINE I *ile*
LEUCINE L *leu*
PROLINE P *pro*
VALINE V *val*
PHENYLALANINE F *phe*
TRYPTOPHAN W *trp*
TYROSINE Y *tyr*
ASPARTIC ACID D *asp*
GLUTAMIC ACID E *glu*
ARGININE R *arg*
HISTIDINE H *his*
LYSINE K *lys*
SERINE S *ser*
THREONINE T *thr*
CYSTEINE C *cys*
METHIONINE M *met*
ASPARAGINE N *asn*
GLUTAMINE Q *gln*

COMPOUND INTEREST
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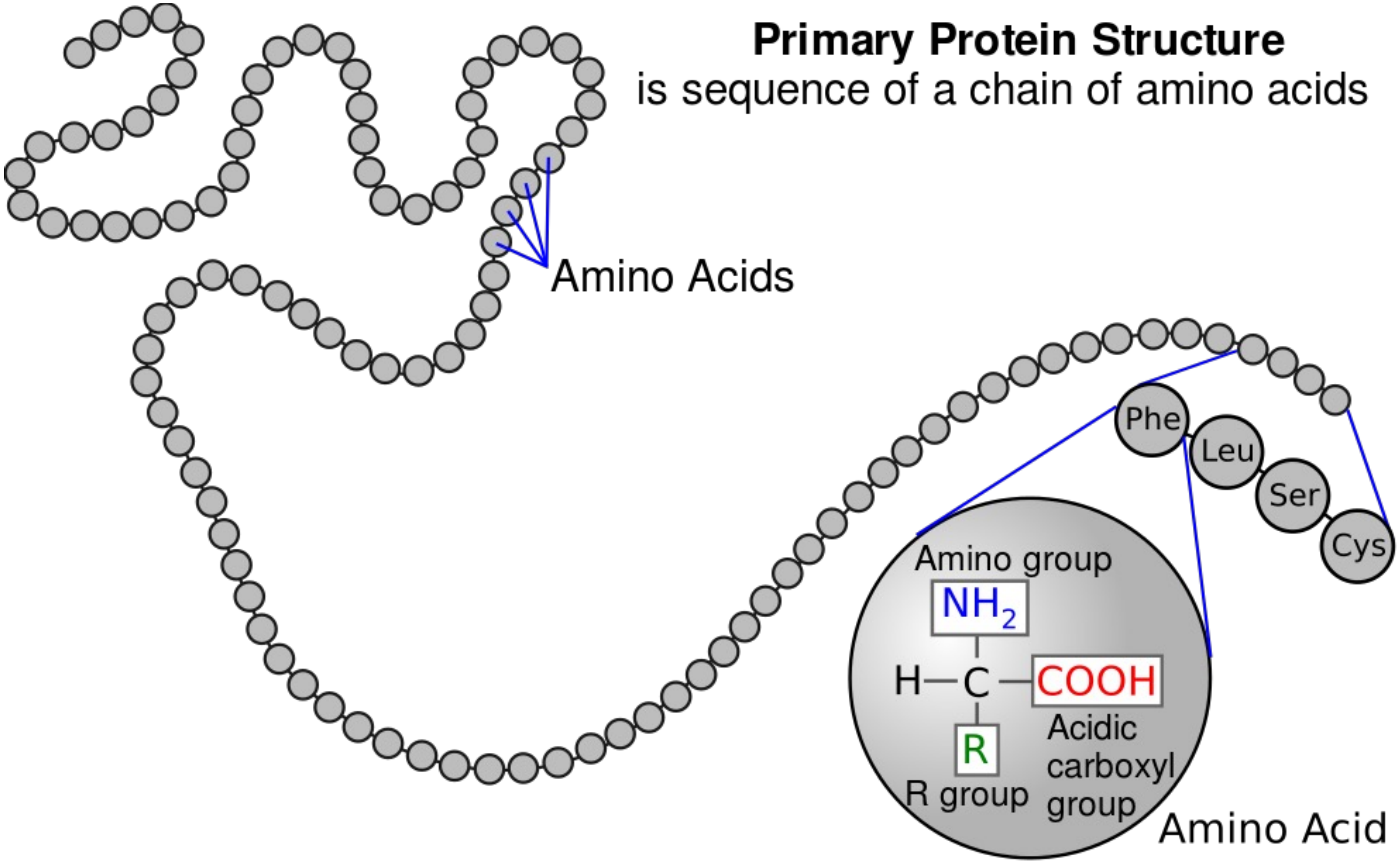
Amino Acids Connect to Form Polymers (Polypeptides/Proteins)



The order is very important for function

There is an enormous number of possible combinations of amino acids: even with only 40 units, there are 20^{40} ($\approx 10^{52}$) possibilities

Image by Wikipedia

Connection Between Amino Acids = Peptide Bond

Amino acids connect together to form polymers (polypeptides or proteins) of 40 to 10,000+ amino acid units

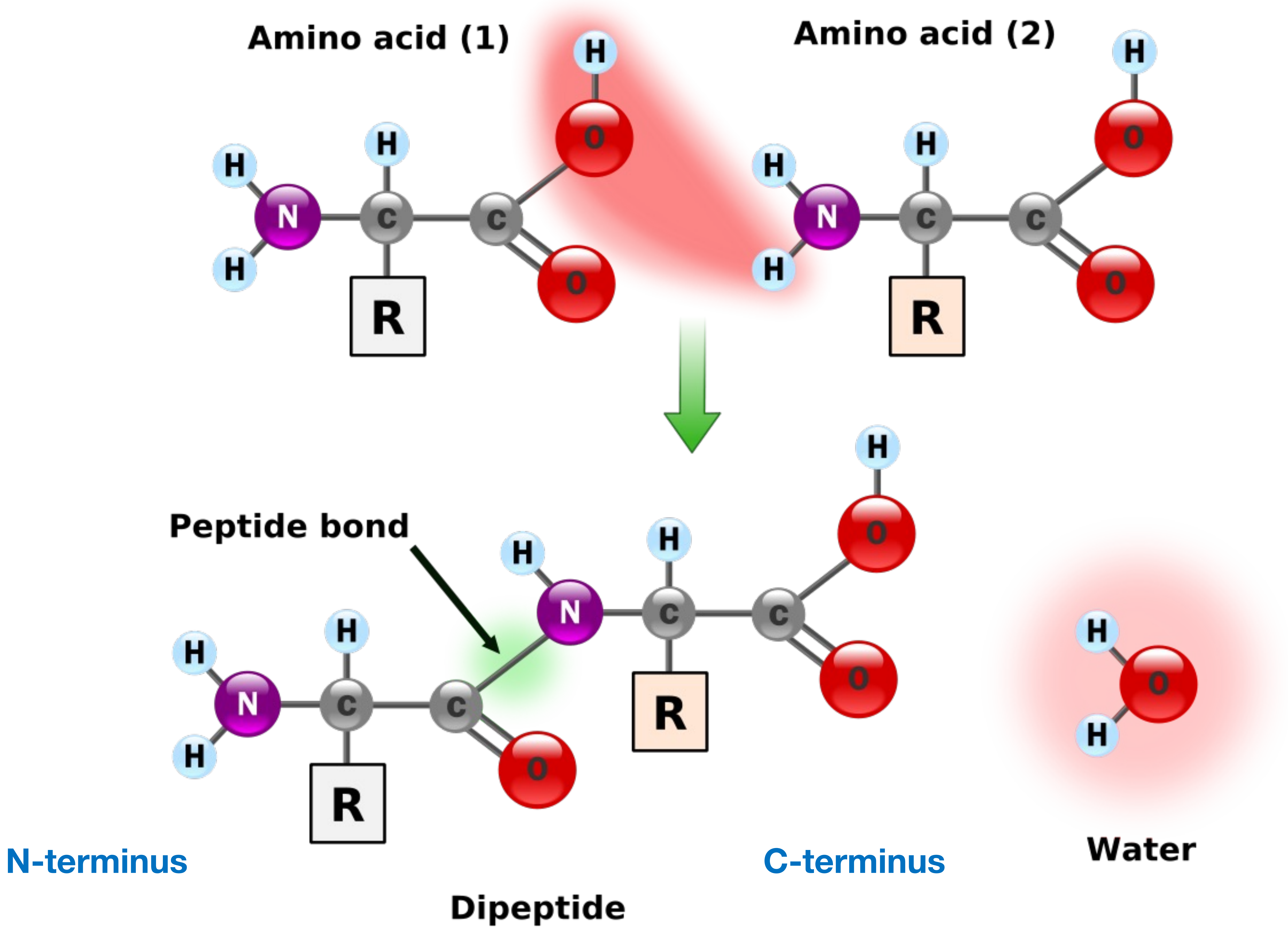
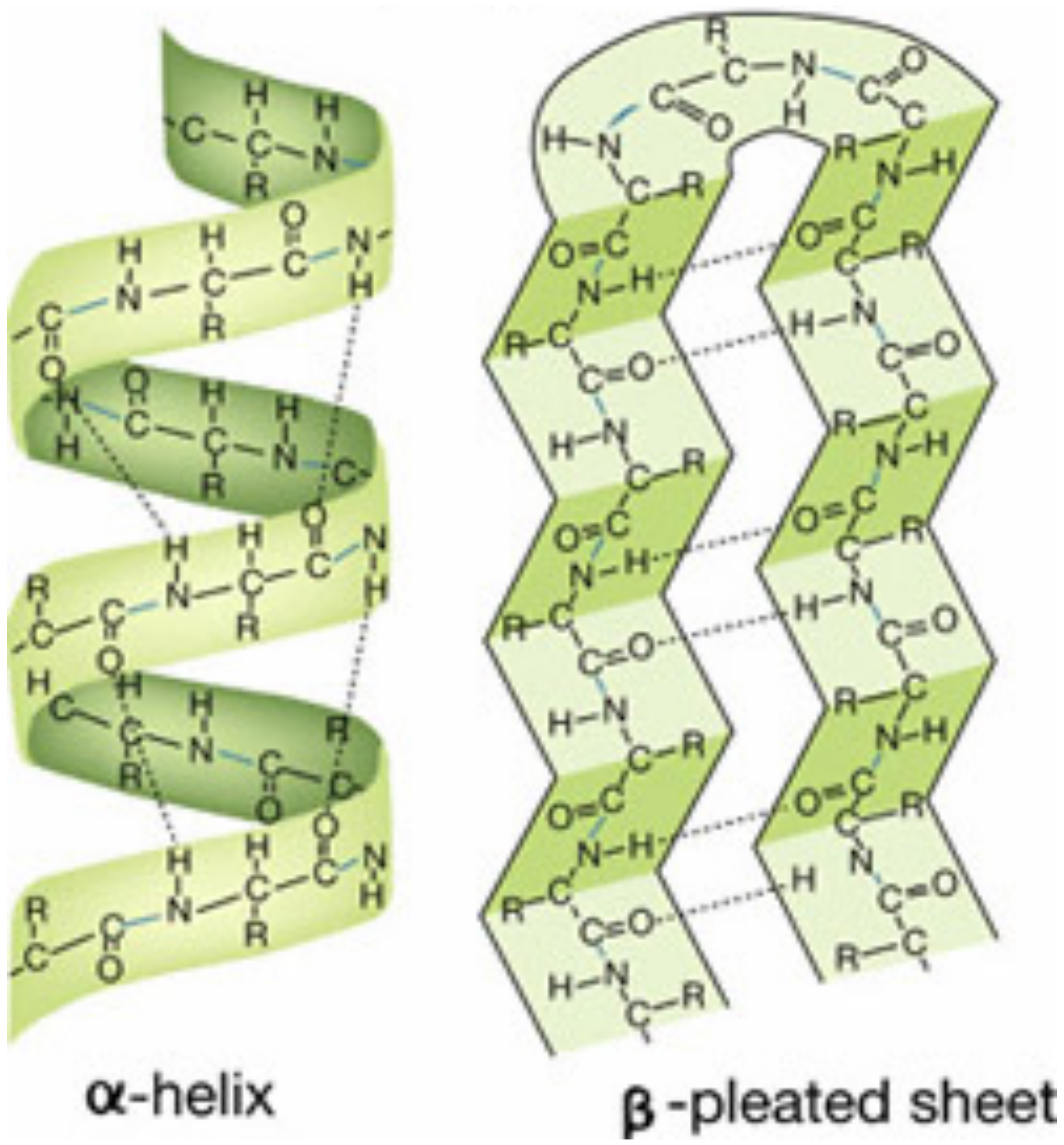


Image by Wikipedia

Protein Secondary and Tertiary Structures

Secondary structure



The polypeptide chain can hydrogen bond to itself, to produce the secondary structure

Tertiary structure

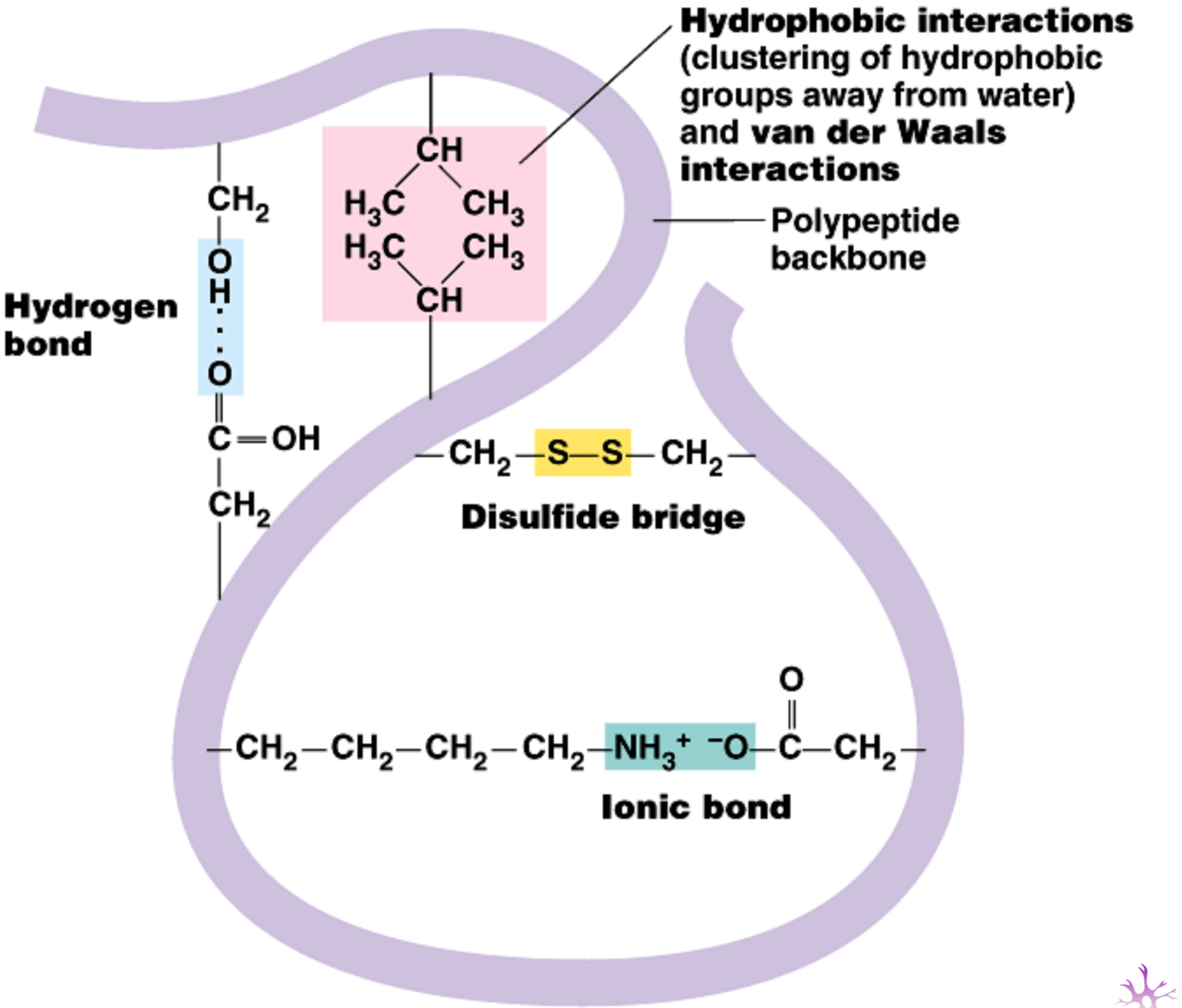
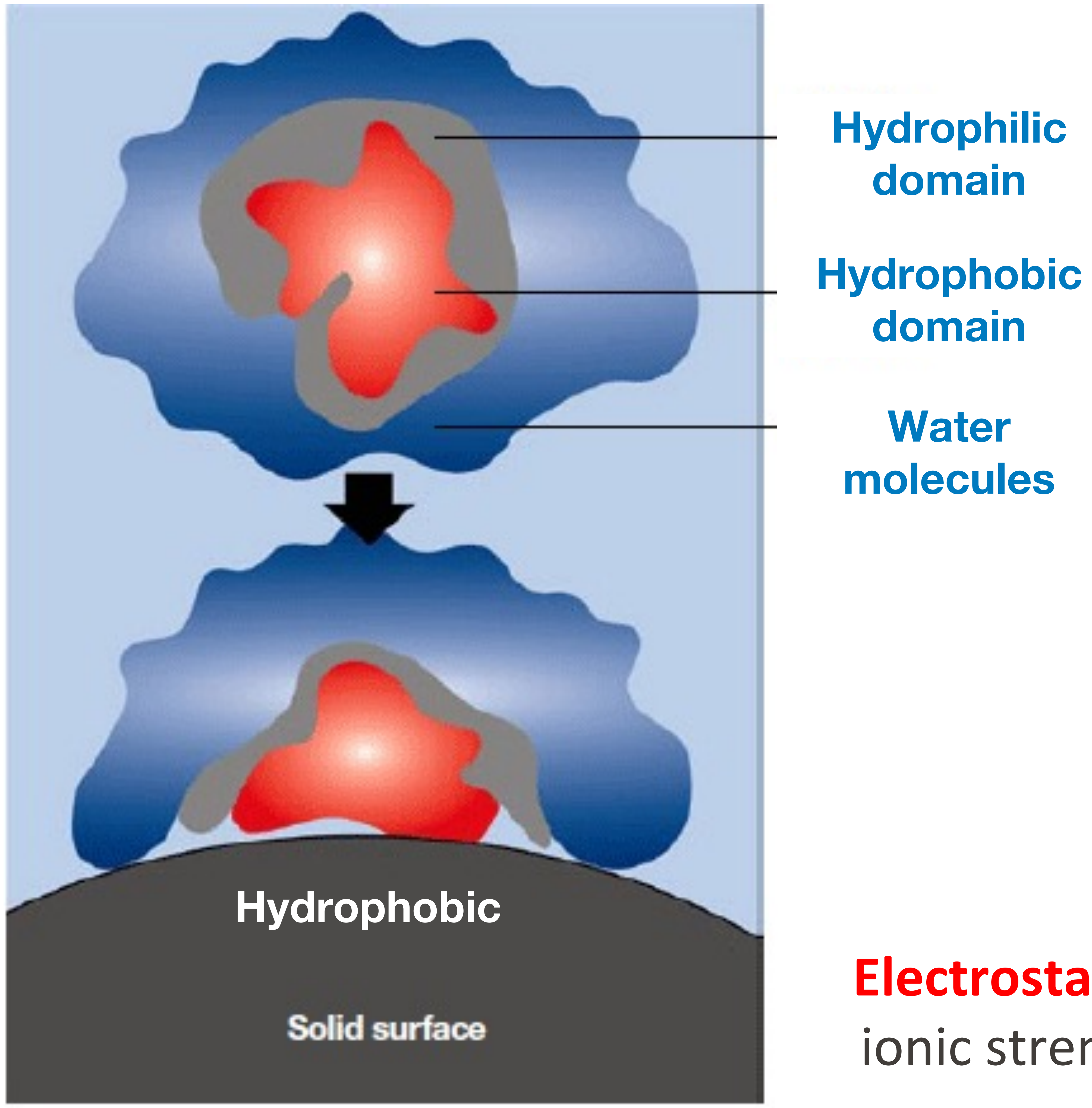


Image by Wikipedia

Proteins on Surfaces – Adsorption and Denaturation

Proteins adsorb on surfaces to lower the free energy of the system



Hydrophobic interactions

Hydrophobic groups on the protein: tend to be located inside of the overall protein structure

↓

Shielded from aqueous surroundings

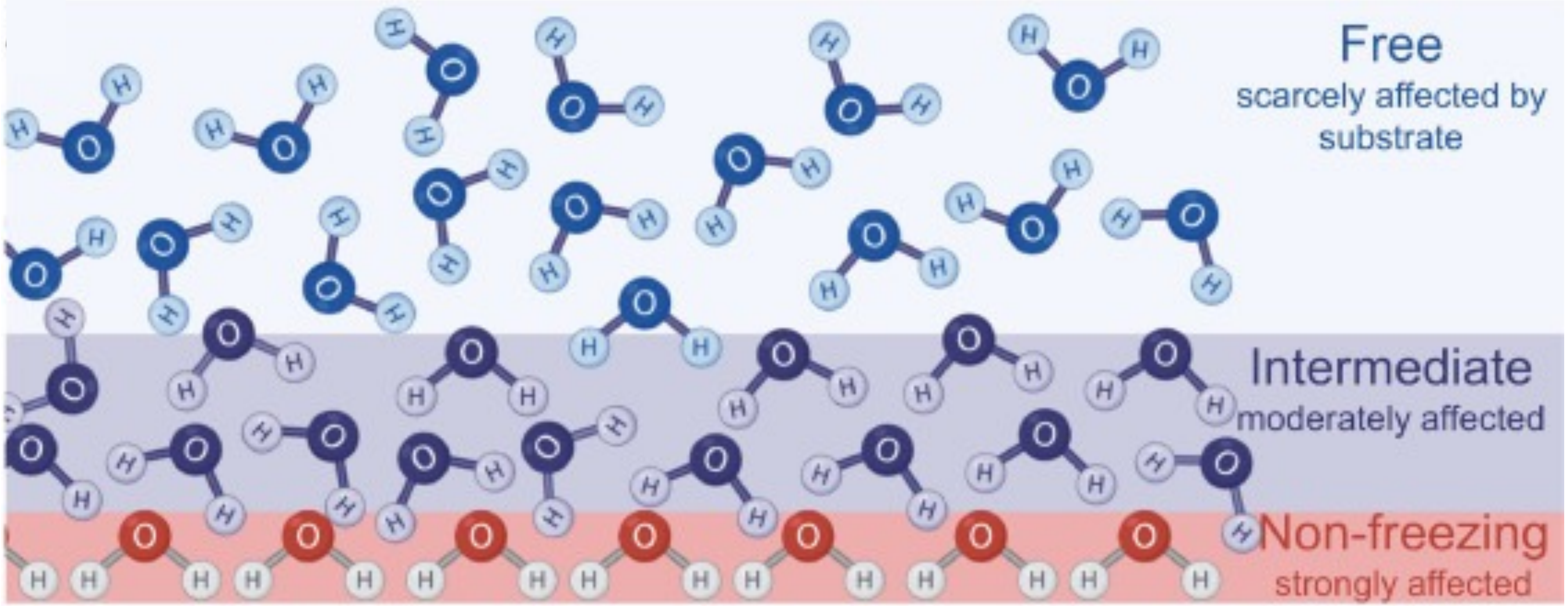
Upon encountering a hydrophobic surface, it is energetically favorable for hydrophobic amino acids to be close to the surface

↓

Unfolding or denaturation of the protein

Electrostatic interactions with the surface are often important → pH and ionic strength of the solution can significantly influence protein adsorption

Hydration Layer on the Surface Composed of Multiple Layers



"Bulk" water
1-2 nm from
surface

1-2 orders slower
kinetics than
"free" water

Tightly bound
water with slow
dynamics

The interactions of water with the surface can drive how proteins stick to surfaces

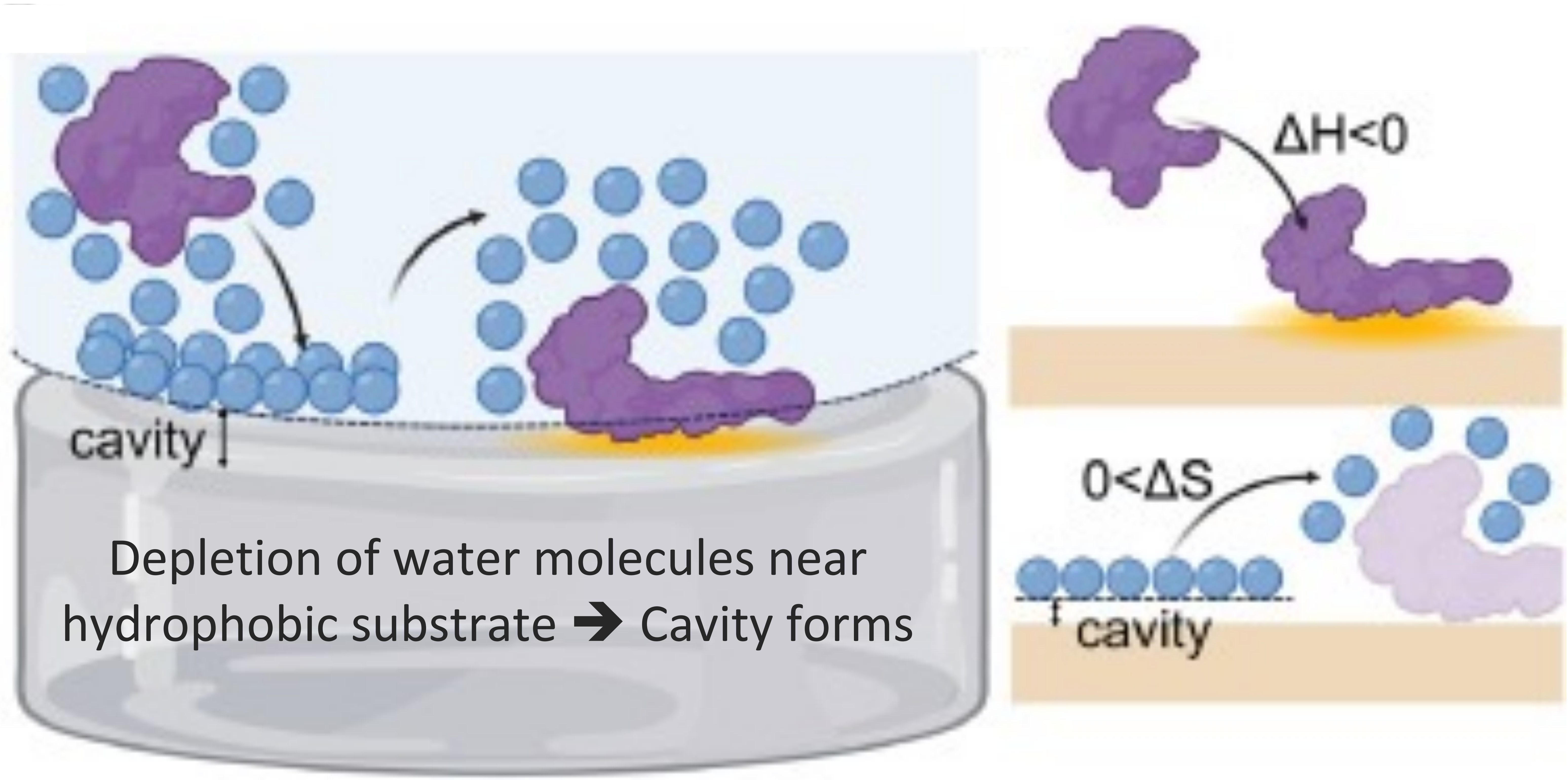
Crago et al. | Acta Biomaterialia| 2024

Thermodynamics of Protein Adsorption on Hydrophobic Surfaces

Hydrophobic surfaces don’t have functional groups to form hydrogen bonding or strong polar or electrostatic interactions

H_2O molecule stick together (H-bonds) since they avoid the surface

Reorganize into tight, ordered layer



Depletion of water molecules near hydrophobic substrate ➔ Cavity forms

Hydrophobic bonds between hydrophobic amino acids and surface

Protein pushes bound water away

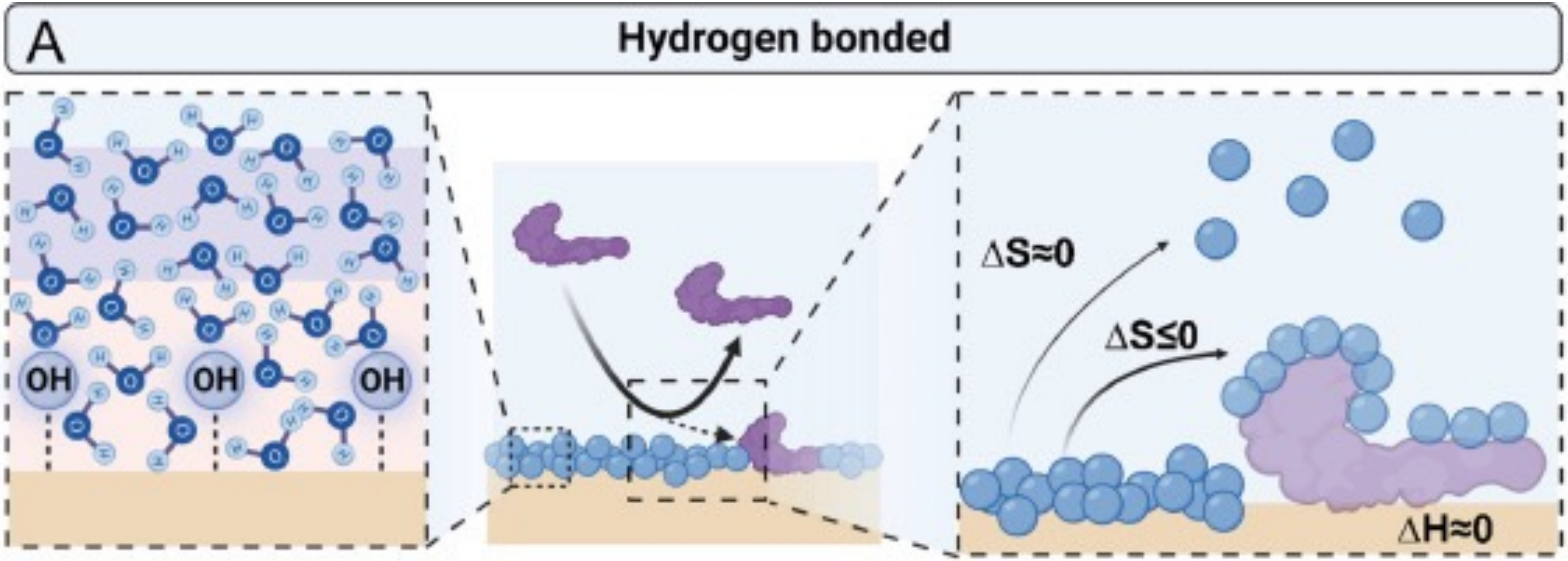
⬇

More freely moving water

Crago et al. | Acta Biomaterialia| 2024

Thermodynamics of Protein Adsorption on Hydrophilic Surfaces

Hydrophilic surfaces can provide more energetically stable bonds with proteins and water molecules like polar and hydrogen bonding



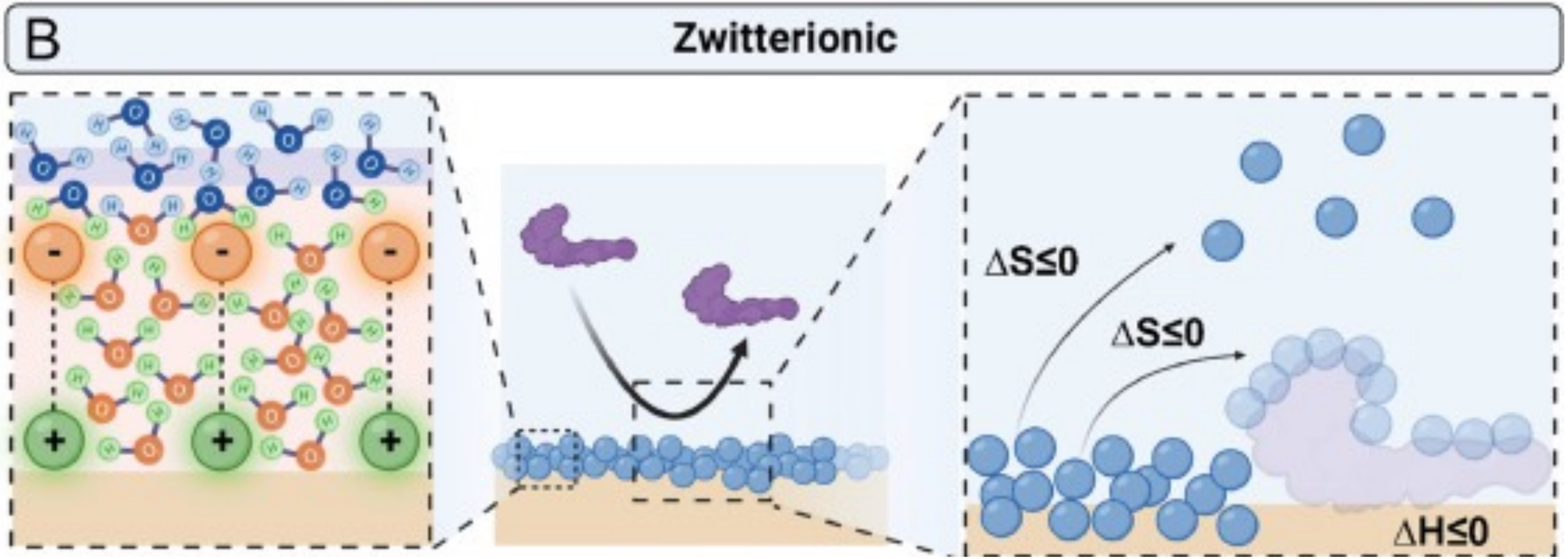
Water sticks to surfaces through H-bonds

To stick, protein must gain more H-bonds to the surface than the water-surface H-bonds being broken (protein adsorption not favorable)

Crago et al. | Acta Biomaterialia| 2024

Thermodynamics of Protein Adsorption on Hydrophilic Surfaces

Zwitterionic surfaces have both + and – charges ➔ surface is overall neutral
This allows water near the surface to keep its natural H-bonding network



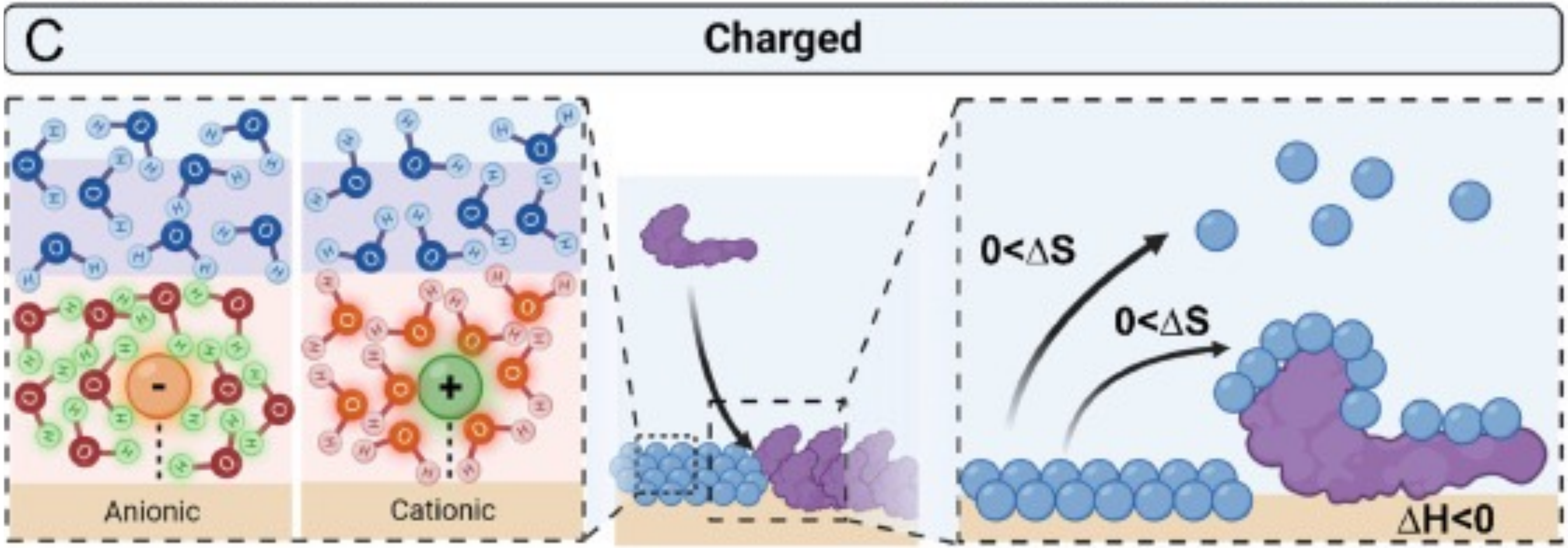
Water in happy state

Zwitterionic surfaces resist protein adsorption because the water near the surface is already stable, so removing it costs entropy

Crago et al. | Acta Biomaterialia | 2024

Thermodynamics of Protein Adsorption on Charged Surfaces

Charged surfaces (+ or – charges) make water near the surface very ordered ➔ water must align around the electric field (restricted motion)



Ordered water

Ordered water release leads to entropy increase
Protein forms electrostatic interactions with the surface

Crago et al. | Acta Biomaterialia | 2024

Thermodynamics of Protein Adsorption Summary

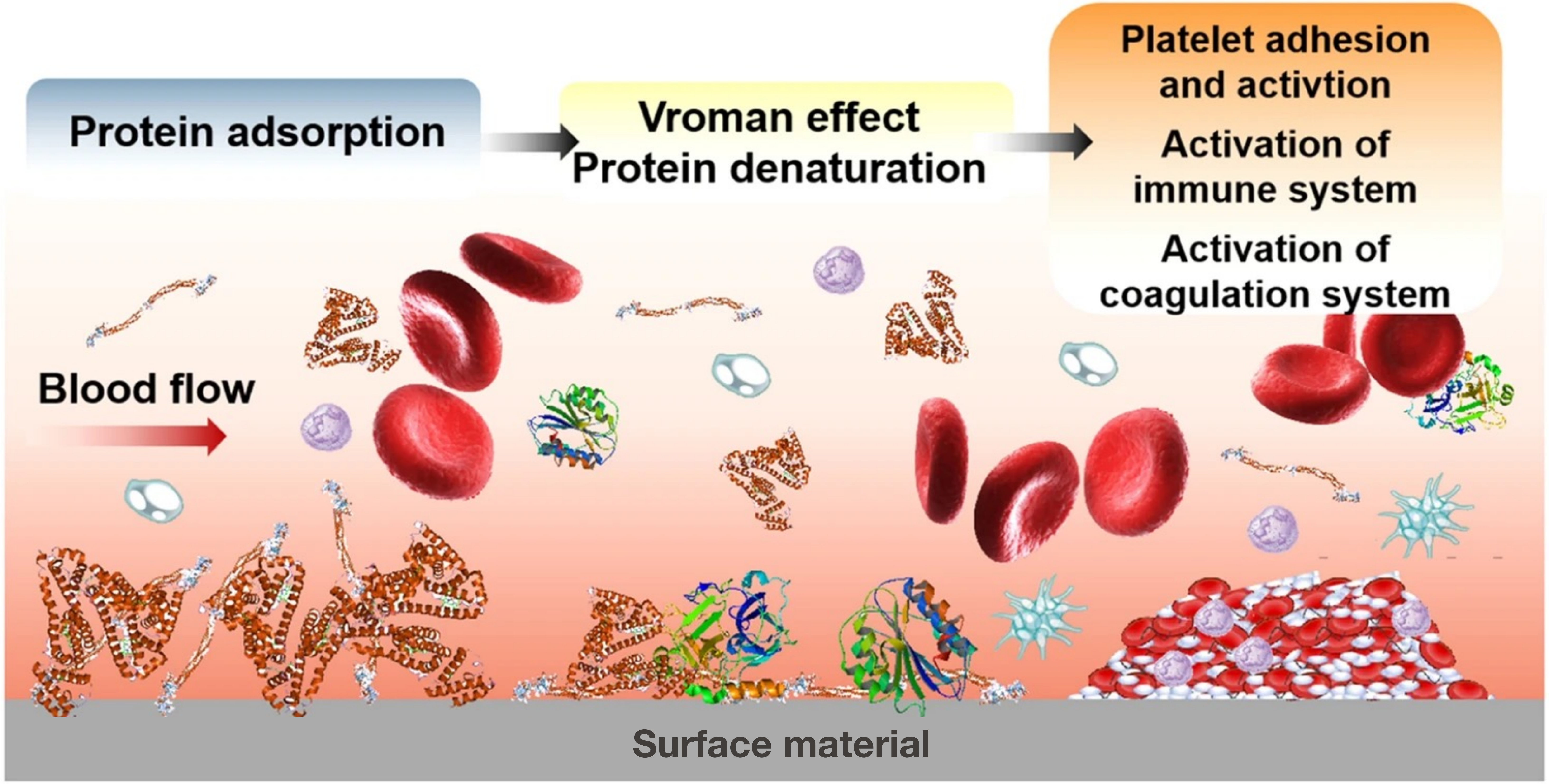
Surface Property	**Water at Surface**	**Entropy Effect**	**Enthalpy Effect**	**Protein Adsorption Strength**
Hydrophobic	Water is highly ordered (unhappy)	$\Delta S > 0$	Hydrophobic contacts give $\Delta H < 0$	Strong (can denature protein)
Hydrophilic / Hydrogen-Bonding	Water is stable and hydrogen-bonded naturally	$\Delta S \approx 0$	Only favorable if protein forms extra H-bonds	Weak–Moderate
Zwitterionic	Water remains very stable, highly "bulk-like"	$\Delta S \leq 0$	Electrostatics small $\Delta H \leq 0$	Very Weak (Protein-Resistant)
Charged (Anionic / Cationic)	Water highly oriented by electric field (low entropy)	$\Delta S > 0$	Electrostatic binding gives $\Delta H < 0$	Strong

Crago et al. | Acta Biomaterialia| 2024

Proteins on Surfaces – Vroman Effect

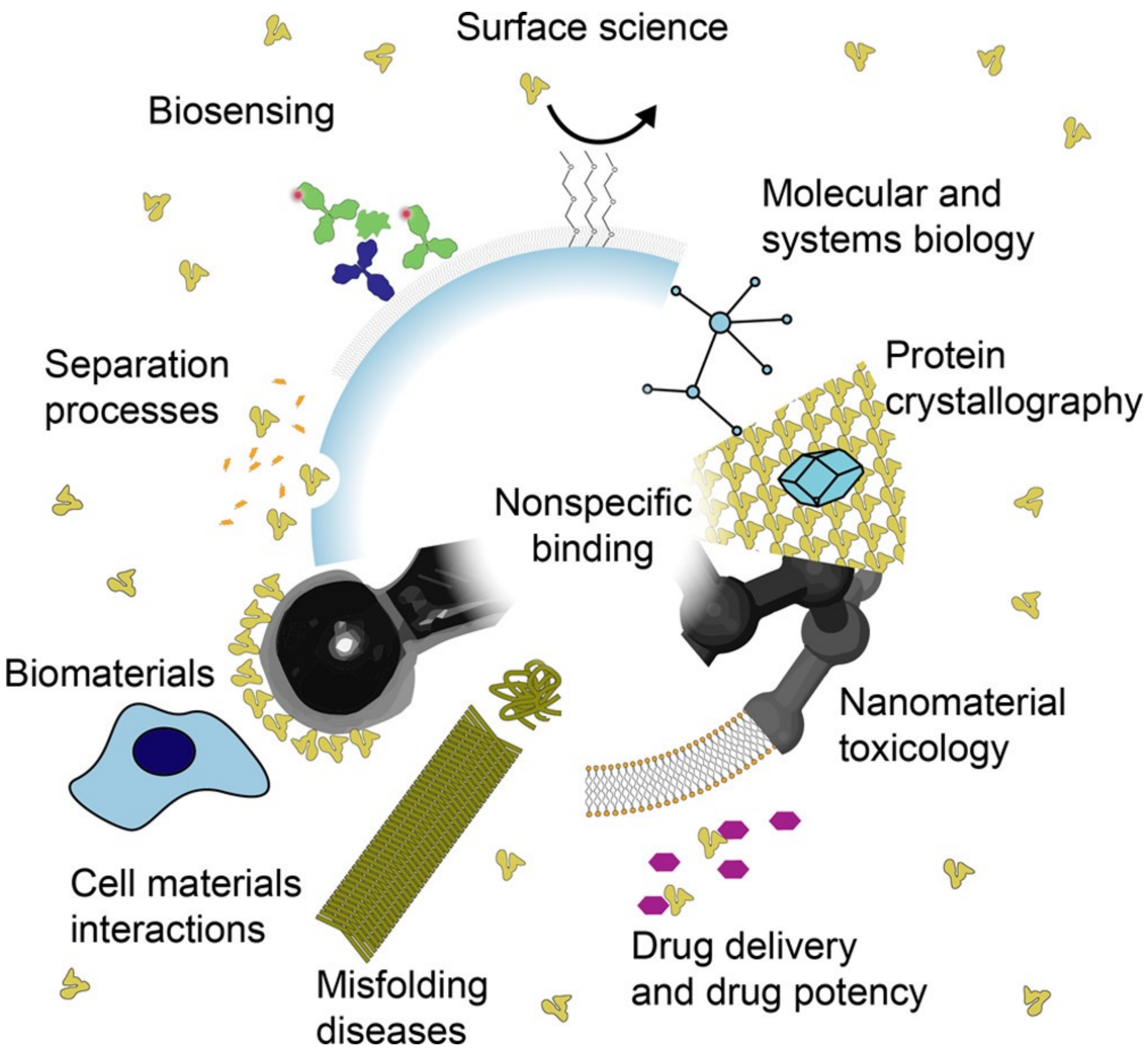
Small, abundant molecules (albumin, fibrin) will rapidly and reversibly coat a surface, gradually being replaced by larger molecules with higher affinity for the surface

Conformational change of many proteins upon nonspecific adsorption to the interface



Ji, *et al.* | *Adv. Fiber Mater.* | 2023

Proteins on Surfaces has Major Implications in Many Fields



Surface science

Biosensing

Molecular and systems biology

Protein crystallography

Separation processes

Nonspecific binding

Biomaterials

Nanomaterial toxicology

Cell materials interactions

Misfolding diseases

Drug delivery and drug potency

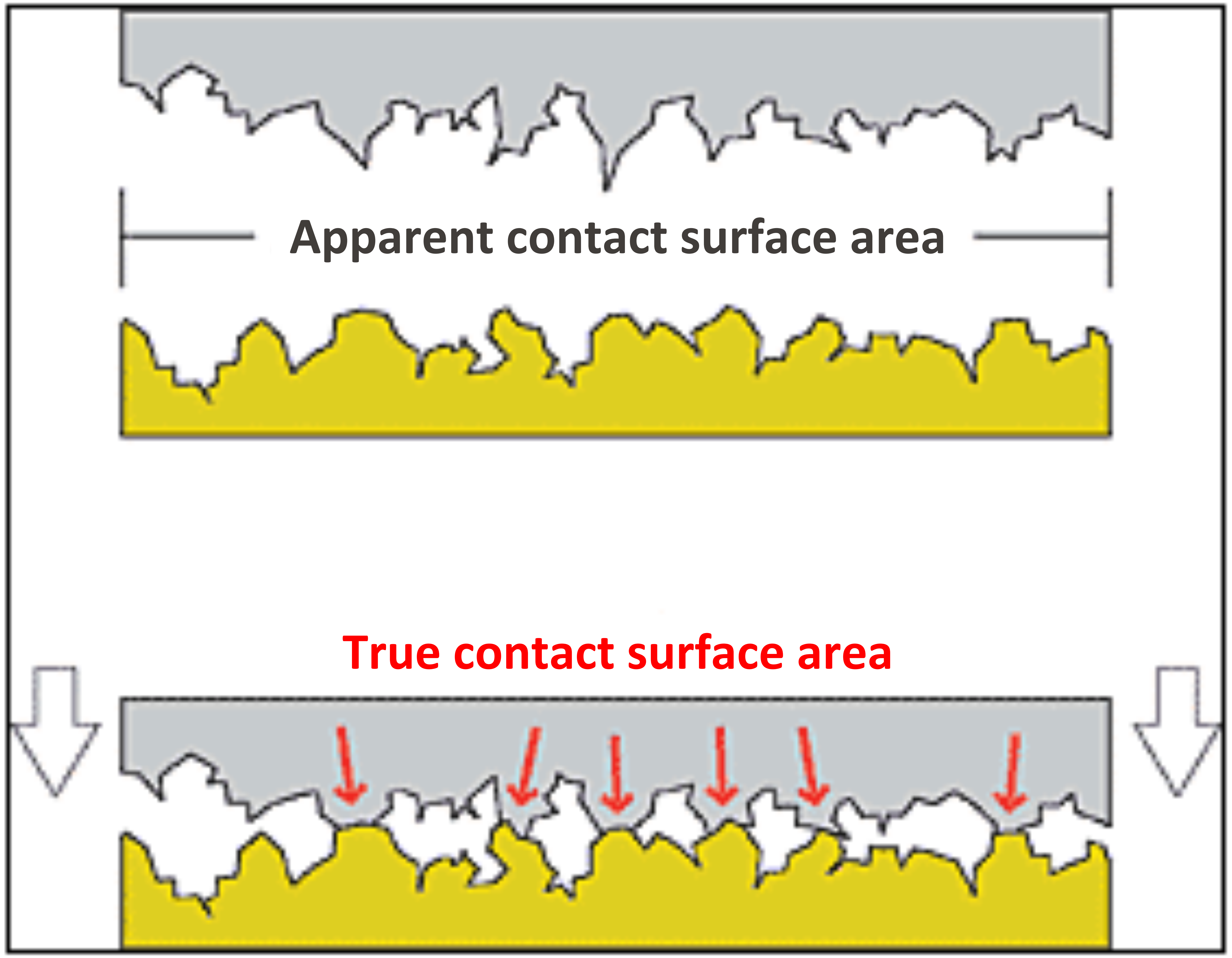
Frutiger, *et al.* | *Chem. Rev.* | 2021

Case Study of Proteins on Surfaces: Synovial Fluid in Joints

Synovial fluid contains lubricin and hyaluronic acid that **adsorb** to cartilage surfaces ➔
Hydrated brush-like layer reduces friction

Renjian *et al.* | Nat. Biomed. Eng. | 2021

Tribology: Rubbing of Surfaces that are Never Perfectly Flat



The normal load is borne by the asperities on each surface coming into contact with each other

Contact areas are small (**asperities**)

↓

Pressures are large

↓

Asperities become elastically and plastically deformed upon contact with each other

↓

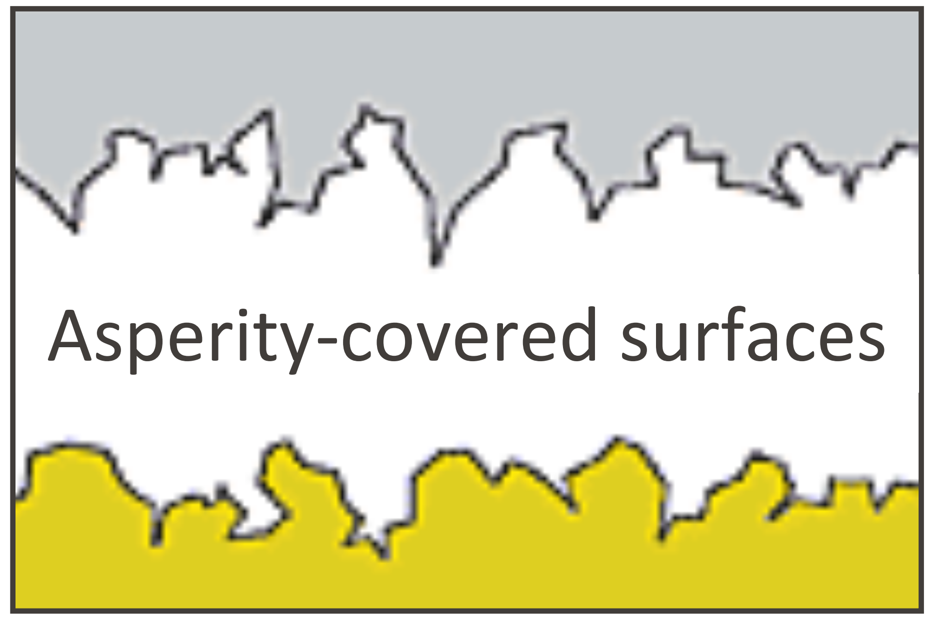
Contact areas increase

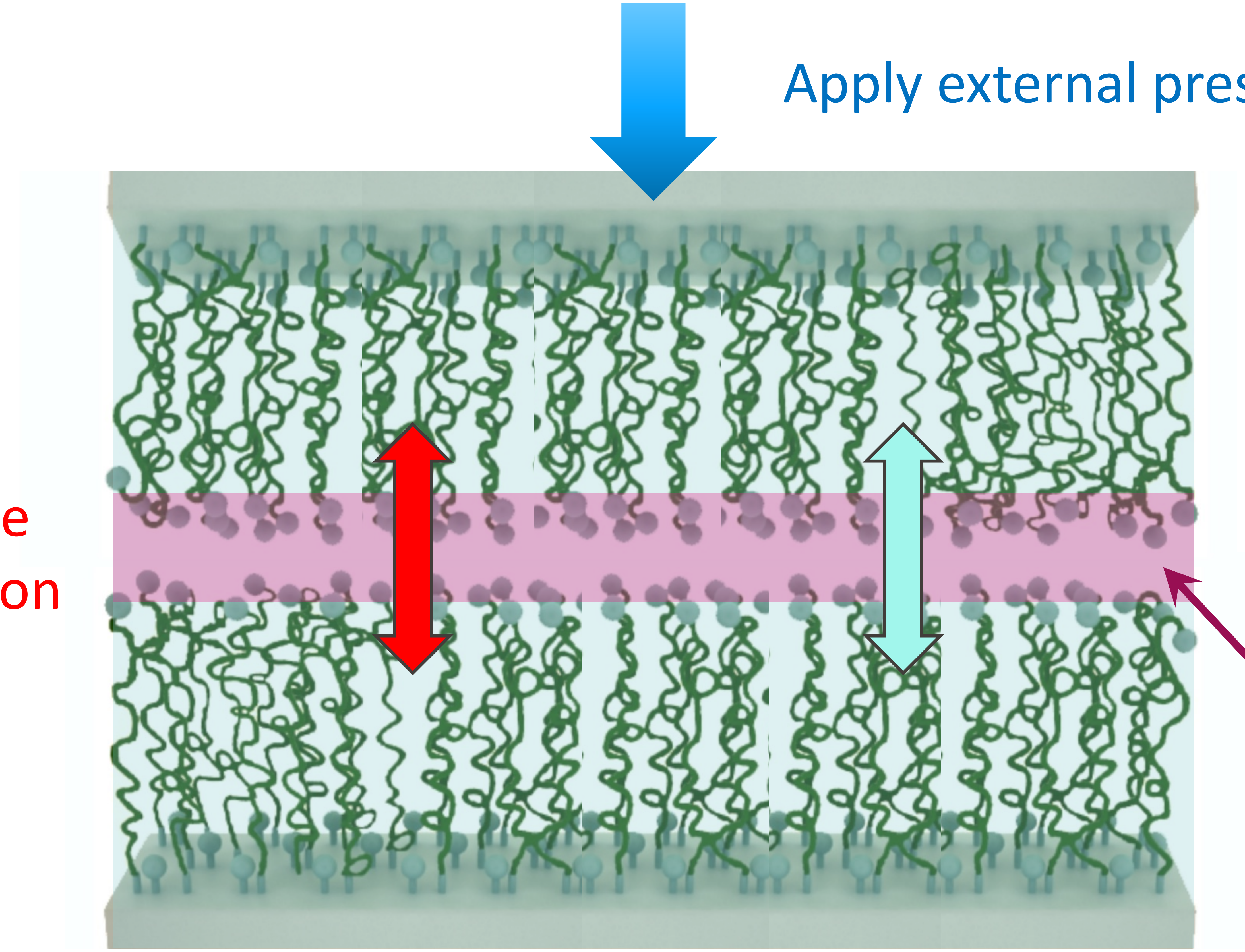
↓

Contact pressure may eventually exceed the elastic limit of the material (wear)

Source: http://images.google.ch

Polymer Brushes Reduce Friction by Acting as Lubricating Layers


Asperity-covered surfaces


Apply external pressure

Osmotic pressure
Resists compression

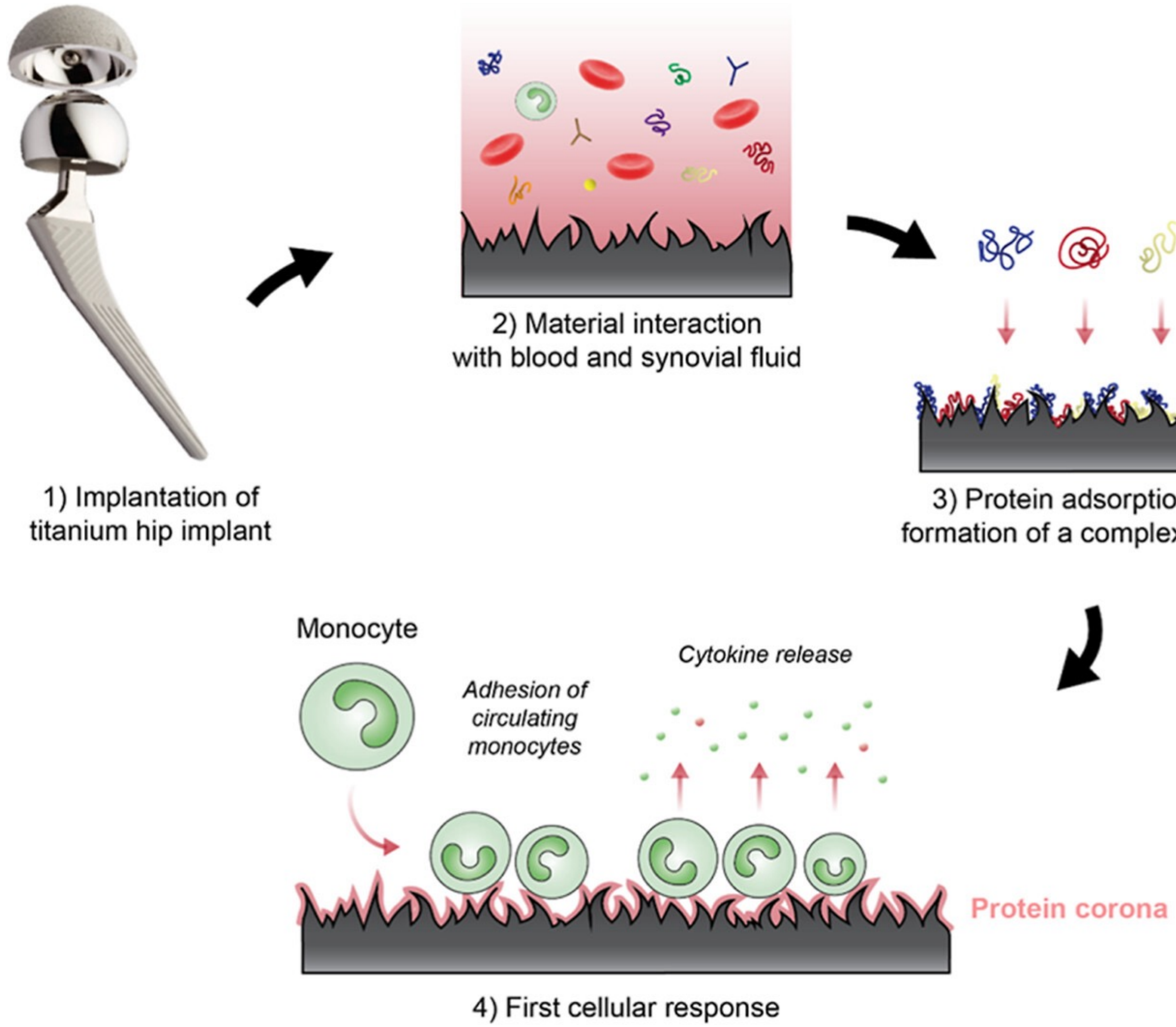
Entropic forces
Resists interpenetration

Hydrated fluid film
enables smooth sliding

Polymer brush-coated surfaces

Polymer brushes lubricate by effectively reducing contact between the hard, asperity-covered surfaces, and replacing it with brush-brush contact

Synovial Proteins Rapidly Adsorb to Implant Materials



1) Implantation of titanium hip implant

2) Material interaction with blood and synovial fluid

3) Protein adsorption and formation of a complex corona

Monocyte

Adhesion of circulating monocytes

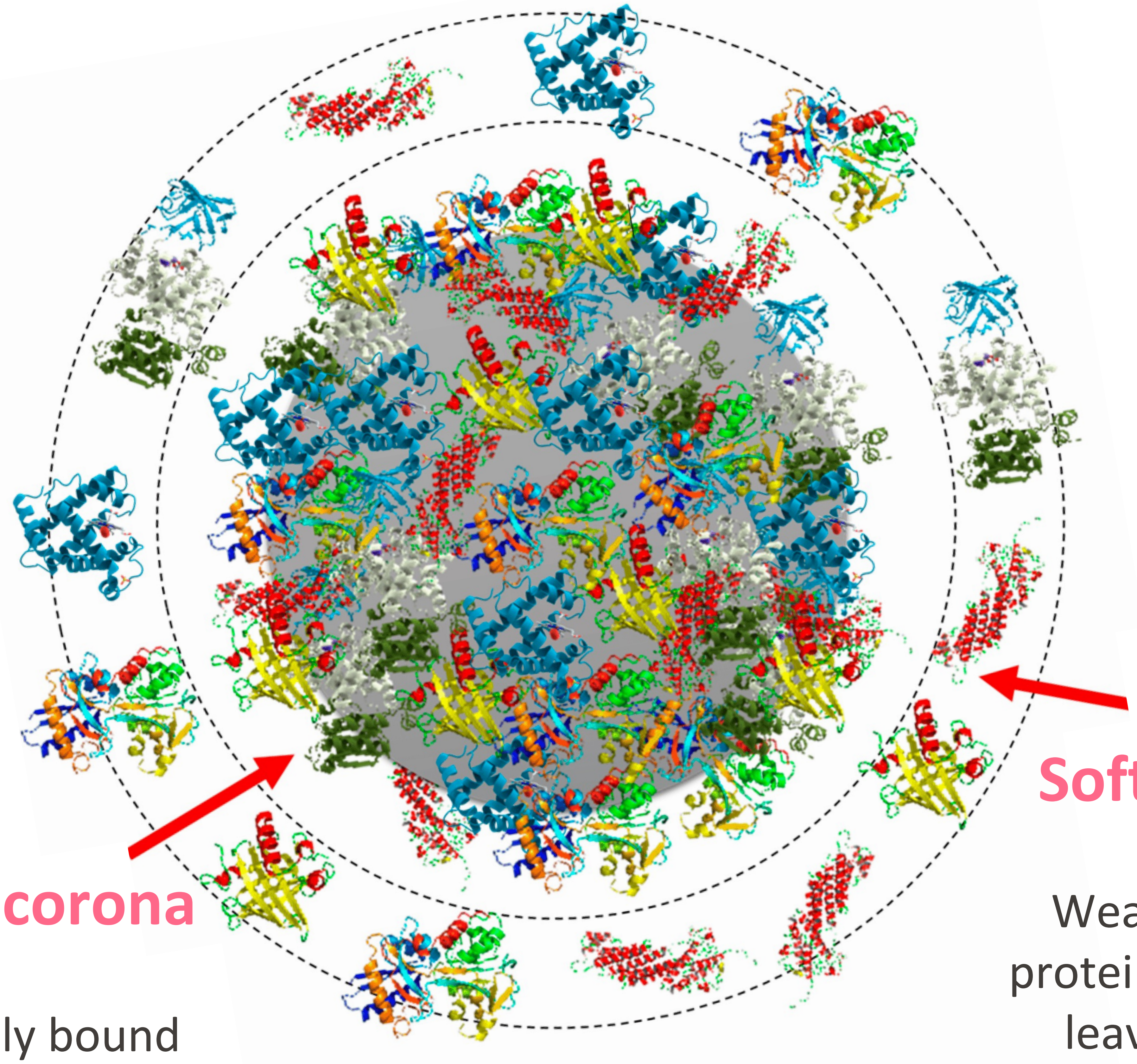
Cytokine release

Protein corona

4) First cellular response

Visalakshan *et al.* | *ACS Appl. Mater. Interf.* | 2022

Case Study of Proteins on Surfaces: Biosensors vs. Biofouling



Hard corona

Strongly bound proteins

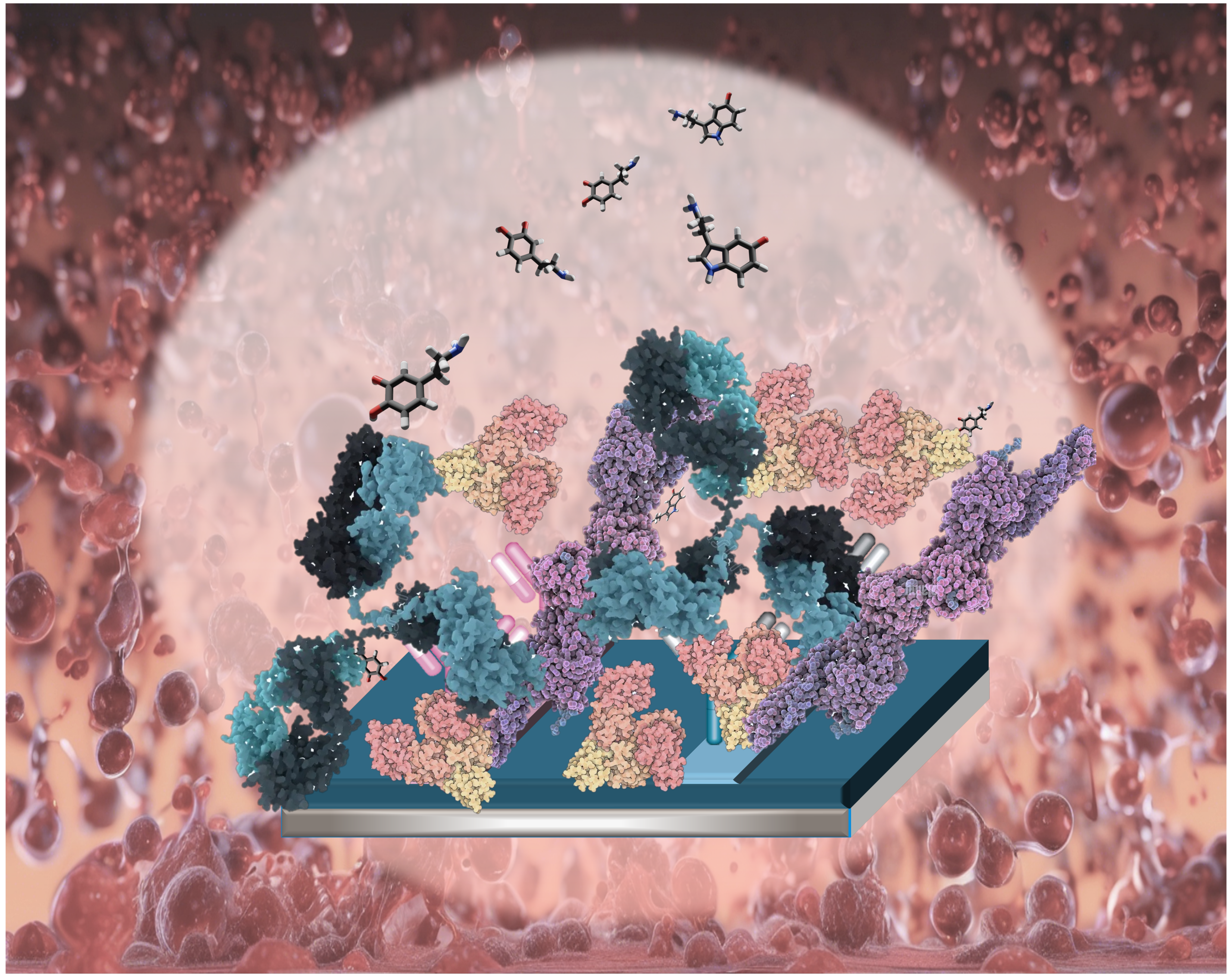
Seconds to form

Soft corona

Weakly bound proteins can easily leave surface

Hours to form

Source: Wikipedia

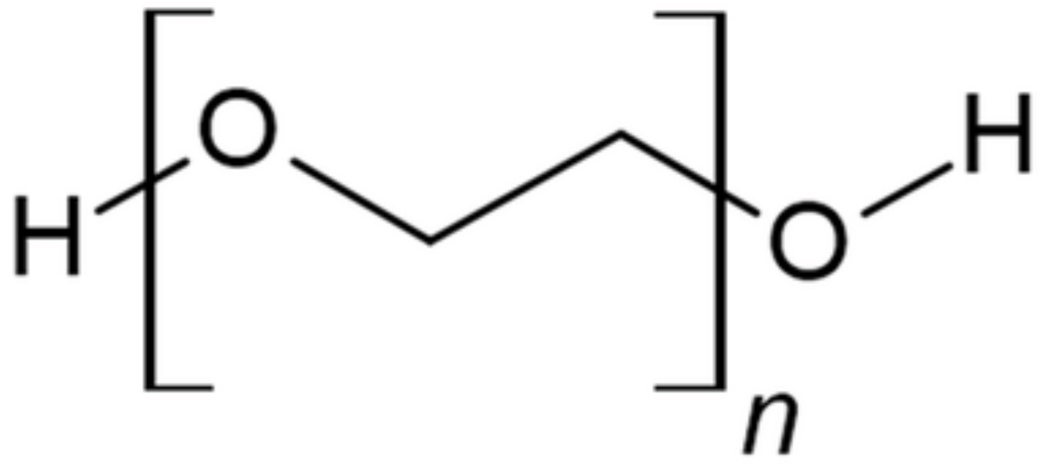


Key Takeaways

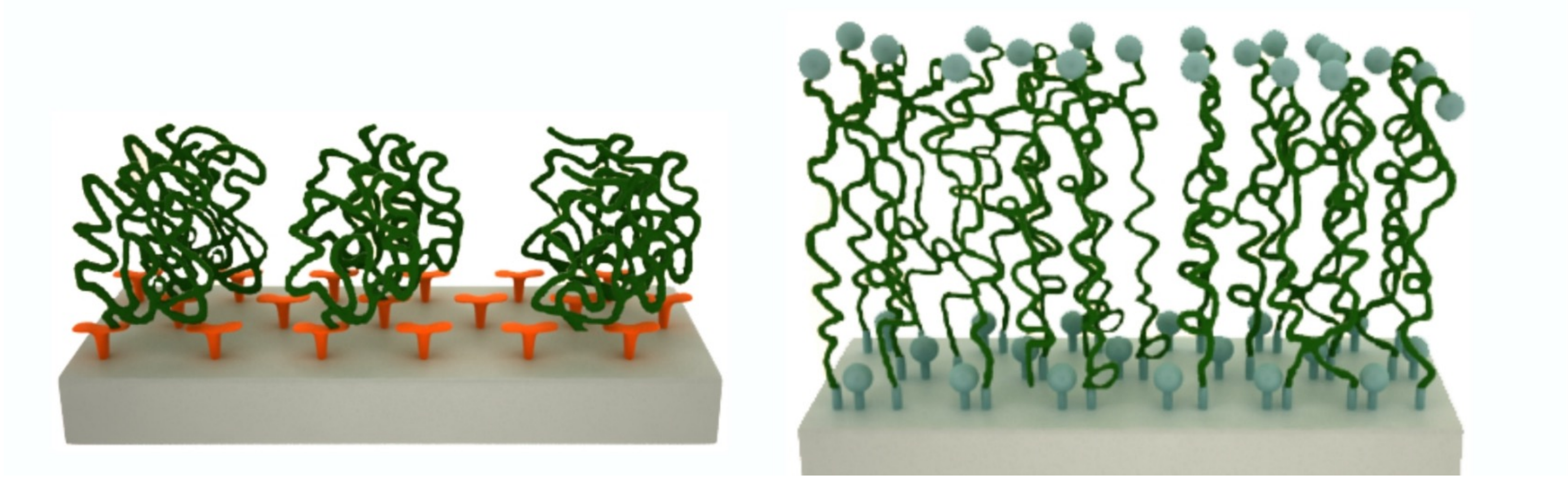
- One of the biggest challenges surfaces face in biological systems is nonspecific binding of proteins
- Proteins stick to surfaces through intermolecular interactions
- Surface properties (hydrophilic/hydrophobic) drive the propensity for proteins to stick to surfaces
- The Vroman effect explains the dynamics of protein adsorption over time
- Challenges and opportunities of protein interactions

How To Control Protein Adsorption Using Polymer Brushes

Certain polymer brushes have been shown to be highly effective in preventing protein adsorption



Poly(ethylene) glycol (PEG)



Neutral brushes

Highly hydrated and flexible

Antifouling benchmark

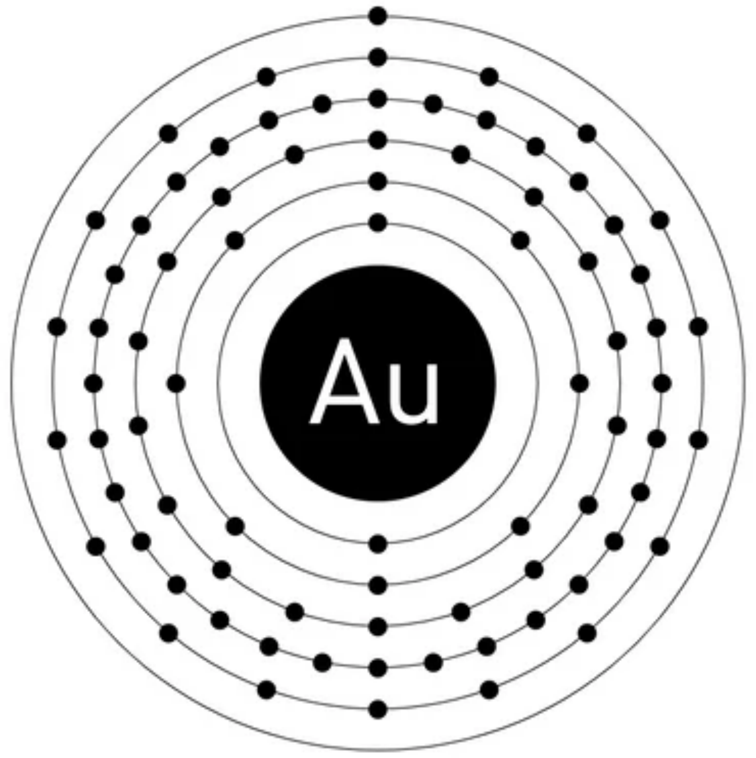
Polymer layer prevent proteins reaching the solid surface beneath

- non-charged (neglible electrostatic interactions with proteins)
- hydrophilic (no hydrophobic interactions with proteins)
- free-energy (penetration of a protein into the brush is unfavorable)

Visalakshan *et al.* | *ACS Appl. Mater. Interf.* | 2022

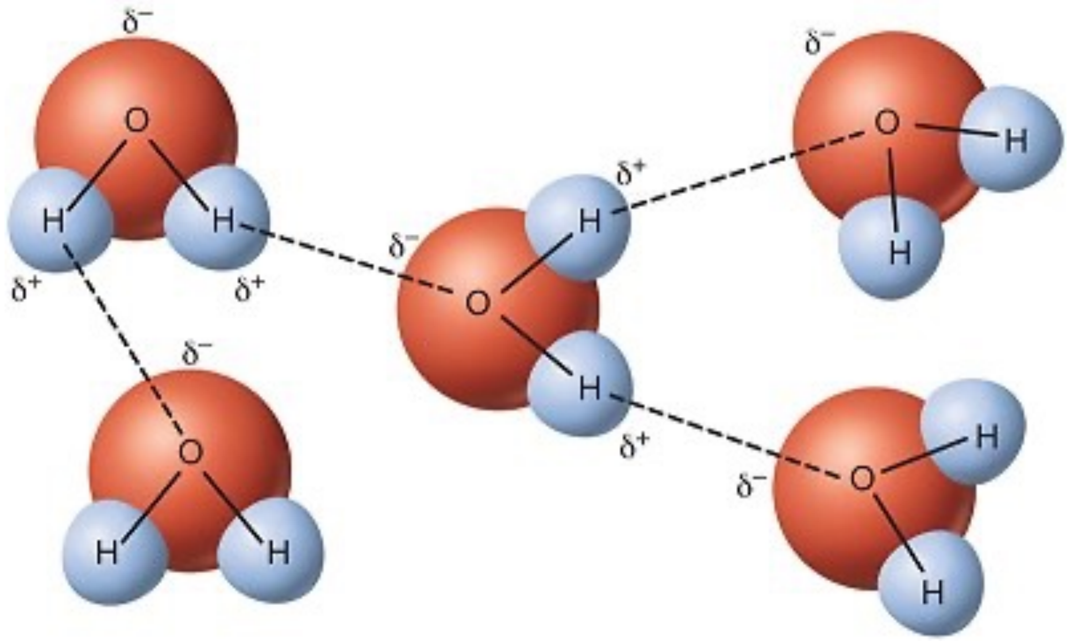
What is a Polymer?

Metal



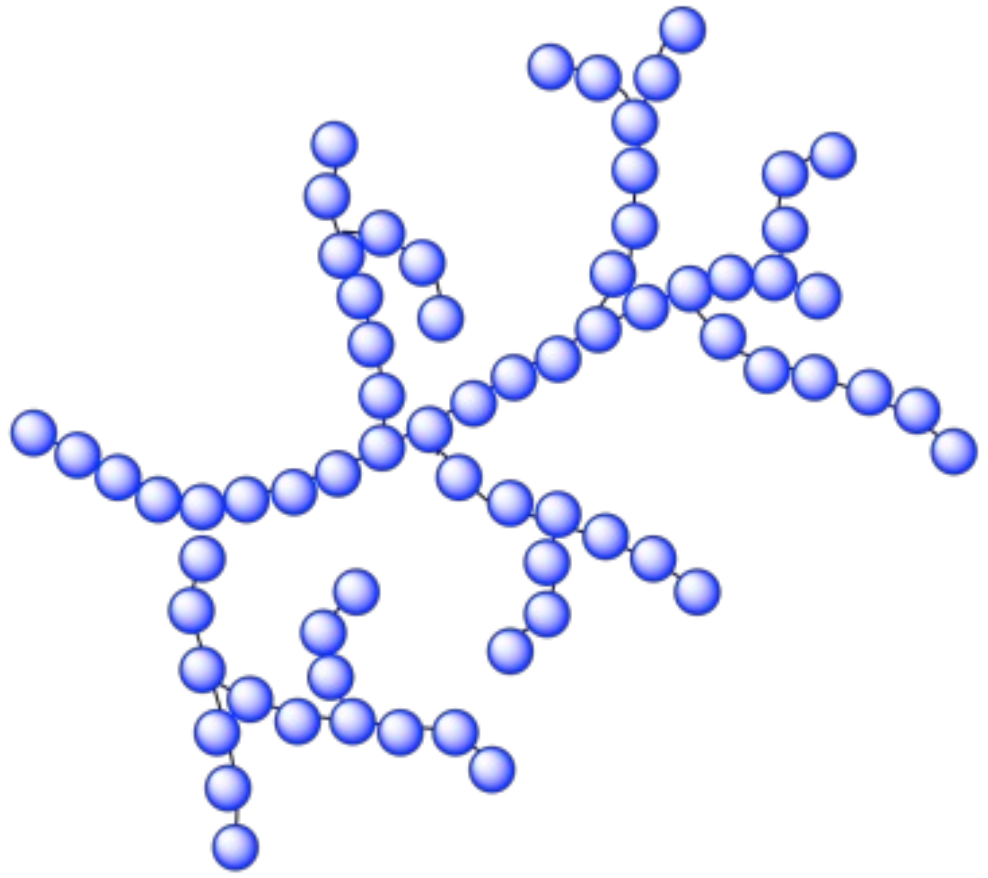
Atoms

Water



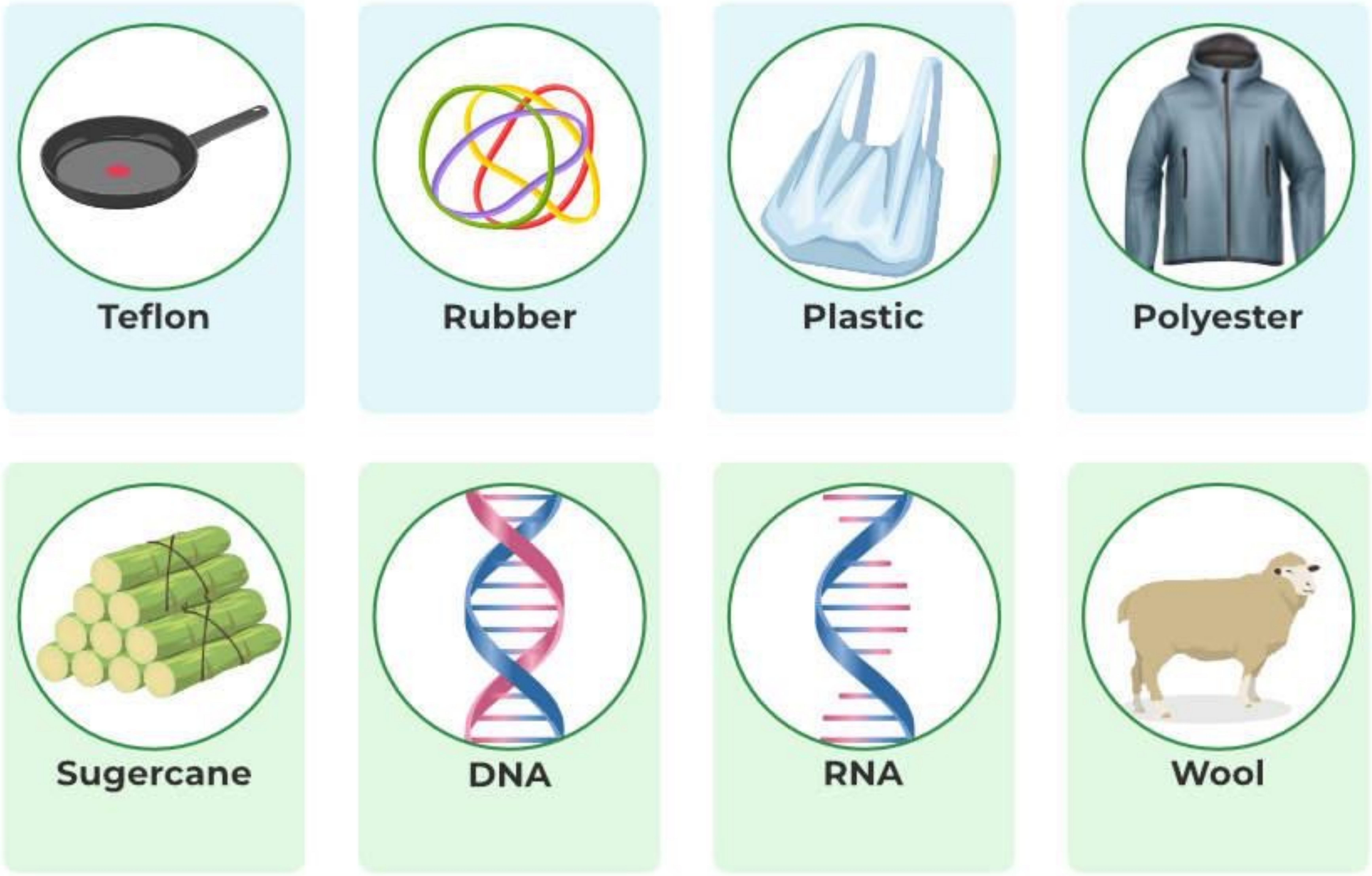
Molecules

Polymer

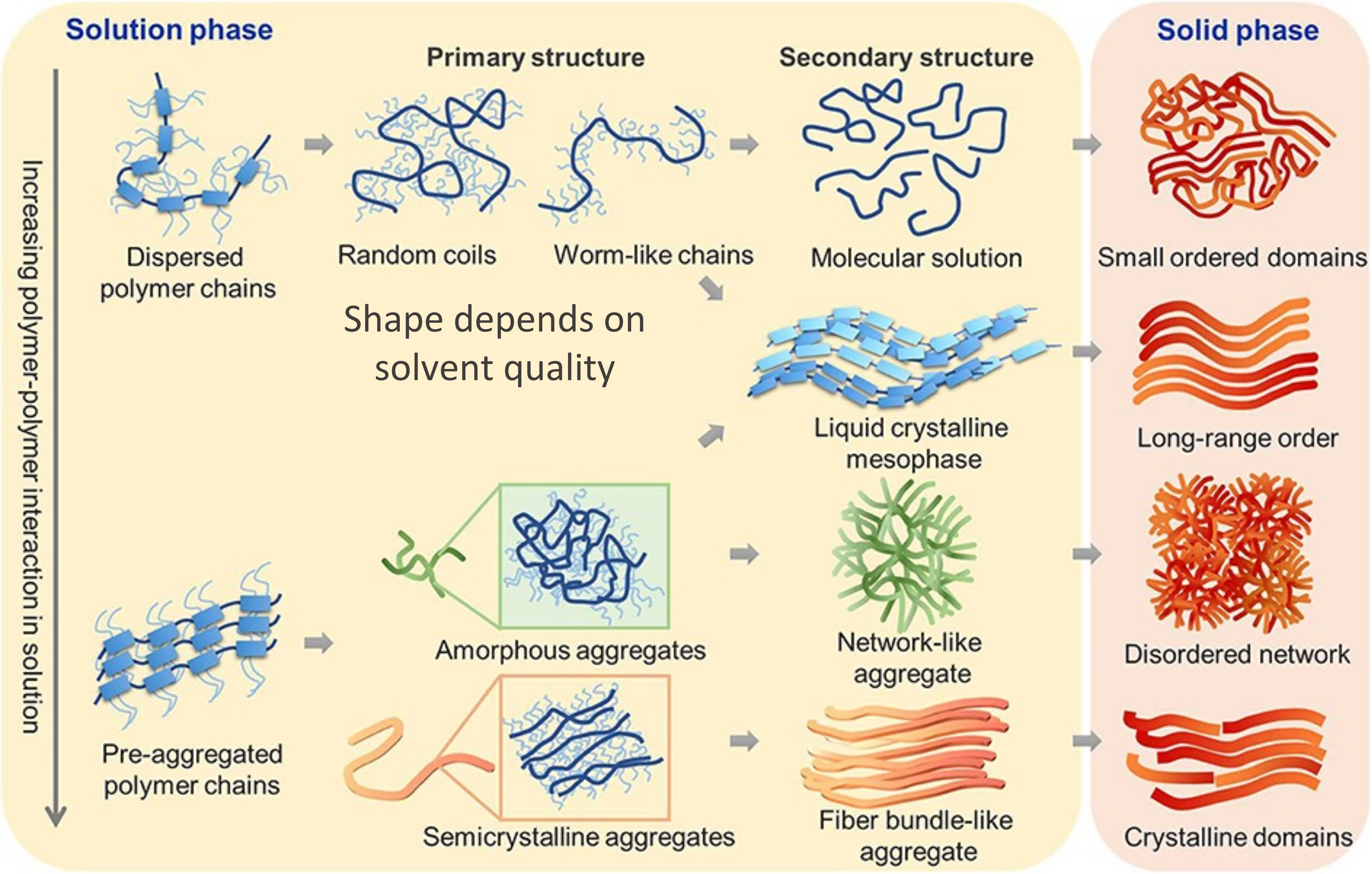


Chains of molecules

Polymers are All Around Us



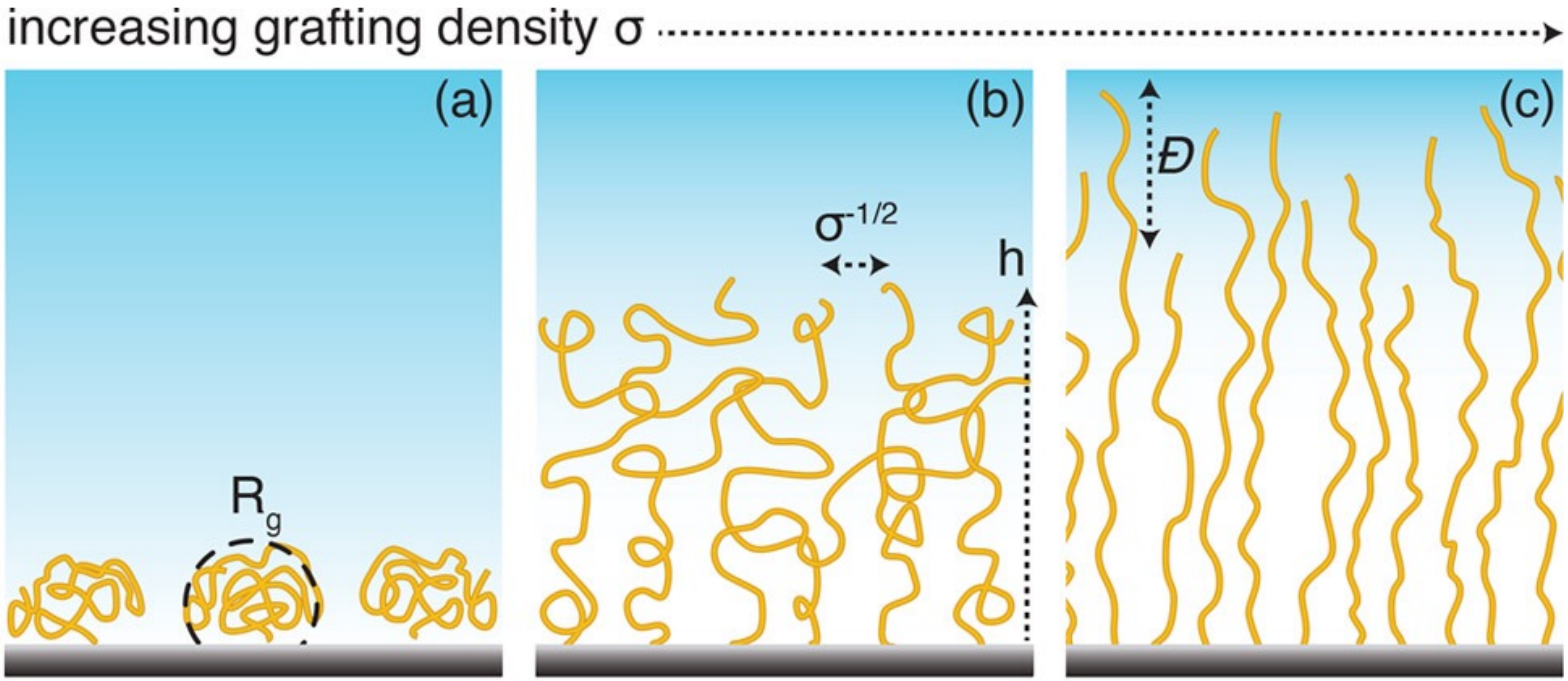
Polymer Chain Conformation from Solution to Solid Phases



Shape depends on solvent quality

Xu et al. | Front. Chem.| 2020

Polymers on Surfaces – Grafting Density Influences Structure



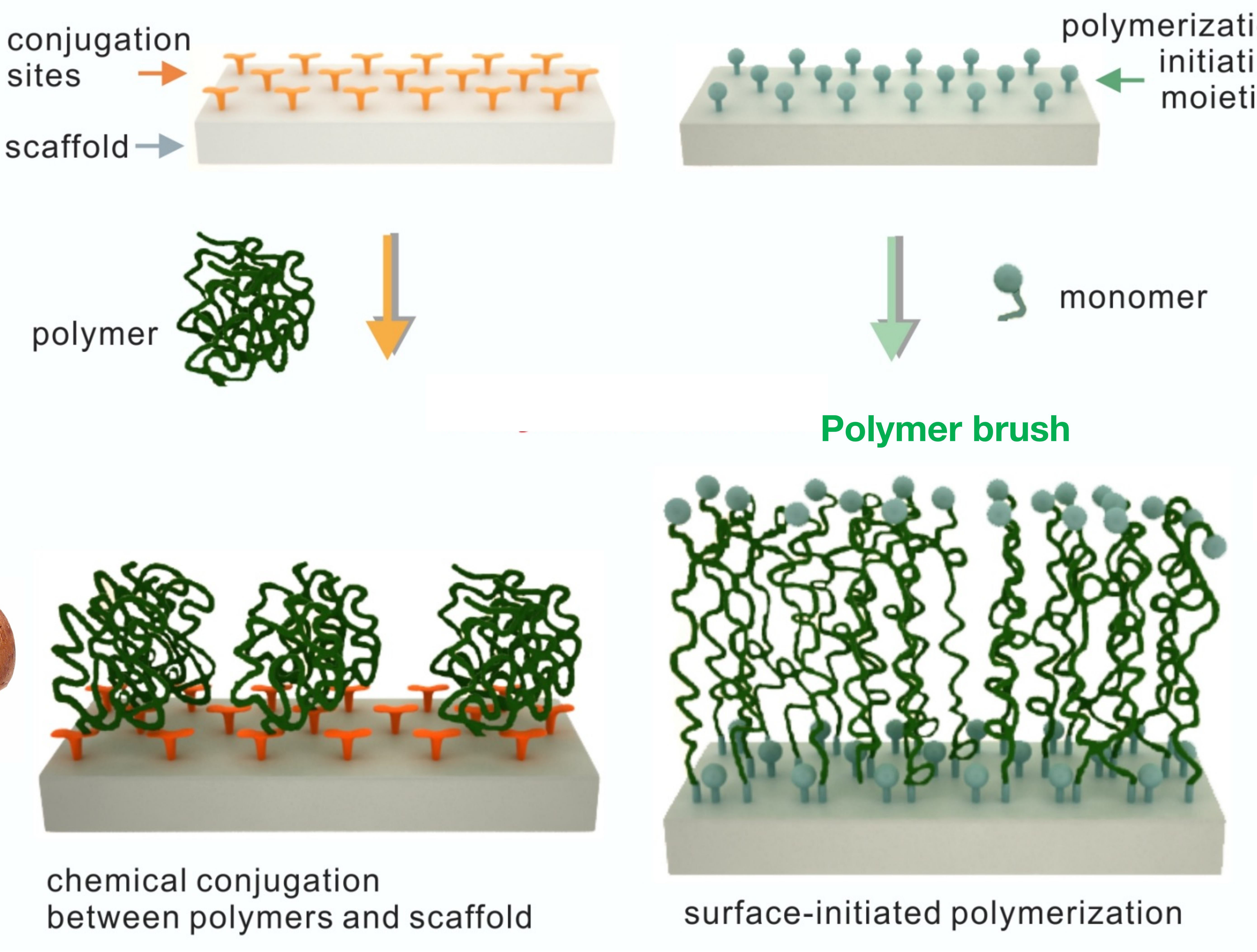
Low density:
chains behave independently

Middle density:
Overlapping separated chains

High density:
crowding ➔ chain extension

Conrad & Robertson | JACS Au | 2023

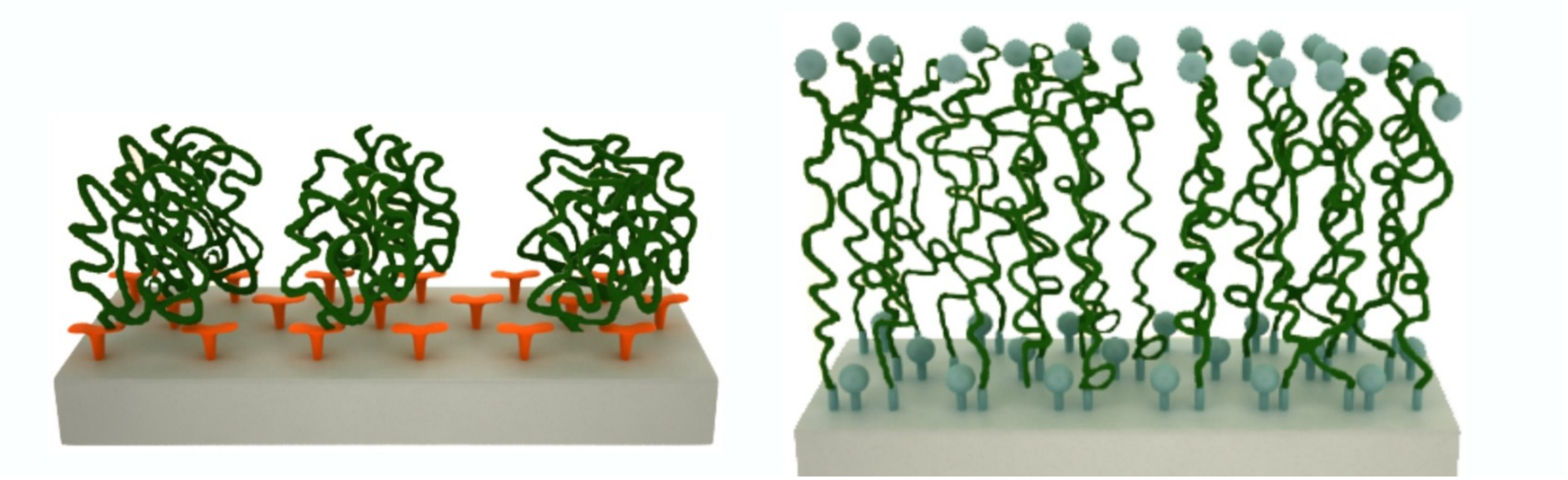
Polymers on Surfaces – Grafting Density Influences Structure



Polymer brush

Kim & Jung | *Phys. BMB Rep.* | 2016

Polymers on Surfaces – Grafting Density Influences Behavior

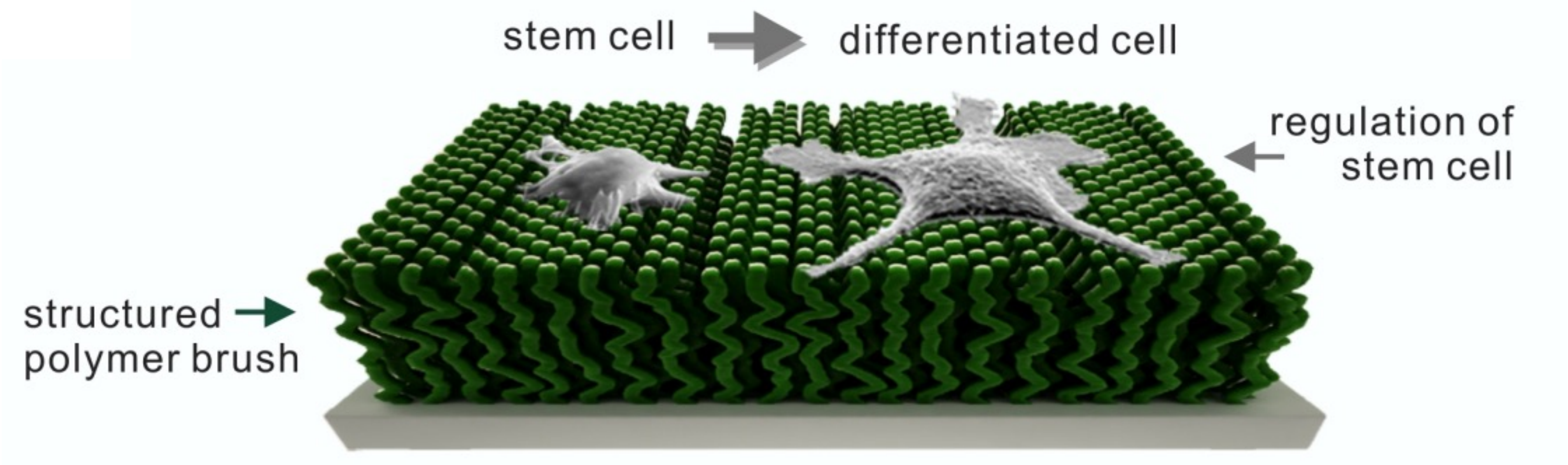


Polymer brush

$$D < 2R_g$$

Distance between adjacent grafting points

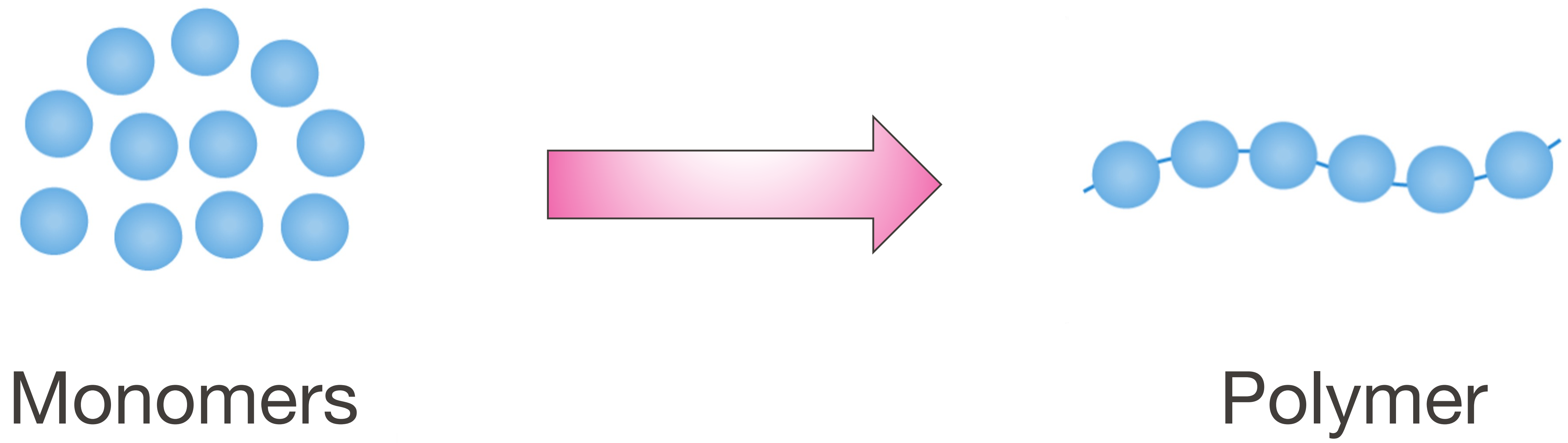
Radius of gyration of polymer



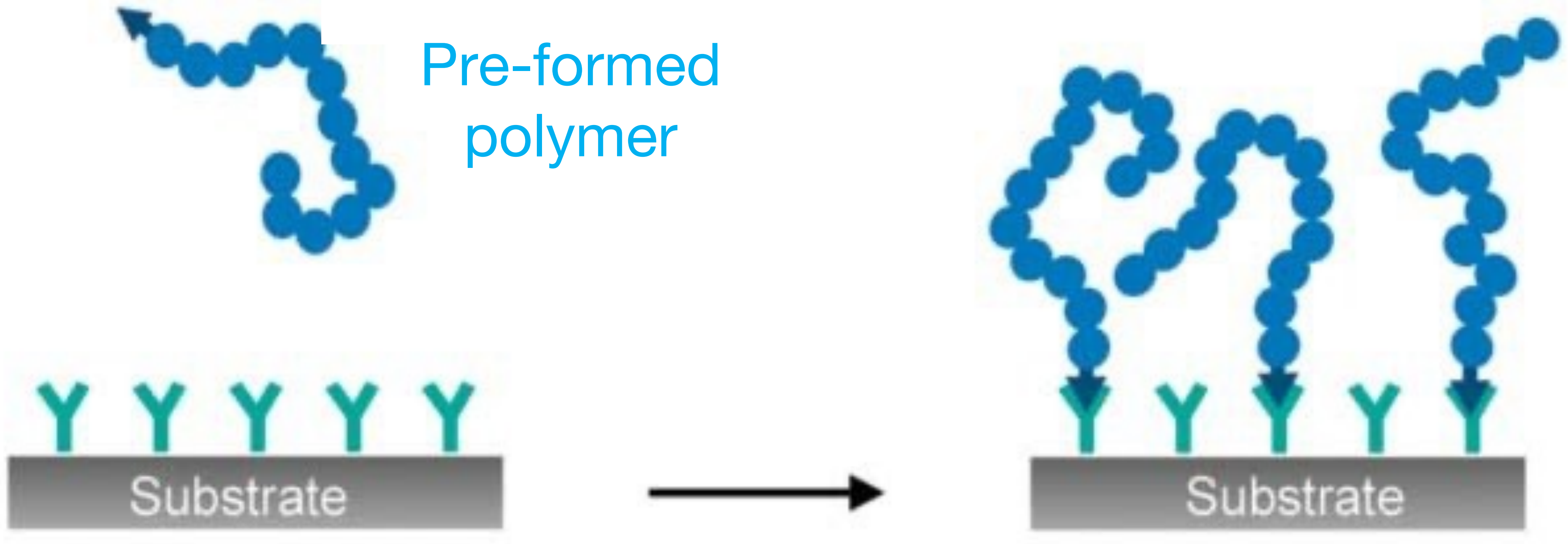
Stem cell differentiation

Kim & Jung | *Phys. BMB Rep.*| 2016

Surface Assembly of Polymers on Surfaces



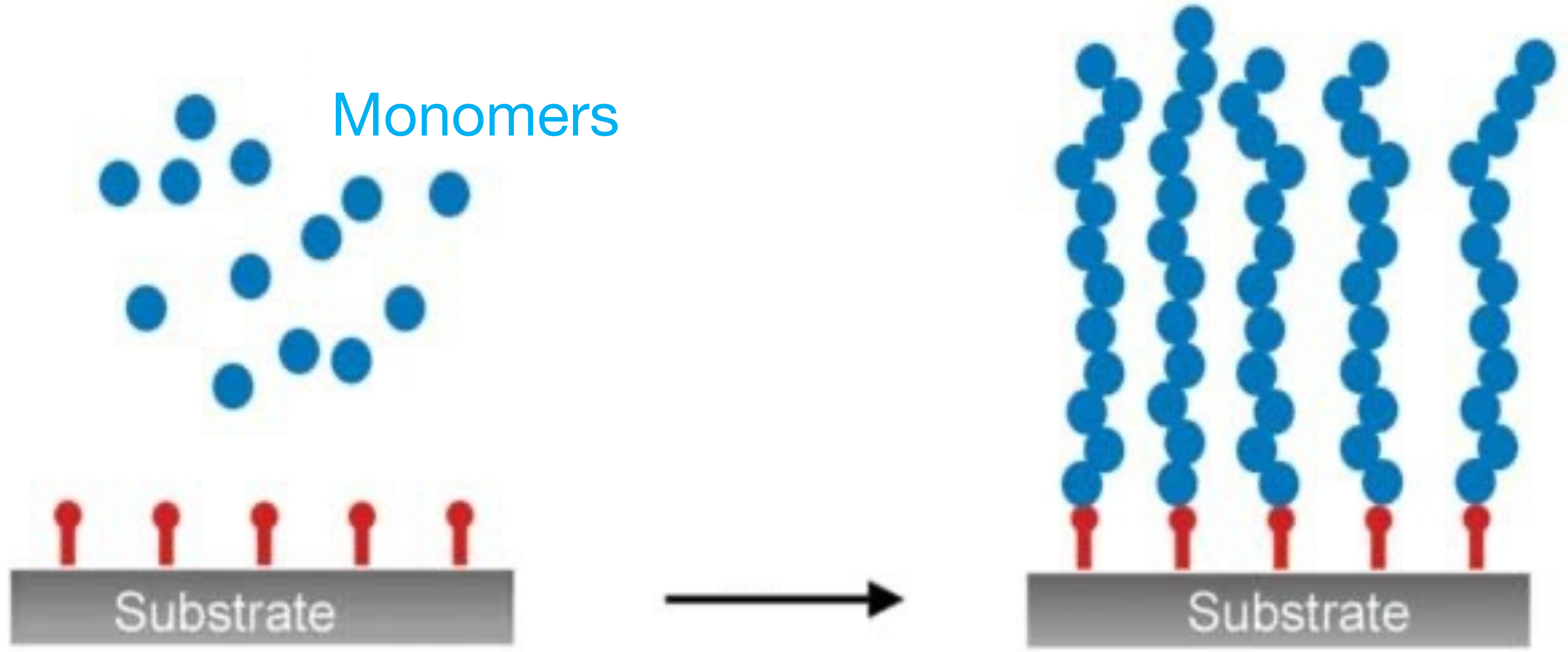
Top-down:
Grafting-to approach



Control over polymer properties

Limited surface density steric hindrance

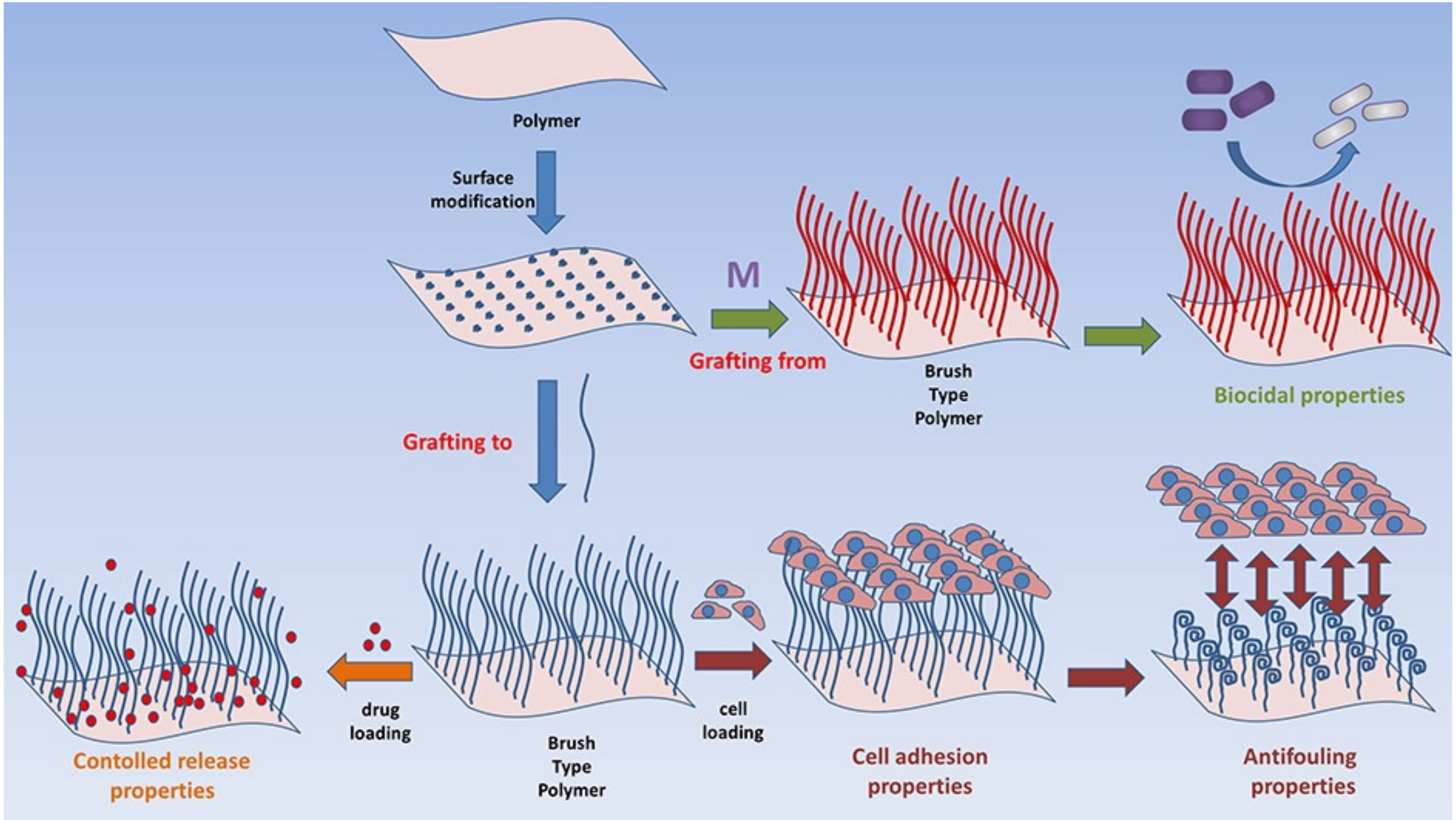
Bottom-up:
Grafting-from approach



High grafting density and stronger bonding

Less control over polymer properties

Different Grafting Routes for Different Applications



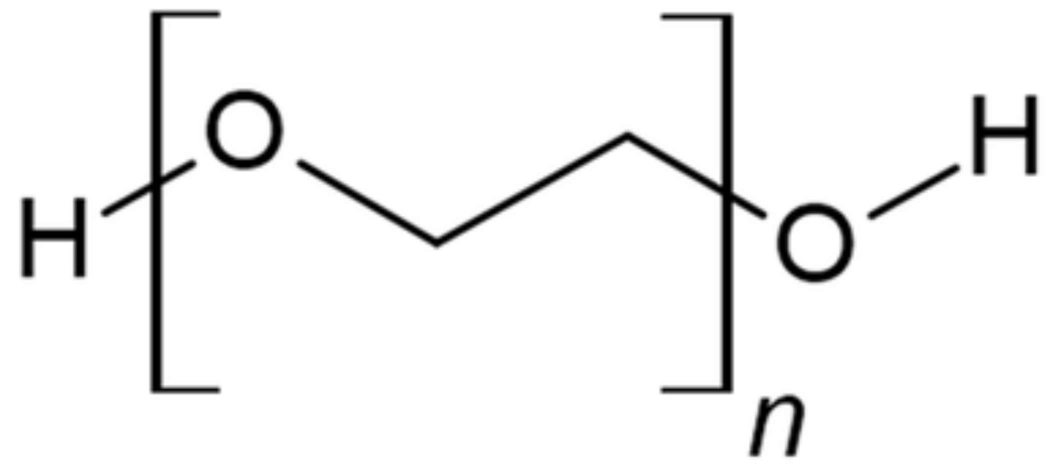
Acari et al. | Adv. Colloid Interf. Sci.| 2022

Comparing Polymer Brushes to SAMs

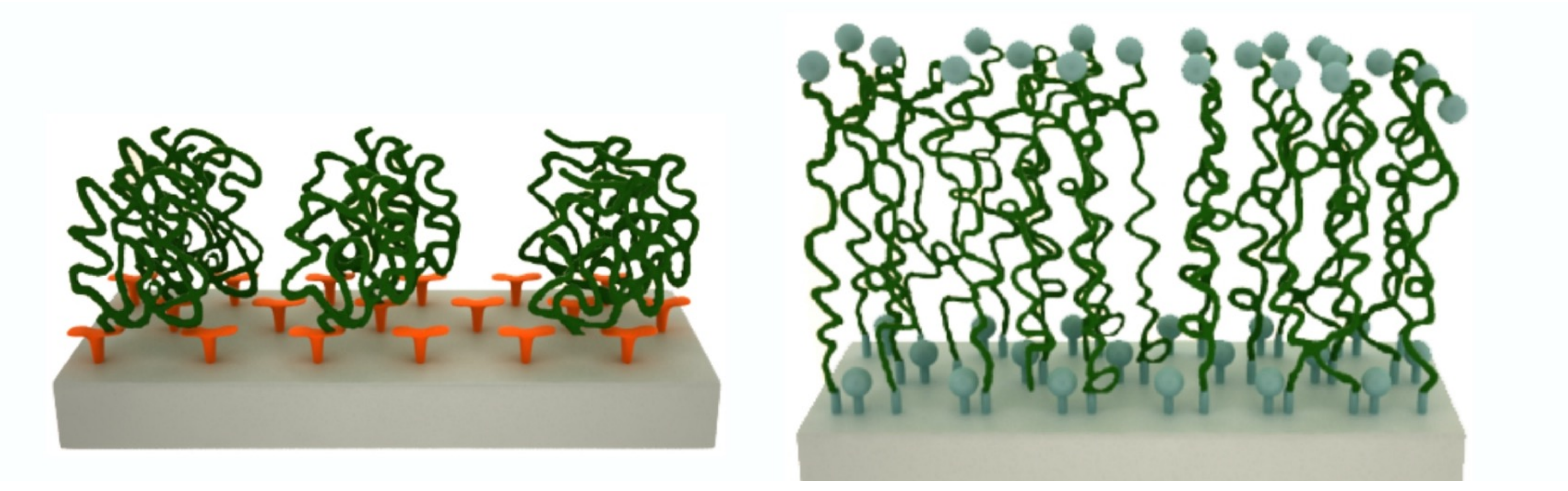
	Grafting-to Polymer Brush	**Grafting-from Polymer Brush**	**SAM**
Fabrication	Attach pre-made polymers	Grow polymers from surface	Molecules self-assemble
Density	Low	High	High
Stability	Good in biological media	Very good in biological media	Lower in biological media
Defects	More gaps	Fewer (self-repair)	Can have pinholes
Thickness	Medium	Thick, tunable	Very thin (1 layer)

Kim & Jung, *Phys. BMB Rep.,49, 12,* **2016**

Different Types of Polymer Brushes: Neutral



Poly(ethylene) glycol (PEG)

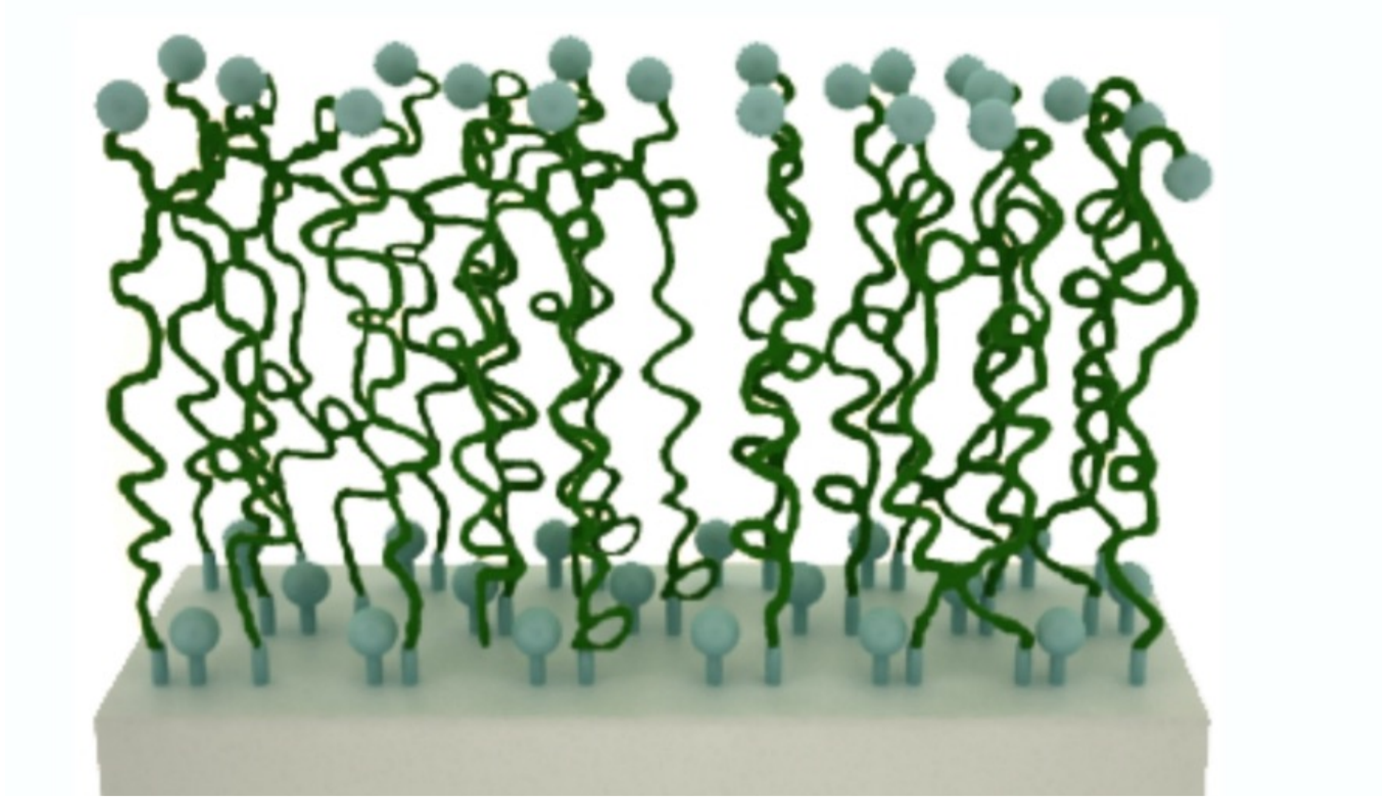


Neutral brushes

Highly hydrated and flexible

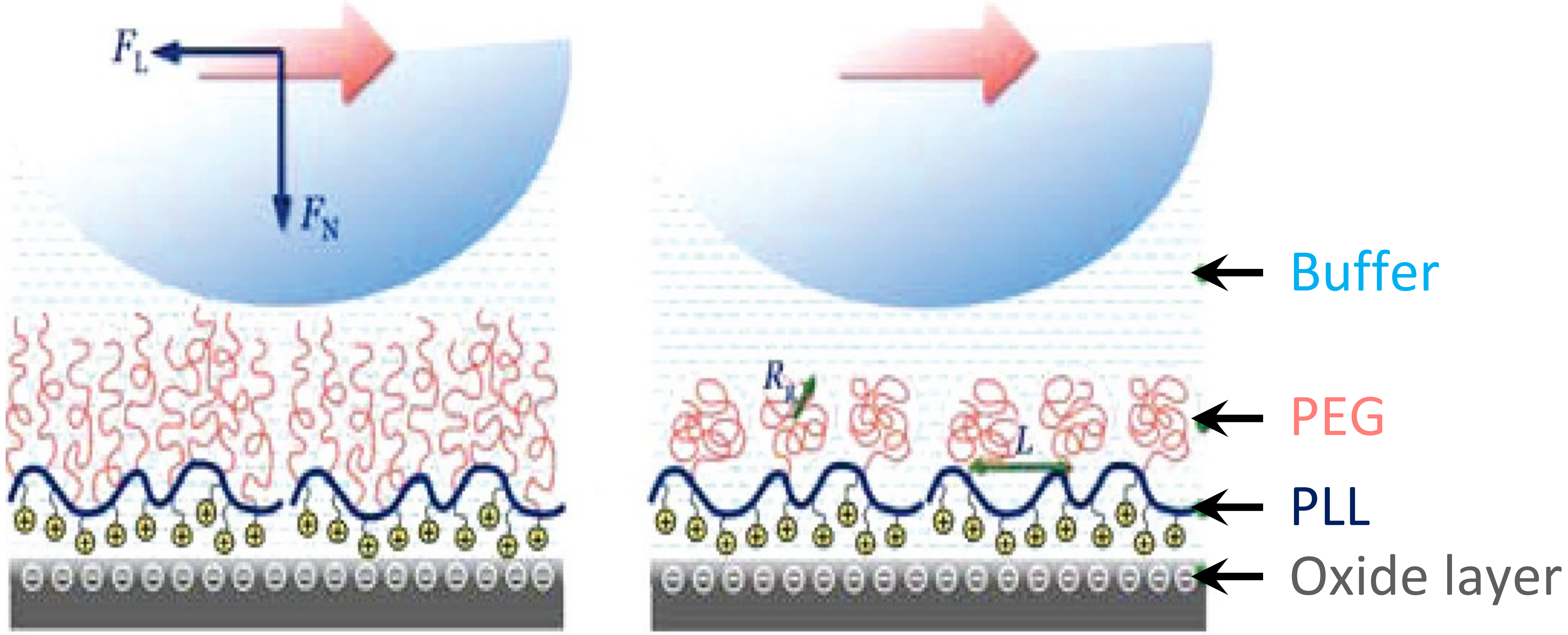
Antifouling benchmark

1. Dense PEG layer = steric barrier



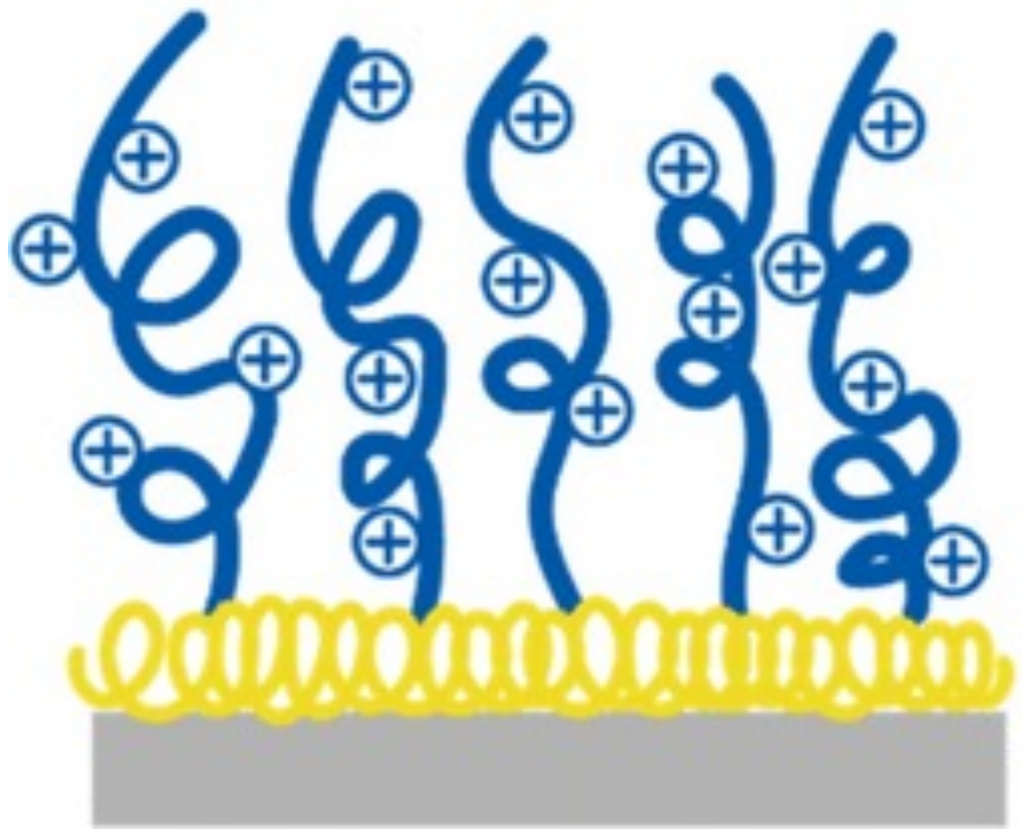
Durmaz et al. | ACS Appl. Polymer Mater.| 2021

2. Hydration and dynamic flexibility of PEG brush

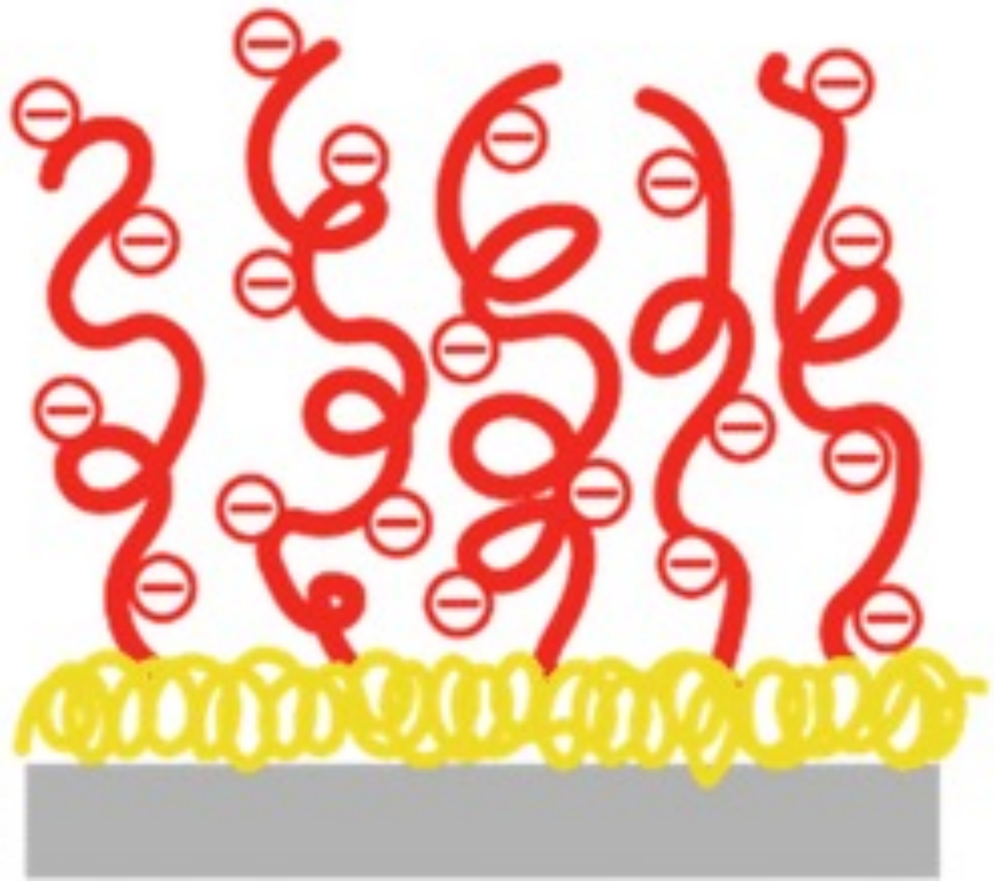


Wei et al. | *ACS. Appl. Mater. Interf.* | 2009

Different Types of Polymer Brushes: Charged



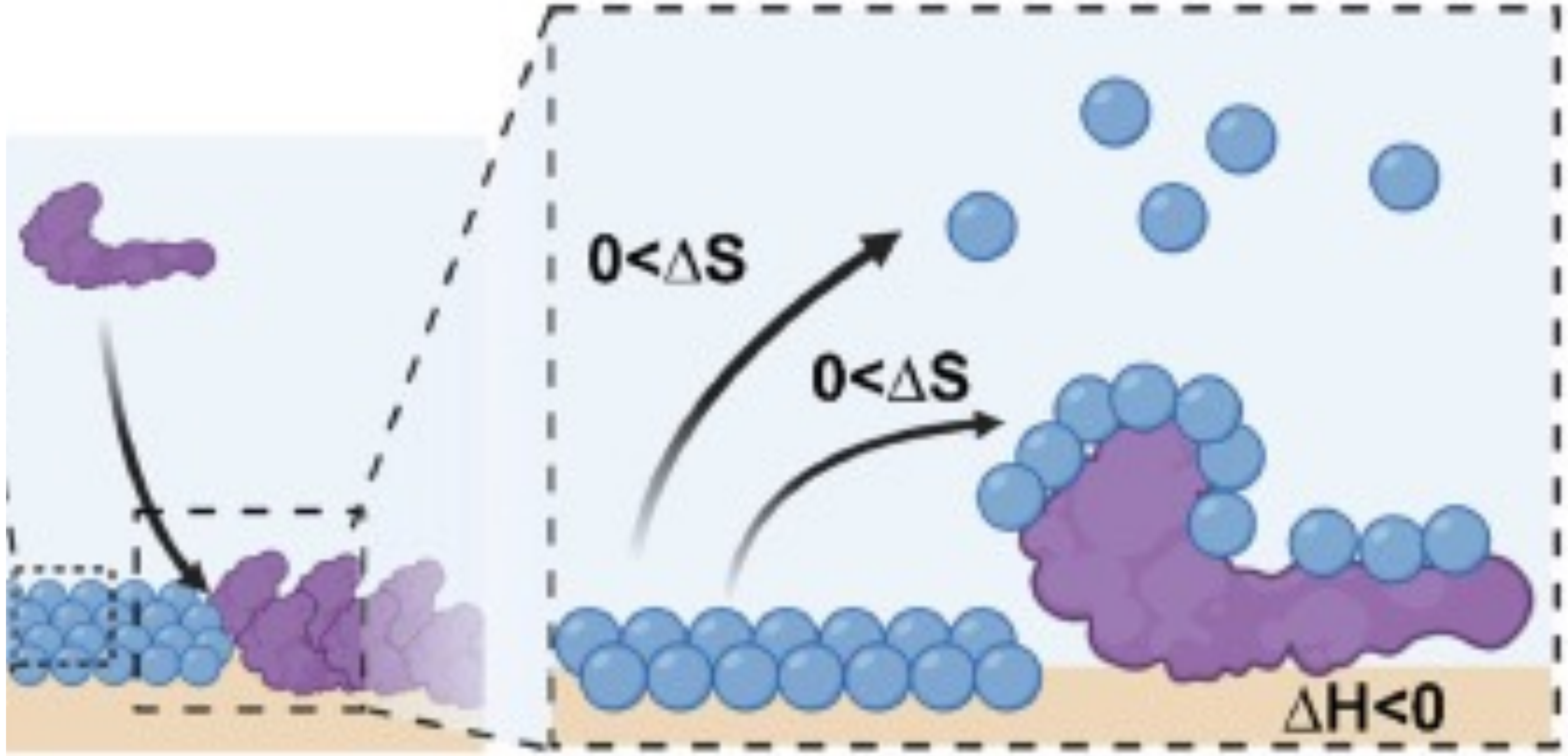
Cationic polymers



Anionic polymers

Charged polymers
promote electrostatic
adhesion

At physiological pH, majority of proteins are negatively charged

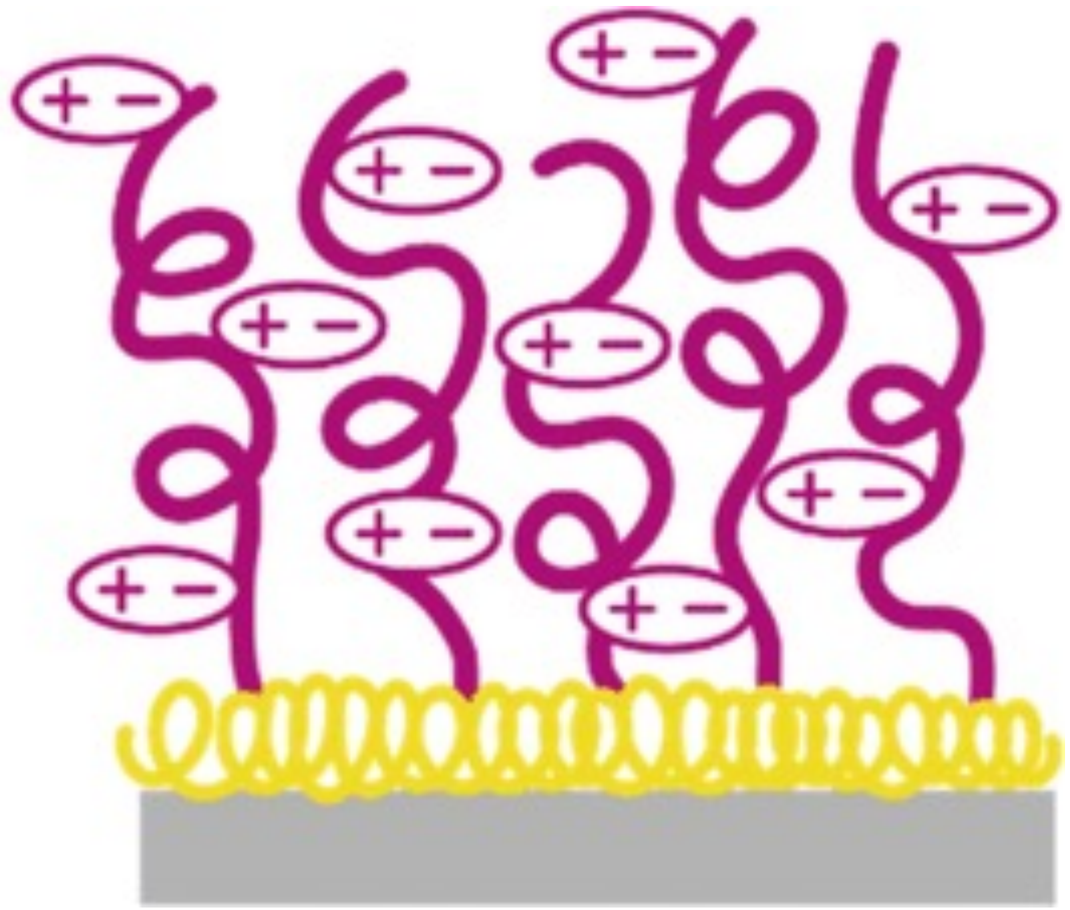


Ordered water release leads to entropy increase

Protein forms electrostatic interactions with the surface

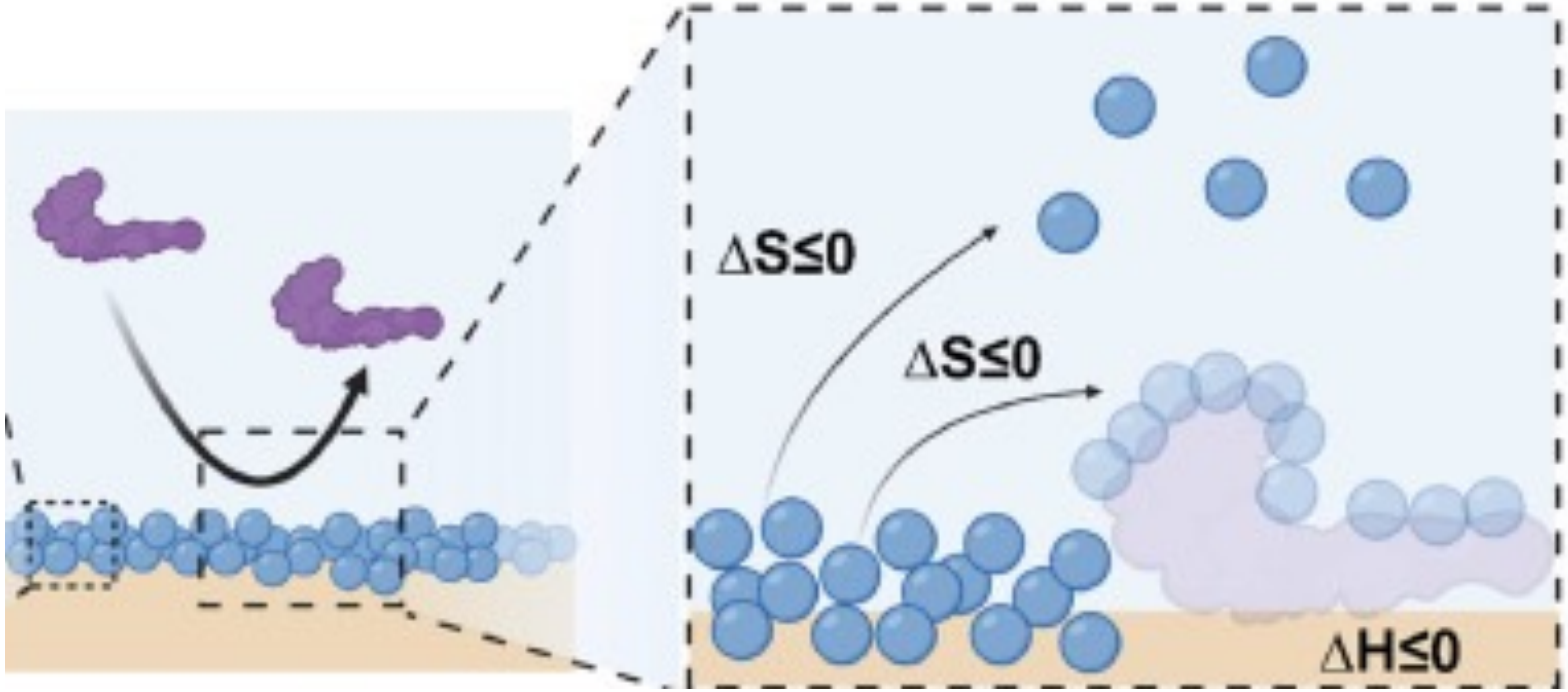
Durmaz et al. | ACS Appl. Polymer Mater.| 2021

Different Types of Polymer Brushes: Zwitterionic Polymers



Zwitterionic polymers

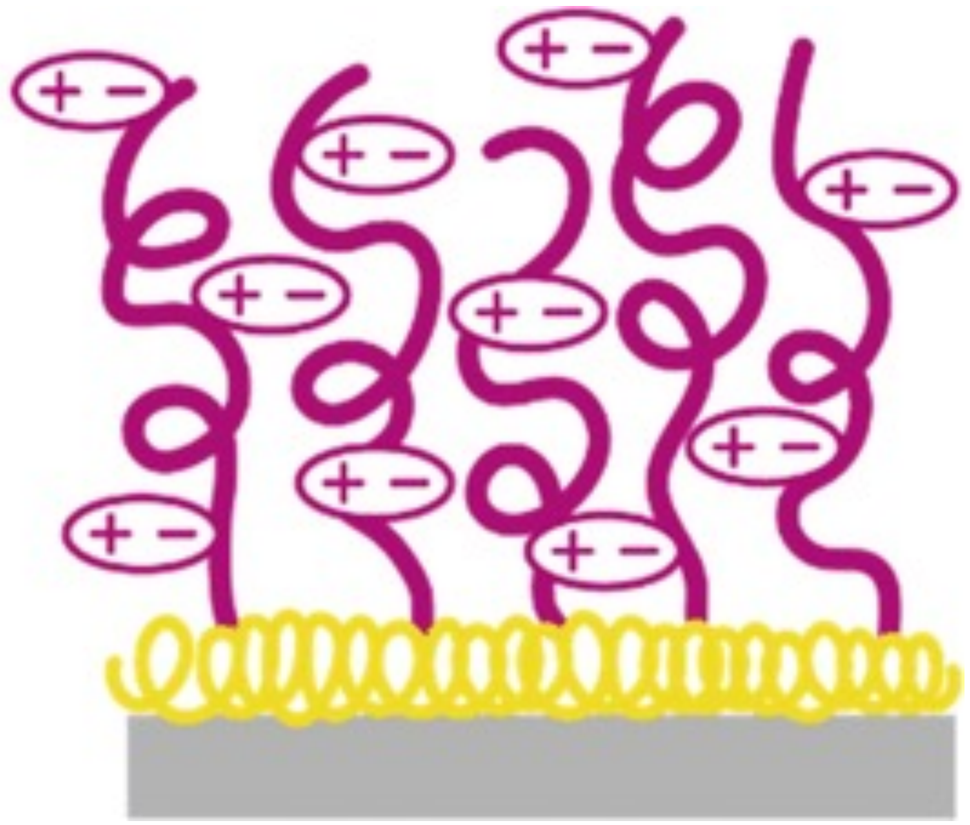
Stronger hydration layer than PEG – better at resisting protein adsorption



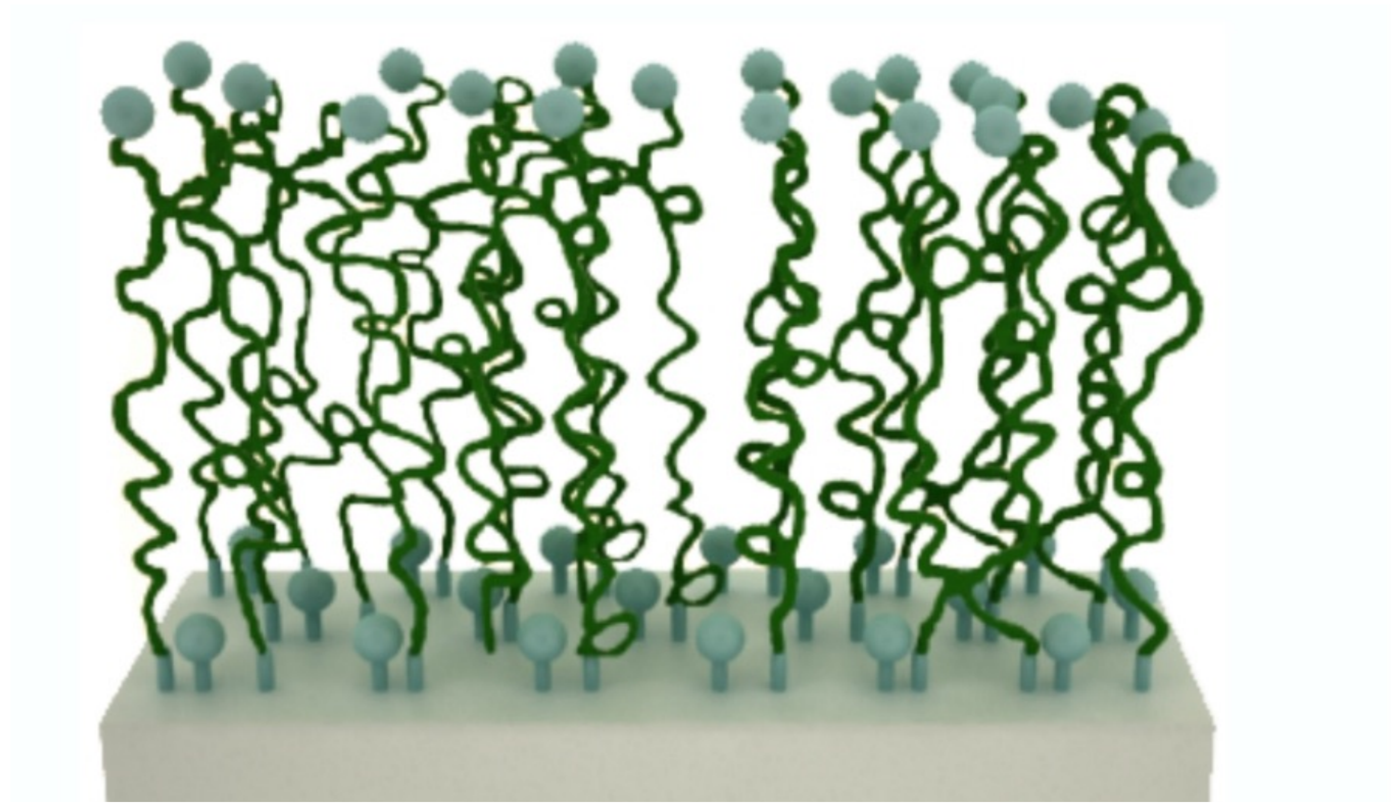
Zwitterionic surfaces resist protein adsorption because the water near the surface is already stable, so removing it costs entropy

Durmaz et al. | ACS Appl. Polymer Mater.| 2021

Different Types of Polymer Brushes: Zwitterionic Polymers



Zwitterionic polymers

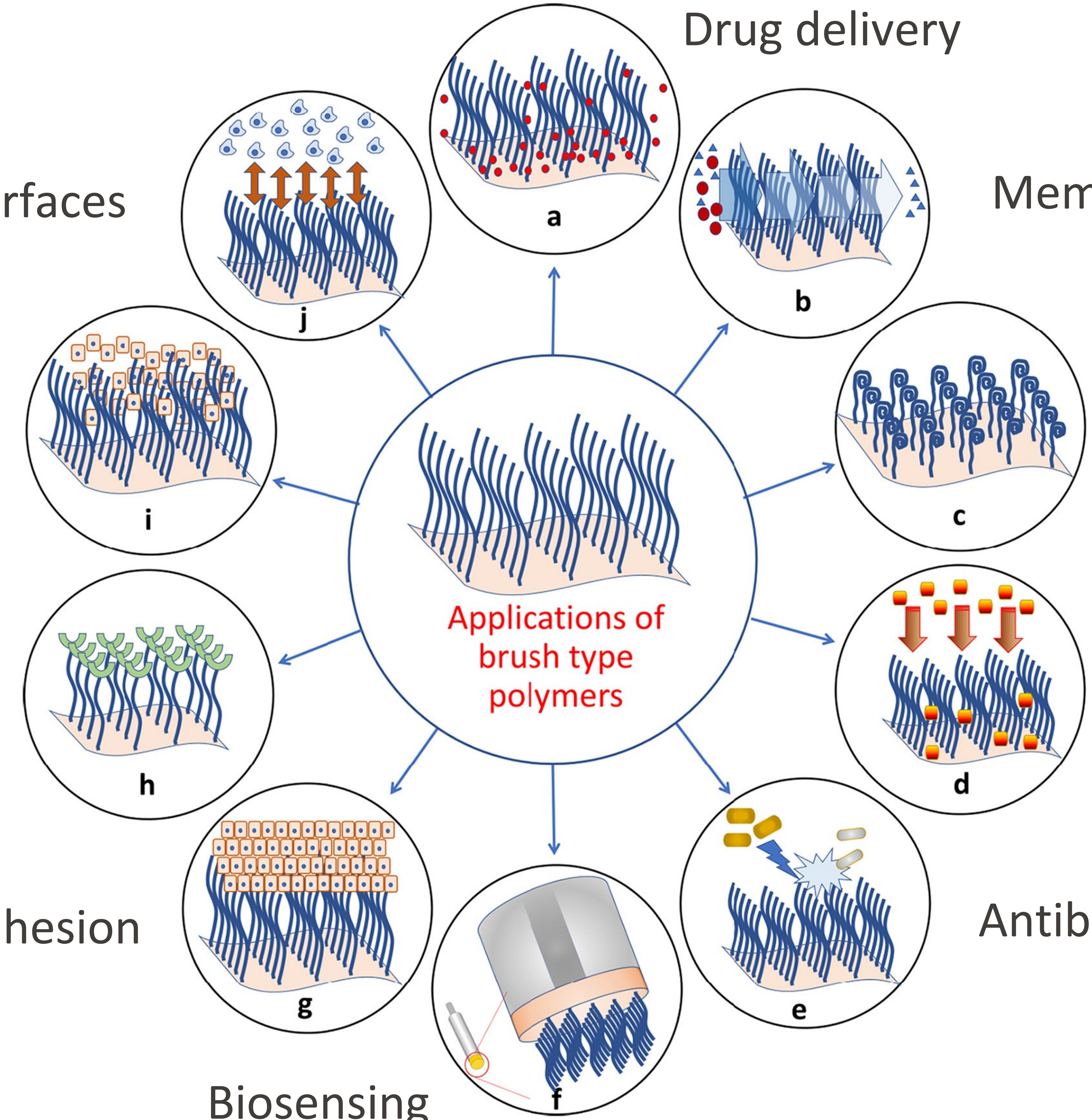


Neutral PEG

Type of interaction	Ion–dipole (electrostatic)	Hydrogen bonding (dipole–dipole)
Hydration layer strength	Strong, stable	Moderate, dynamic
Water exchange rate	Slow (tight binding)	Fast
Ionic strength sensitivity	Robust (maintains hydration)	Sensitive (can collapse)
Antifouling performance	Often superior in biological fluids	Excellent

Durmaz et al. | ACS Appl. Polymer Mater.| 2021

Biomedical Applications of Brush-Type Polymers



Drug delivery

Membrane

Surface property tuning

Biosorption

Antibacterial surfaces

Biosensing

Cell adhesion

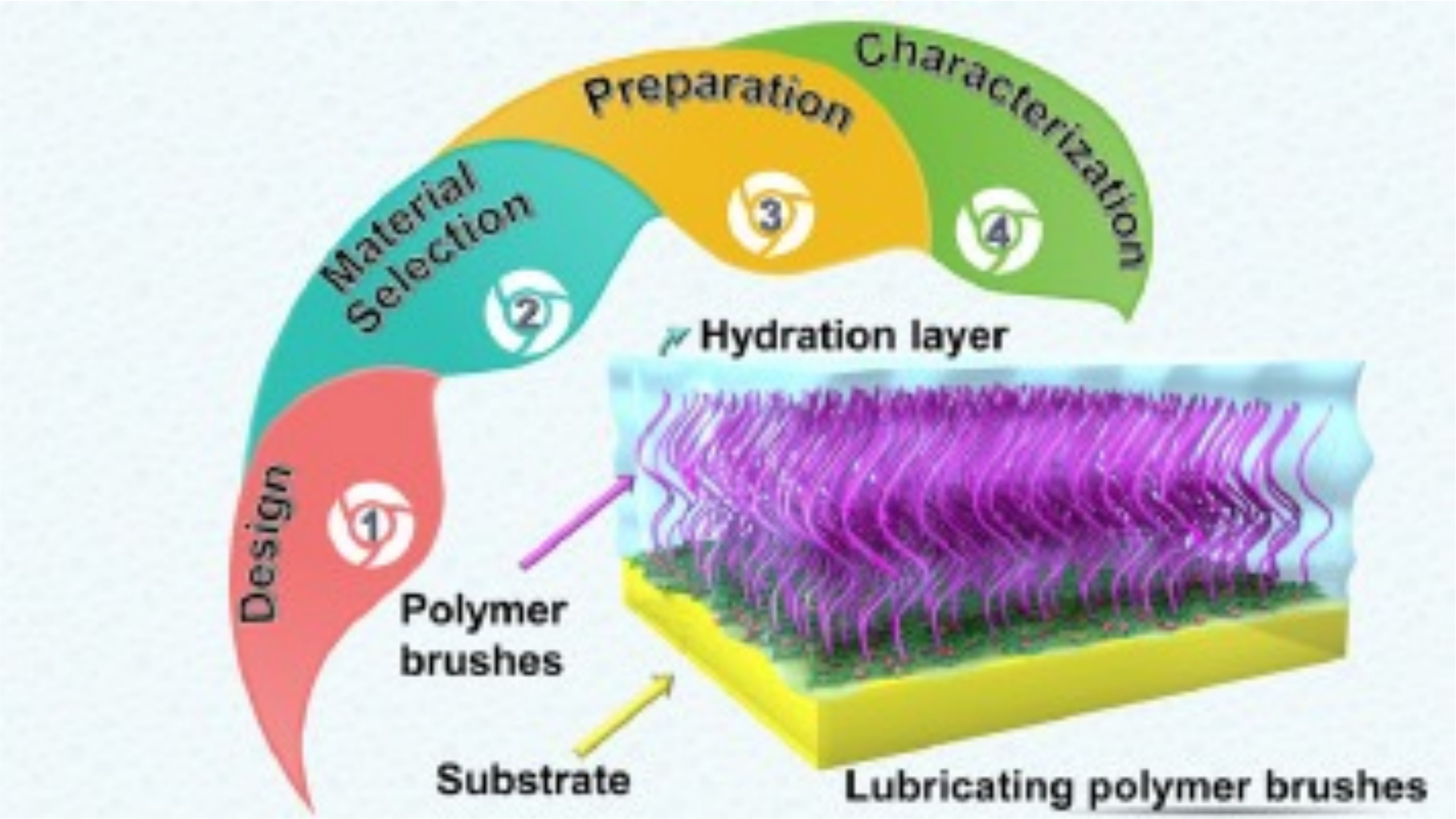
Biocompatible coatings

Tissue engineering

Antifouling surfaces

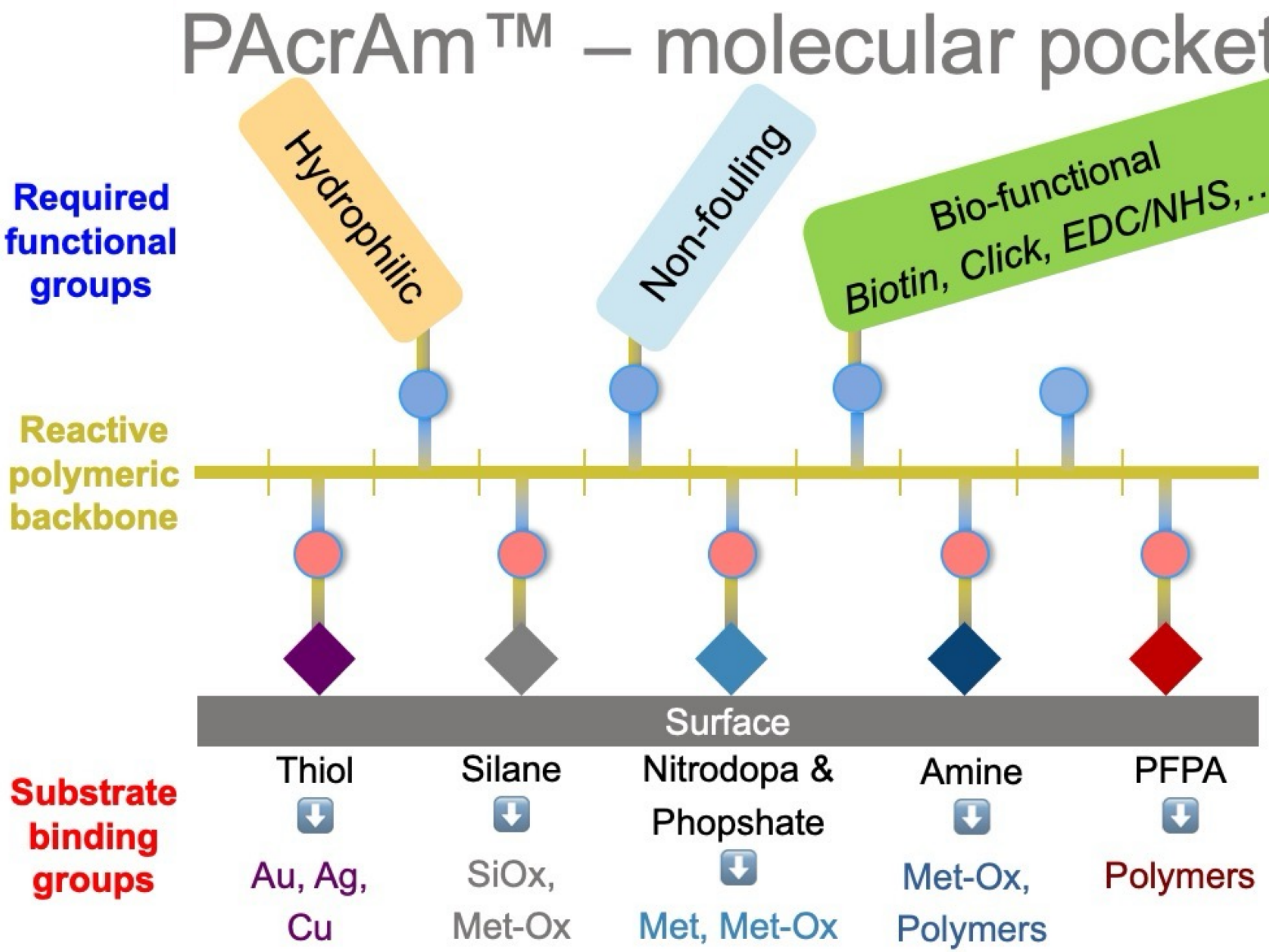
Acari et al. | Adv. Colloid Interf. Sci.| 2022

From Design to Characterization of Polymer Brushes



Song *et al.* | *Acta Biomaterialia.* | 2024

The “Swiss Army Knife” of Surface Chemistry with Polymers



PAcrAm™ – molecular pocket-knife

Required functional groups

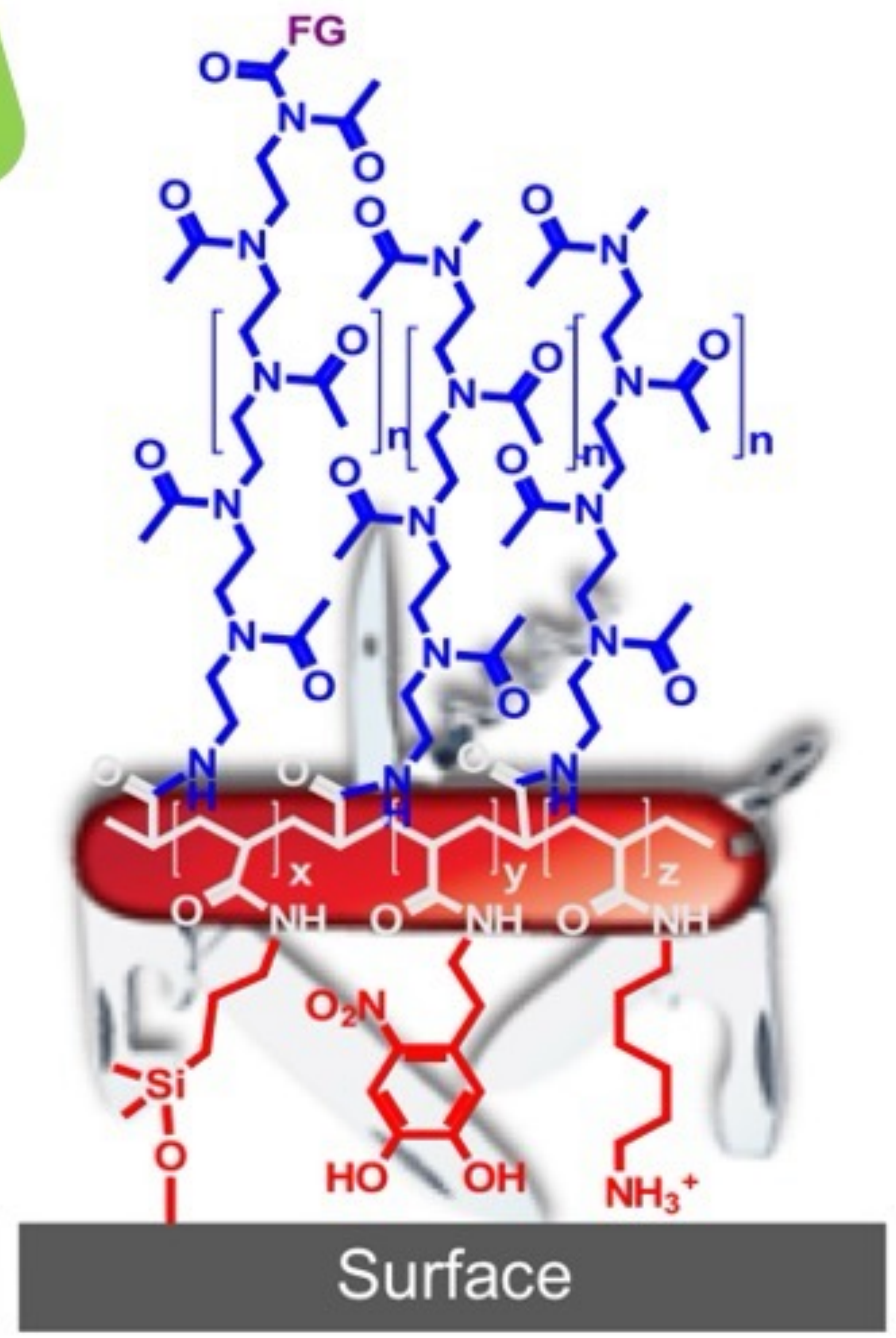
- Hydrophilic
- Non-fouling
- Bio-functional
  Biotin, Click, EDC/NHS,…

Reactive polymeric backbone

Surface

Substrate binding groups

Thiol	Silane	Nitrodopa & Phopshate	Amine	PFPA
⬇	⬇	⬇	⬇	⬇
Au, Ag, Cu	SiOx, Met-Ox	Met, Met-Ox	Met-Ox, Polymers	Polymers

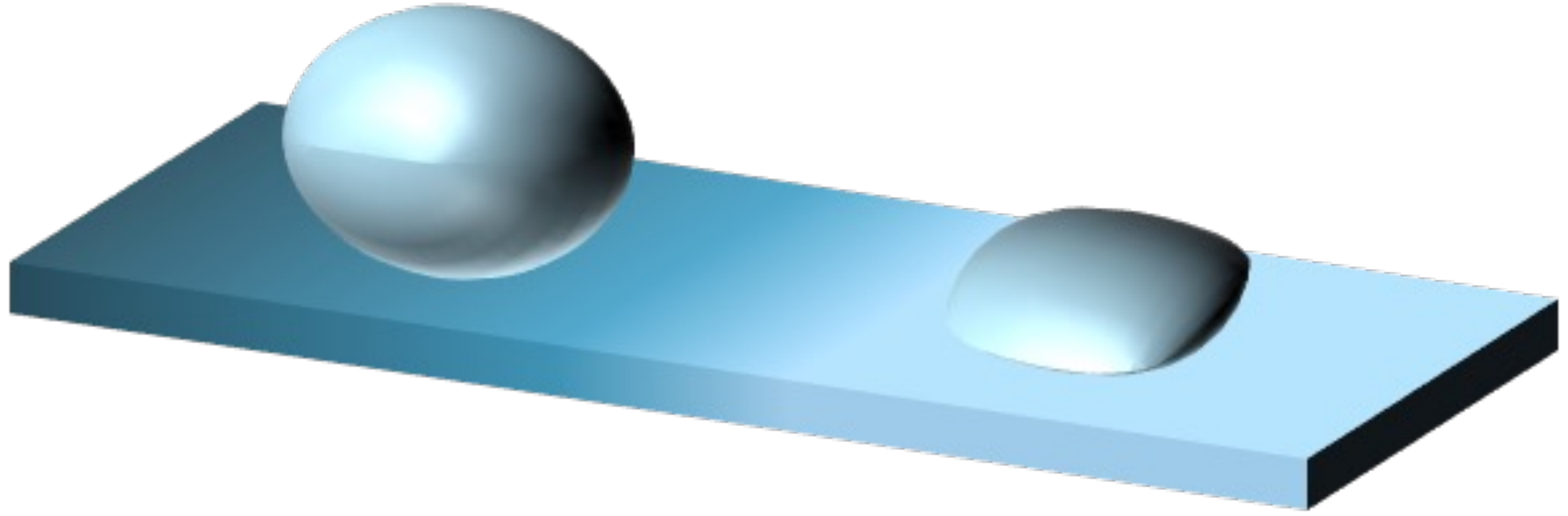


SuSoS
SURFACE TECHNOLOGY

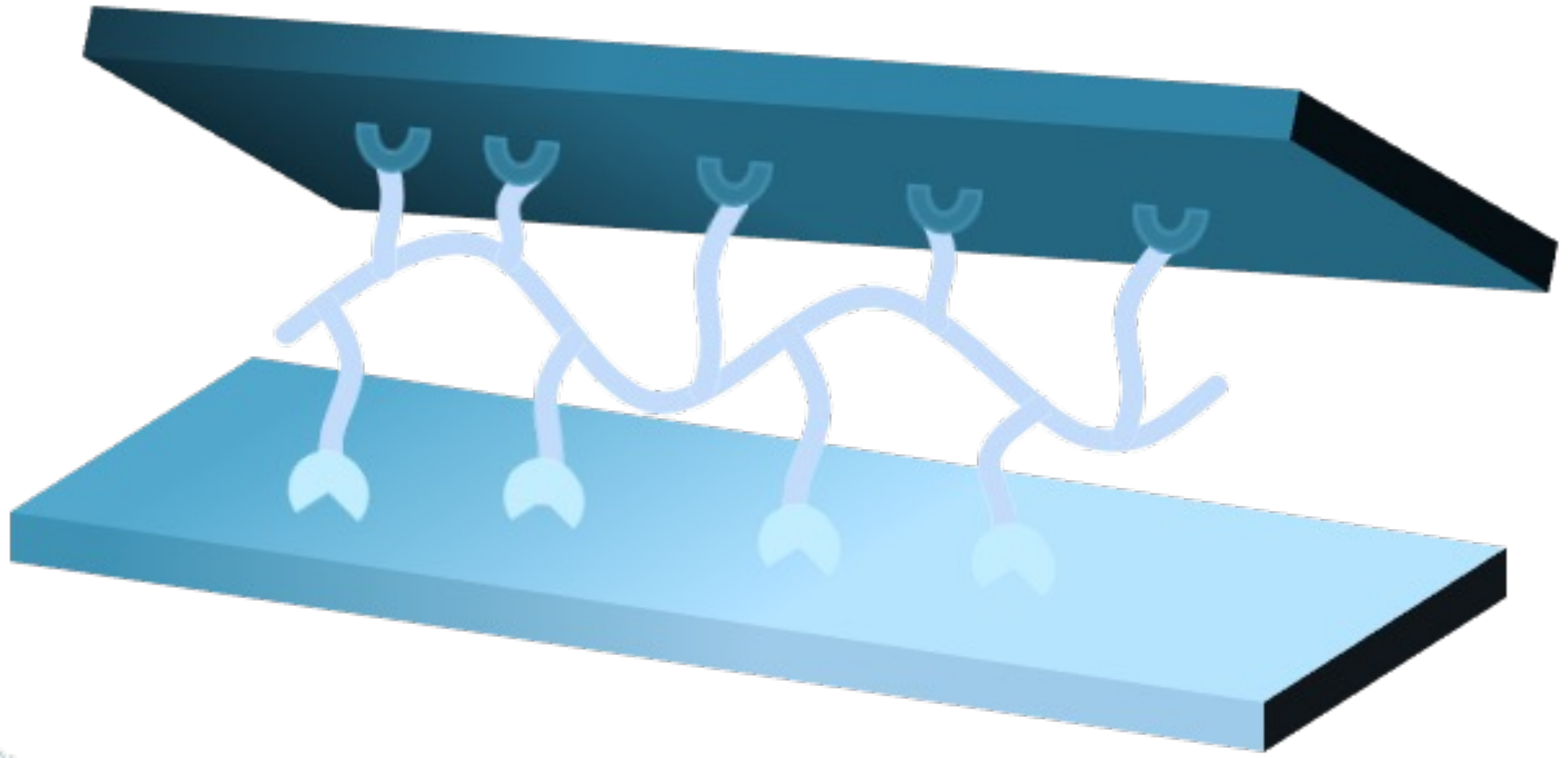
CHEMINA

Core Applications for “Swiss Army Knife” Polymers

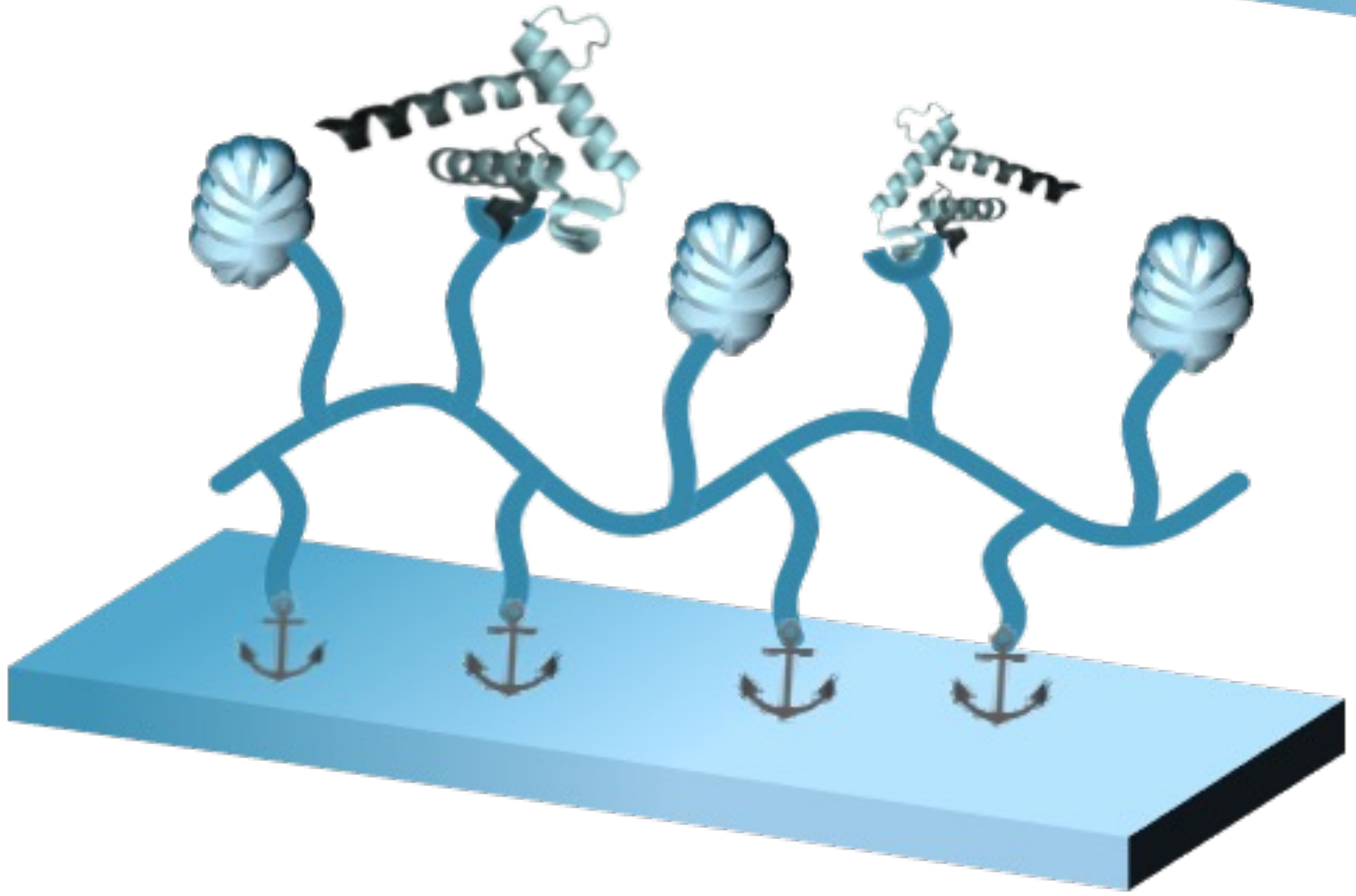
Tuning surface energy using functional molecular layers allow control of the wettability of surfaces



Molecular “super glue” bonding two surfaces together with polymer layers

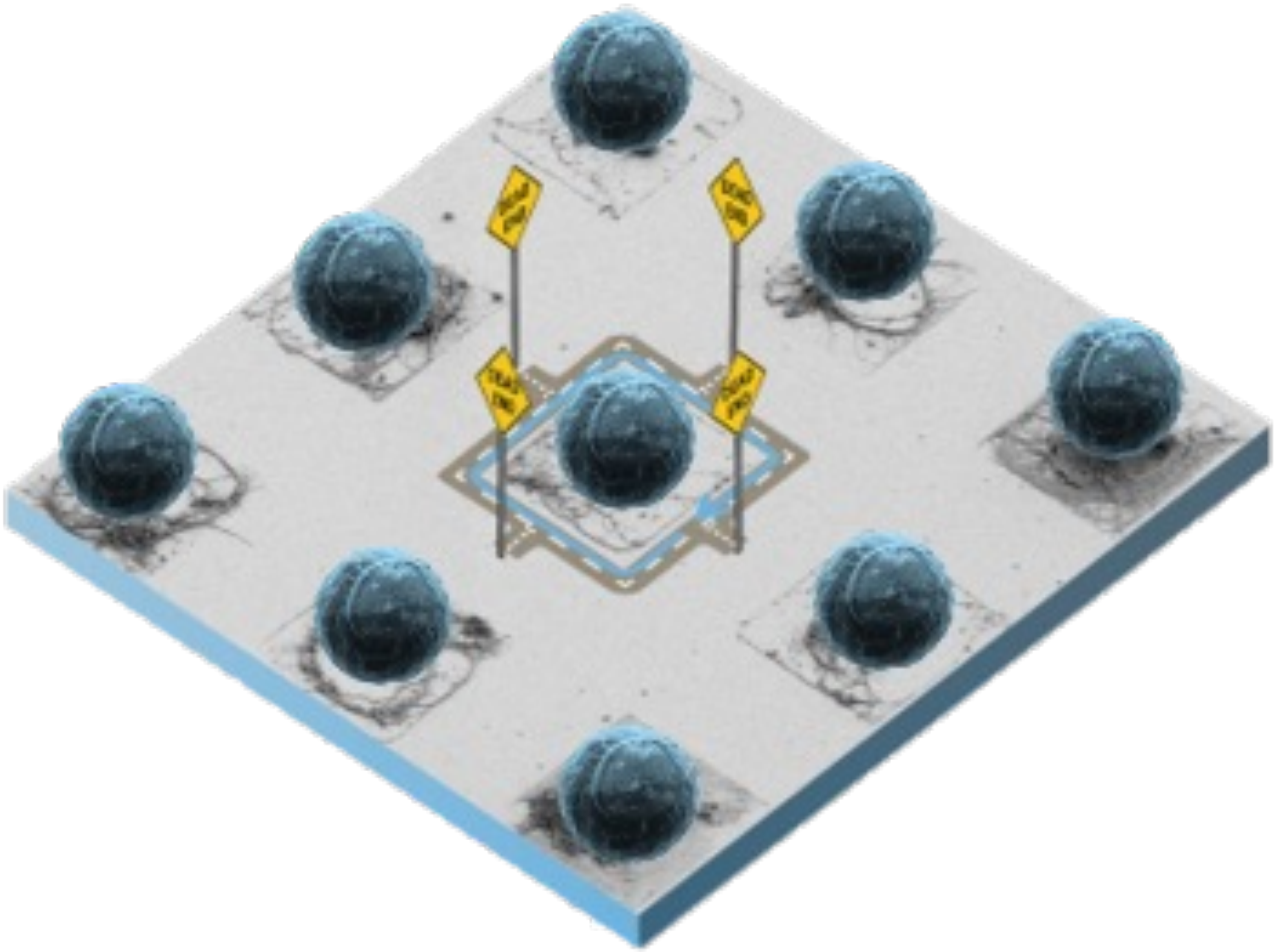


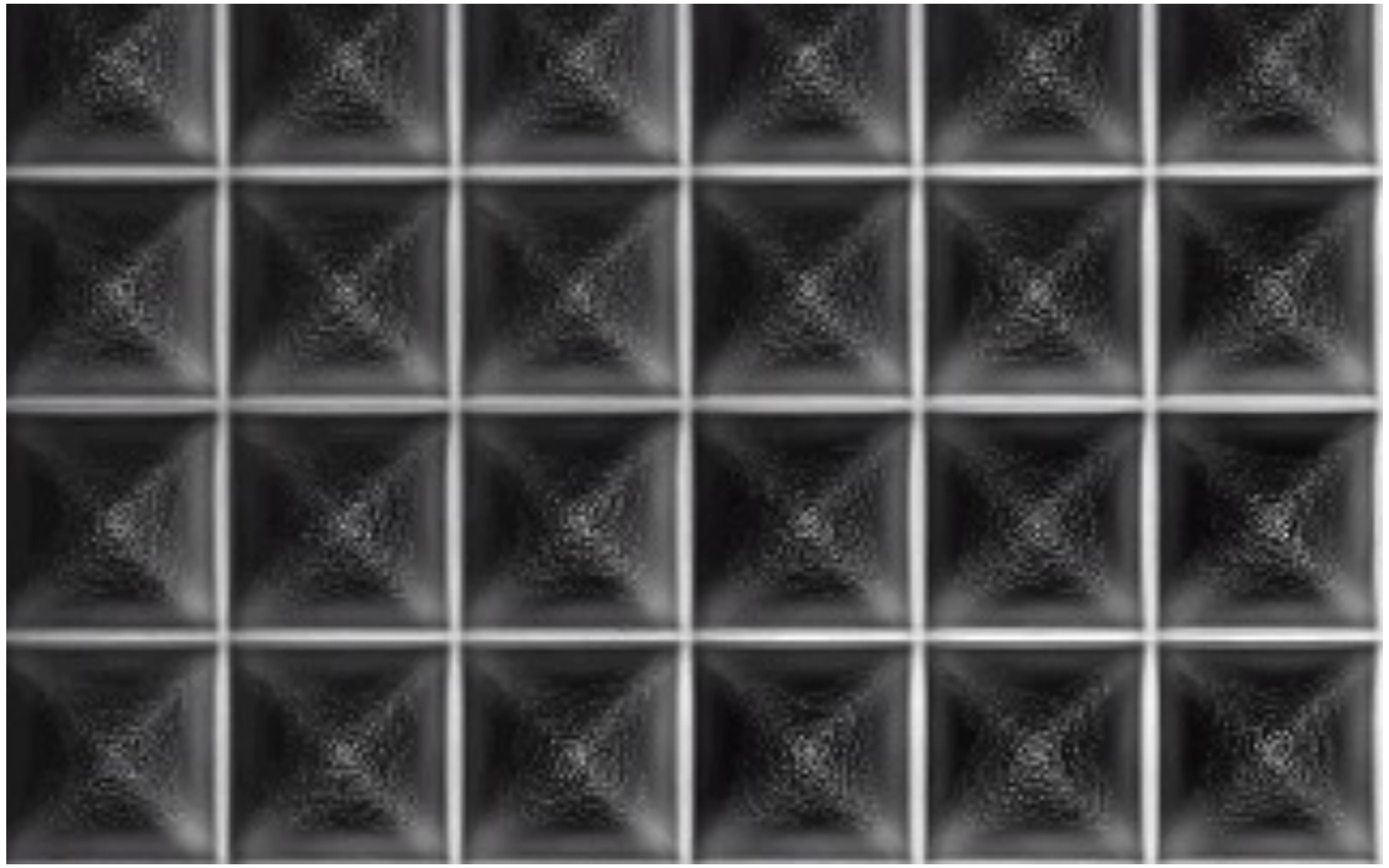
Specific bio-functionalization with specific binding sites surrounded by non-fouling groups



Core Applications for “Swiss Army Knife” Polymers

Formation of spheroids (3-D cell aggregates) as *in vitro* models in wells coated with polymers





Key Takeaways

- Polymer brushes (neutral, zwitterionic) minimize protein adsorption
- Polymer chains on surfaces – grafting density and structure
- Polymers on surfaces can influence biological behavior
- Assembly routes for polymers on surfaces
- Multifunctional polymers for diverse applications

Summary of Today's Class

- Coupling chemistries at surface
- Molecular patterning on surfaces from micro to nanoscale
- Nonspecific protein binding on surfaces – thermodynamic mechanisms
- Controlling protein adsorption through polymer brushes with specific properties
- Tuning surface properties using surface chemistry and molecular assembly

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