Design of Active Interfaces Using Responsive Molecular Components

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Responsive interfaces are interfaces that show a defined and reversible change in physical properties in response to external stimuli. Typically, responsive interfaces result from the immobilization of responsive molecular components at the interface that translate a nanoscale signal into a macroscopic effect. Responsive interfaces can also be obtained if the topology of the interface can be reversibly changed using an external stimulus. As the surface of any material is its connection to the environment, responsive interfaces provide opportunities for interactive materials which are not only able to change properties upon demand, but also sense their environment and act autonomously. The application of responsive molecular components at interfaces, however, requires chemical and physical compatibility with the material surface of interest, posing a challenge not least in the retention of the responsive functionality. The state of the art in “active” interfaces which display responsive wettability, permeability, or adhesion is discussed, with a particular emphasis on microscale and nanoscale patterning since patterned interfaces can give rise to unique material properties. Finally, perspectives in the development of responsive interfaces, as well as promising approaches for bypassing the most prominent challenges are discussed.

1. Introduction

In recent years there is a clear trend in materials science to move from “passive” to “active” materials.[1–4] Passive materials are materials with sophisticated and tailor-made properties depending on their composition and structure that cannot be modified post-synthesis. Active materials are materials that have properties that can be changed after their synthesis, either by applying an external stimulus or by autonomous mechanisms embedded in the material.[5] Typical external stimuli include light,[6,7] magnetic field,[8] or electrical bias,[9] which can lead to a reversible change of structure, stability, permeability, porosity, conductivity, etc. of an active material. Additionally, self-healing is a compelling property of autonomous active materials.[10] Since the surface of a material is where it connects to its environment, a similar trend from “passive” to “active” interfaces is leading to functional interfaces that respond to external stimuli and enable versatile material interfaces with tunable and reversible properties such as wettability and adhesion.[11] Potential applications are found in a wide range of areas such as electronics and energy materials,[2,12,13] biotechnology and biomaterials,[14–18] sensing,[15,17,19] additive manufacturing,[20] and many more.[1,21–23]

A powerful strategy to move from passive to active interfaces is the integration of active molecular components that can translate a molecular signal (such as a change in charge or dipole or conformation) into a change in a macroscopic movement.[18,24,25] An overview of such active molecular components is shown in Figure 1. Prominent examples include acids and bases, which change electrostatic charge upon deprotonation and protonation and hence can induce significant interfacial effects upon a change in pH.[26,27] While a change in pH is easily realized by addition of acid or base, the application of a liquid, the slow response and the extreme pH necessary in order to achieve the desired effect are often drawbacks. Similar effects can be induced using electrochemistry: redox active groups can be reversibly charged by oxidation and reduction.[28–30] In this case, the change in redox state is instantaneous at the electrodes and can effect an immediate macroscopic response, but the interfacial volume that lies beyond relies on redox-hopping and can delay the response time significantly. Molecular photoswitches such as azobenzenes,[31,32] diarylethenes,[33,34] and spiro-pyranes[35–37] show a change of conformation and dipole or charge distribution upon irradiation. Although prolonged UV irradiation can cause degradation, in general light as a trigger is highly advantageous as it is easily applied and provides spatiotemporal control over functionality at interfaces. Thermoresponse can be obtained by polymers with a lower critical solution temperature (LCST), which desolvate and collapse above a threshold temperature.[38–41] Disadvantages here include poor reversibility of the fully collapsed state, as well as the lower response time due to heat dispersion in the system. Lastly, also intermolecular interactions—covalent as well as noncovalent—can be controlled...
by external stimuli. One major advantage is that although the synthetic effort is generally higher, substrates are selective for specific reactive groups only. On the other hand, the response time is limited by the rate of the reaction. Typical examples include dynamic covalent bonds such as boronate esters, hydrazones, and disulfides which respond to pH changes, the addition of competing reagents, or (in some cases) irradiation or redox reactions. Noncovalent interactions such as hydrogen bonding, pi-stacking, or host–guest chemistry are also highly sensitive to even minor changes in pH or temperature, so that the properties of supramolecular materials and their interfaces can be easily tuned by external stimuli.

It should be emphasized that in addition to the interface chemistry, also the interface topology (e.g., surface curvature, micro/nanopatterning) is a key factor determining the interface properties. This implies that active interfaces can also be obtained if the topology of the interface can be reversibly changed using an external stimulus. Furthermore, the presence of a critical threshold for such topologically dependent macromolecular features imparts enhanced sensitivity to the responsive molecular components, making them ideal for forming synergistic high-performance active interfaces.

In this progress report, we highlight some of the most recent advances to attain active interfaces by functionalizing interfaces with responsive molecular components. Typically, two approaches are applied, where molecular changes in either affinity (i.e., hydrophobicity, hydrophilicity, or electrostatics) or shape (i.e., packing parameter, host–guest interactions) dictate macroscopic properties at the interface. However, we also show how this “bottom-up” chemical approach toward active interfaces can be complemented and even enhanced by combination with “top-down” physical approaches to active interface topologies. Rather than providing a comprehensive overview, we have selected stimulating examples from the recent literature. We have focused on reports in which interfacial properties are determined by nanoscale molecular layers on solid substrates and we have excluded quasi-3D materials such as surface molecular organic frameworks (MOFs) and studies on responsive liquid–liquid and liquid–gas interfaces. We have organized the progress report in four subsections which each focus on a particular surface functionality. The most straightforward and probably most investigated interfacial property is responsive wettability (Section 2). With increasing complexity of the interface, the wettability at porous surfaces can effect changes in permeability (Section 3). Furthermore, complementary surface functionalization can enable tunable multivalent interactions that are strong enough for macroscopic adhesion (Section 4).

Lastly, we will cover examples which show molecular design that has been enhanced by patterning to achieve functionality that goes beyond that of the molecular components, generating increasingly complex and valuable interface functionality (Section 5). Finally, we will briefly discuss future perspectives and potential solutions for current challenges in the field.

2. Responsive Wettability

The properties of functional surfaces are defined by the molecular interactions found at the interface of materials and their surrounding and are reflected by their ability to attract or repel this environment. Solid–liquid interfaces, specifically, are ubiquitous in nature and serve a range of purposes in complex biological systems key to their survival, exhibiting how an ensemble of nanoscale interactions can bring about vital macroscopic properties. By attempting to mimic nature, we gain an increasing understanding of the complex underlying mechanisms that govern these biomolecular functions, not least through the effect of subtle structural changes that result in unprecedented properties. For example, surface porosity, a feature which nature gratefully utilizes, can have a substantial...
effect on the fashion in which droplets sit on the surface through the added interfacial interaction with a thermodynamically stable void or lubricating liquid in its nanogaps.[70–73] An archetypal example is the lotus leaf, which through a combination of a hydrophobic molecular ensemble and its surface roughness achieves a superhydrophobic state that allows for a self-cleaning functionality,[74] a function that has been mimicked repeatedly with various molecular components.[75–78] Though the molecular interactions by themselves serve an important part in the overall wettability, the surface roughness can amplify this functionality by forming a further micro- or nano-scale physical separator between the surface and the interfacial material,[79,80] or even at both length scales to enhance surface wettability even further.[81] When such physical separation is present at rough surfaces we speak of a Cassie–Baxter state,[82] or Cassie state, whereas the intrusion of this interstructural surface space by the interfacial material, thereby strengthening its interaction with the surface, is referred to as a Wenzel state (Figure 2A). This nanorough structuring facilitates a sharp transition between wetting states as the threshold for crossing wetting states is subtle and the gain in contact area steep. Many reports make use of such surface roughness to imbue their functional interfaces with enhanced oil/water contact angles. Beyond having amplified static contact angles, however, functional interfaces require reversible changes in wetting states that empower control over surface properties. Thus, a combination of addressable molecular components and the enhanced interactions attained by nanorough structuring is exemplary in their state of the art.

For instance, Han et al. applied a multicomposite ZnO nanorod assembly with lubricant fluid to create cooperatively responsive rough slippery surfaces, responding to a combination of electrical input and photogenerated current (Figure 2B).[84] Through self-assembly of zinc-nanorods on a spin-cast ZnO on indium tin oxide (ITO) on glass slides a nanorough structure was obtained that was modified with cis-bis(4,4′-dicarboxy-2,2′-bipyridine) dithiocyanato ruthenium(II), a typical redox sensitizer capable of photoinduced electron transfer.[85] Subsequent self-assembly of 1H,1H,2H,2H-perfluorodecylmethoxysilane and lubrication with silicon oil ensured the intrinsic hydrophobic nature of the Cassie state structured surface, with retained excited state transfer kinetics of the sensitizer underneath. Han and coworkers thus defined three stages for their dually responsive modular slippery surface, pertaining to 0.4 V intervals, in which various responses were observed with and without excitation of the ruthenium redox sensitizer.[84] In the initial stage, a potential range between 0 and 0.4 V, the water droplet has a sliding angle of 13.3°±2.1° due to the inherently superhydrophobic silicon oil-imbued fluoralkyl interface. The sliding angle remained unchanged upon photoexcitation in this potential regime, as well as upon advancing up to 0.8 V in the dark. However, upon irradiation with light while raising the potential from 0.4 to 0.8 V the sliding angle gradually increases to 88.5°±1.5° due to the additional photoelectric response of the ruthenium sensitizer, causing the interfacial silicon oil to compress so as to facilitate Wenzel state wetting (Figure 2B). Though the pinning of the water droplet is also achieved in the dark upon applying potentials above 0.8 V the sliding angle gradually increases to 88.5°±1.5° due to the additional photoelectric response of the ruthenium sensitizer, causing the interfacial silicon oil to compress so as to facilitate Wenzel state wetting (Figure 2B).
Table 1. Overview of active interfaces and their components covered in this progress report.

| Interface                      | Stimulus          | Molecular component                  |
|-------------------------------|-------------------|--------------------------------------|
| Wettability                   |                   |                                      |
| ITO on glass                  | Photoelectric     | Ru-sensitized ZnO nanorods\(^\text{[84]}\) |
| Electrospun polymer           | Piezo             | Polyanhydride fluoride\(^\text{[86]}\) |
| Copper mesh                   | Thermo            | Poly(N-isopropylacrylamide)\(^\text{[86,87]}\) |
| Si                            | Acido             | Amino polycrystal\(^\text{[91]}\)      |
| Cotton                        | Solvato           | Mixed acrylate blockcopolymer\(^\text{[88]}\) |
| C, Pt                         | Mechano           | Surface curvature\(^\text{[49]}\)       |
| Glass, PDMS, PMMA, Al, paper  | Magneto           | Carbonyl iron particles in PMMA\(^\text{[90]}\) |
| PDMS                          |                   | Carbonyl iron particles in PDMS\(^\text{[139]}\) |
| Acrylate polymer              |                   |                                      |
| PDMS                          |                   |                                      |
| Permeability                  |                   |                                      |
| Electrospun polymer           |                   |                                      |
| Cotton                        |                   |                                      |
| Textile                       |                   |                                      |
| Polyacrylate                  |                   |                                      |
| Copper mesh                   |                   |                                      |
| Steel, PDMS, Al, Cu, Ni, Si   |                   |                                      |
| Carbon                        |                   |                                      |
| Titanium mesh                 |                   |                                      |
| Liquid crystal polymer network|                   |                                      |
| PDMS/graphene                 |                   |                                      |
| Nylon                         |                   |                                      |
| Adhesion                      |                   |                                      |
| Si                            |                   |                                      |
| Poly(ionic liquid)            |                   |                                      |
| Cu, Al, stainless steel, Cu,  |                   |                                      |
| bone, wood                    |                   |                                      |
| Glass                         |                   |                                      |
| Mylar                         |                   |                                      |
| Glass                         |                   |                                      |
| Glass                         |                   |                                      |
| Polypropylene on glass        |                   |                                      |
| Actuation                     |                   |                                      |
| Liquid crystal network        |                   |                                      |
| Magneto                       |                   |                                      |
| Humidity                      |                   |                                      |
| Graphene oxide                |                   |                                      |

off/on control over droplet mobility as well as a quasipermanent “writing” functionality. Similarly, piezoresponsive copolymer strings consisting of alternating polyvinylidenefluoride (PVDF) and polymethylmethacrylate (PMMA) fibers were employed by Guselnikova et al. to modulate between Cassie and Wenzel wetting states through magnetism. (Figure 2C).\(^{[86]}\) The excellent processability of PVDF allows for electrospinning fibers intertwining with PMMA, while simultaneously maintaining their ionic conductivity and piezoelectric properties. Postmodification of the copolymer anchor polymer and an increased exposure of the hydrophilic block, resulting in a superhydrophilic surface (Figure 2D, left). Subsequent drying at 95 °C in air stimulated the hydrophilic portion to return to the interface, thereby restoring the Cassie state and resulting in a superhydrophobic surface (Figure 2D, right). Hence, such functionality may find application in textile finishes that enable natural antifouling features while still being susceptible to the laundry washing cycle.

Although Cassie and Wenzel states provide great opportunity to control wettability at the nanoscale, larger structures can
rely on changes in contact area to drive a substantial change in wettability. While this can be achieved with surface modifications (vide infra), it is worth noting that also the global shape of surfaces themselves can induce changes in wettability. Zhu et al. report that the wettability for platinum and carbon surfaces vary with curvature on account of a change in orderliness of water.

Figure 2. A) The interactions of a droplet or bubble at a structured surface, categorized in Cassie and Wenzel states. The use of lubricant micro/nanodrops or airpockets adds an additional layer of interaction which can assist in tuning the desired surface properties. B) Approach of Han et al. to achieve switchable wettability by a cooperative input at multicomposite ZnO nanorod assemblies with a lubricant fluid. Neither a potential of 0.8 V nor the generation of a photocurrent at the nanorods through ruthenium sensitization immobilizes the water droplet, but the joint stimuli facilitates transitioning of the contact mode to a Wenzel state and thus pin the droplet at sliding angles up to 90°. Adapted under the terms of the Creative Commons License 4.0.[84] Copyright 2019, The Authors. Published by Wiley VCH. C) Electrospun strings consisting of alternating polyvinylidene fluoride and polymethylmethacrylate copolymer fibers are postmodified at the polymethylmethacrylate with perfluorooctyl groups for hydrophobicity. The thus obtained Cassie state can be switched by exposure to an electric field to contract the PVDF fibers, expanding the PMMA fibers and spreading the hydrophobicity sufficiently to allow transitioning into the droplet-pinning Wenzel state. Adapted with permission.[86] Copyright 2018, American Chemical Society. D) Utilizing the interchangeable interactions of aptly designed block copolymers at textile surfaces for antifouling purposes. Prolonged exposure to aqueous and ambient environments can transition the copolymer orientation to alternate its philicity, resulting in a more effective laundry cycle. Adapted with permission.[88] Copyright 2018, American Chemical Society.
at the surface. They show that the very first solvent layer of molecules at the surface dictates the surface properties by being the interface between the liquid–solid attractive forces and the bulk liquid intermolecular forces. For water on platinum, specifically, it was found that the intrinsic attractive forces regulate an interface-structure orderliness at small curvature that overcomes the natural hydrophilicity of platinum. Increasing the curvature, however, disrupts the orderliness and the 2-D H-bond network, leading to a mechanically induced reversible change-over from the hydrophobic to a hydrophilic surface.

Yang et al. were able to switch wettability at surfaces by controlling the contact area of magnetoresponsive micropillars modified with an organometallic molecular component. The micropillars were fabricated on substrates by in situ spray coating and curing a mixture of polydimethylsiloxane, carbonyl iron particles, and toluene in a magnetic field. Impressively, the controlled capture and release of water droplets is realized at various substrates such as PDMS, glass, PMMA, aluminum and paper, owing to its facile magnetic-field-directed production process. Postproduction, the formed magnetorheological elastomer micropillars remain reversibly responsive to an external magnetic field at all substrates, giving modular control over the interfacial contact mode by simply tuning the strength of the applied electromagnetic field. In a weak magnetic field there is no force to sustain the upright orientation of the micropillars, and although some micropillars enter a collapsed state by default, the reorientation is also stimulated upon contact with a water droplet due to its cohesive force. Consequently, the increased contact area at the surface-droplet interface causes an increase in adhesive force that is able to pin the water droplet with no effective sliding angle. Conversely, in a 0.45 T magnetic field the micropillars are stiffened, as they were for the production process, and thus are able to bear the load of a sessile droplet on their pillar tops. The subsequent minimum contact area with the water droplet creates a low-adhesive state in which the droplet reaches sliding angles below 10°. As a proof of principle, Yang and coworkers also demonstrated the water droplet load-transporting ability over short distances at their range of substrates, showcasing the potential as well as the breadth of their facilely applied design strategy.

Alternatively, photodynamic patterning also allows for spatiotemporal control of wettability at surfaces, as demonstrated previously for disulfide formation/reduction strategies. The modularity of the disulfide bond provides the opportunity to attach, exchange and detach different thiol components at a thiol-modified surface without a significant loss of functionality over time. For example, Du et al. demonstrated reversible UV-induced disulfide exchange at porous poly(hydroxyethyl methacrylate-co-ethylene dimethacrylate) surfaces in presence of a photoinitiator. After esterification of the porous polymer with bis(2-carboxyethyl) disulfide they were able to reversibly change the contact angle to 128° and back to 44° upon photodynamic interchanging between with dibutyl...
disulfide and bis(2-carboxyethyl) disulfide, respectively. Furthermore, various disulfide probes in this and in further work by the group demonstrated the extent of spatiotemporal control in being able to control the fluorescence down to a gap resolution of 10 μm by applying photomasks (Figure 3B).[91] The use of disulfide bonds through this approach thus allows for precise control and a high synthetic flexibility, but although the use of UV-light was shown to have a modest impact on interface performance, the use of visible light to exchange surface modifications further broadens the applicability. Diselenide bonds, e.g., have been shown to efficiently undergo metathesis with rapid recombination under visible light irradiation without the use of additional catalysts,[92] showing further promise for bioapplications.[93,94] Recently, Xia et al. have demonstrated their dynamic functionality at various interfaces, including ITO on glass, PDMS and quartz surfaces, showing reversible exchange of selenide surface modifications under visible light irradiation (Figure 3C).[95] Much like with the disulfide photodynamic pattern, the photoactivated process enables the use of photomasks in order to create patterned surfaces, and although the authors do not mention a limit to resolution it is expected to be similar to that seen for the disulfide exchange above. The photodynamic diselenide exchange is rapid, reaching completion within 30 s, and thus is shown to allow for swift adjustment of various modular functionalities such as oil/water wettability, fluorescence, and dynamic bioconjugation. Furthermore, owing to the efficiency at which the exchange occurs such wettability changes in hydrophobic surface-modified capillaries can induce visible light stimulated upward capillary motion of a polyethylene glycol diselenide solution over time, showcasing the versatility of the design strategy (Figure 3D,E).

Interestingly, the state of the art of responsive wettability at surfaces lends itself to yet another application, requiring only a substrate redesign. Many of the functionalities that are attained in the abovementioned examples can potentially be applied to porous substrates also to cause addressable changes in their permeability. For example, poly(N-isopropylacrylamide) modified surfaces, cast from surface-initiated atom-transfer radical polymerization (SI-ATRP), were previously found to undergo efficient thermal wettability changes.[96] Recently, Liu et al. demonstrated such changes in wettability at poly(N-isopropylacrylamide) modified electrosyns policlactone porous membranes. Additionally, the changes in wettability led to changes in permeability, allowing for partial moderation of oil separation efficacies, and although the changes are modest this example highlights the potential toward switchable permeation (Section 3).[97] Thus, merging of micromolecular (wettability) and macromolecular (porosity) design can yield a new level of complex functionality, i.e., permeation, with tunable response depending on the molecular components. Moreover, as laid out below, their functionality can be tuned beyond the exemplary adjustment of oil/water separation efficiencies alone, to create nearly full control over which component of various mixtures is allowed passage.[98]

3. Responsive Permeability

Over the past billions of years nature has accurately demonstrated that cooperative ensembles of interacting molecular components can be of vital importance, with, e.g., membranes arguably having played a crucial role in the survival of species.[99,100] The complex gating developed by nature showcases, however, that although pore size plays an undeniable key role in such matching and mismatching interactions with its environment, to be able to controlably and reversibly gate particles similar or even larger in size than their counterpart necessitates the utilization of molecular interactions that go beyond size alone, i.e., electrostatics.[101] The modularity at interfaces shown in Section 2 provides ample opportunity for such synergy to be reversibly addressed at porous substrates, making them ideal candidates for addressing challenging medical and socioeconomical issues.[102,103] In particular, oil–water separation is an ecologic topic that has received widespread attention over the last decades, finding application in resolving societally pertinent issues such as waste water treatment and oil spillage recovery.[101] Separation of oily wastewater, for one, can be performed with aptly designed molecular systems, albeit their efficacy generally reduces significantly over time as such membranes get blocked with the separation product. Being able to control separation reversibly brings about significant advantages as the efficacy of membranes can be recovered by restoring the original unobstructed material. To this end, surface modifications that govern the interfacial interactions and do so reversibly through an external stimulus are highly desirable. For example, pH dependent functional groups provide facile access to distinct electrostatic states at varying pH, interacting differently with disparately charged molecular components. The electrostatic interactions are sufficient to bring about structural changes, i.e., changes in porosity, as well as to alter the interaction with the to be separated molecular components. In several recent examples, Shami et al.,[104] Zeng et al.,[105] and Chen et al.[106] show effective oil–water separation through pH-responsive electrostatic interactions in an carboxylated electrosyn polymer mesh, a carboxylated click-functionalized fabric and a UV-cured amino-functionalized polyurethane textile, respectively. The modularity of this approach is demonstrated by the efficient water separation at low pH paired with efficient oil separation at high pH for the carboxylated systems, whereas the reverse functionality is realized for the amino-functionalized textile.

Although these systems are capable of demonstrating remarkable separation efficiencies, the extreme pH required does leave room for milder triggers. For example, Li et al. impart CO$_2$-response in poly(N,N-dimethylamino-2-ethyl methacrylate) grafted cellulose nanofiber aerogels to effect the desired pH change.[107] The decrease in pH upon bubbling through CO$_2$ results in protonation of the dimethylamino functional groups at the membrane surface, leading to a changeover in oil–water separation over $50 \text{ s}$ as the water contact angle recedes from $130^\circ$ to $0^\circ$. Reversion to the hydrophobic state is readily achieved by bubbling through N$_2$ for 15 min, discarding the need for extreme pH completely and empowering readily available gases as an efficient trigger instead.

Although pH is a practical stimulus, the potential mismatch in processability and sustainability due to the overall basicity and acidity can be overcome by enabling disparate chemical stimuli for reaching the same outcome. Li et al., for example, have designed nanowire membranes capable of reversible oil–water separation upon wetting with ethanol.[108] An easily
prepared superhydrophobic zeolitic imidazolate porous framework grown on copper meshes provided nanorough interfaces as shown above in many design strategies for altering wettability. The rough surface features enabled prelubrication of the nanopockets with ethanol and concomitant switching-on of Cassie state (Figure 2A) superoleophobicity, while attaining full reversion by drying. Thus, high separation efficacy with remarkable flux rates for oil–water filtration were achieved, with high corrosion stability demonstrated in prolonged exposure to pH solutions ranging from 3 to 12.

To imbue a redox-response, Du et al. employed nano fibrous carbon membranes which could be used as a conducting support for electrochemically addressable poly-3-methylthiophene. The porous electro-responsive poly-3-methylthiophene membrane allowed for swift electrochemical switching between a superoleophobic ClO₄-doped and superhydrophilic dedoped state, yielding quickly addressable water- and oil-permeability, respectively. The use of electrical stimuli allows for swift control over properties, as well as being a facilely applied and environmentally friendly trigger.

Likewise, Gao et al. demonstrated reversible oil–water separation albeit by photochemical and thermal stimuli. Treatment of titanium meshes with poly(vinylidene difluoride) and perfluorooctanoic acid-modified TiO₂ nanoparticles generated superhydrophobic and underwater superoleophilic membranes (Figure 4A,B). Owing to the modular surface structure of TiO₂ in presence of H₂O and O₂, a significant increase in hydrophilic Ti-OH surface species can be realized through UV-irradiation for 70 min, while treatment at 120 °C for 90 min restores the original surface coverage of hydrophobic Ti-O. The robustness of the individual components was reflected in the properties of the ensemble, as negligible changes in respective surface wettability before and after UV irradiation were observed upon immersion in highly acidic (pH = 2), highly basic (pH = 13) and highly saline environments for 12 h, as well as under storage over 6 weeks, upon immersion in liquid nitrogen, and exposure to oxygen plasma etching. The demonstrated durability of the membrane and the high repeatability without loss of performance ultimately allows for highly efficient oil/water filtration of corrosive waste.

Yu et al. have also developed corrosion resistant membranes through fabrication of superhydrophobic poly(dimethylsiloxane) and graphene modified copper meshes that are able to attain superhydrophilicity upon O₂ plasma etching for 30 s (Figure 4C–E). The resulting increase in hydrophilic carboxyl groups on the surface can be repeatedly reversed by laser etching, its application to oil–water separation showing separation efficiencies greater than 94% after 15 cycles still. Interestingly, the membrane also responded to abrasion on account of the resulting change in surface roughness, moderately decreasing its water contact angle but, moreover, facilitating complete pinning of water droplets, i.e., increasing its water sliding angle from several degrees to 180. Subsequent flame treatment almost completely recovers the initial surface roughness and degree of superhydrophobicity, while five further abrasion-flame treatment cycles still show promising reversion rates before the performance starts to wear.

Although oil–water separation is a highly sought-after functionality due to its ecological relevancy, permeability shows...
Fan et al., for example, developed a liquid-gating system which makes use of the self-assembly of capillary amphiphilic micelles in water to adjust transmembrane gating in nylon membranes with various pore sizes.\[114\] By regulating the concentration of sodium dodecyl benzene sulfonate the transmembrane interfacial molecules can rearrange to lower the transmembrane critical pressure at increasing amphiphile content. Surpassing the critical pressure of the membrane creates micellar capillary liquid/gas pores fit for transmembrane gating. Interestingly, through this approach a substrate can be selected for its desired pore size while the attained gating functionality operates independently, merely possessing lower base transmembrane critical pressures at larger pore sizes. Moreover, further chemical tuning could be achieved through coordination with various metals, lowering the transmembrane critical pressure as the orderliness of amphiphiles increases, and through adding ethanol to alter the micellar interactions, initially raising the transmembrane critical pressure albeit followed by significant lowering after a 20% content.

Yong et al., on the other hand, make use of reversible Cassie state pretreatment of the substrate to tune its aeroaffinity through aeration of its nanopockets or displacement thereof by ethanol prewetting.\[115\] By laser ablation of substrates in equidistant horizontal and vertical lines, microscale pores at cross-sections and coral-shaped microstructures in untargeted zones were created, each bearing a nanoscale-size rough surface. When using such poly(tetrafluoroethylene) and polydimethylsiloxane substrates, or when Al, stainless steel, Cu, Ni, and Si substrates are postmodified with a fluoroalkyl silane to gain superhydrophobic surfaces, the porous structure yields the surface modification needed to capture an interfacially interacting layer. The resulting surfaces are superaerophilic in nature due to the presence of aerated nanopockets, while pretreatment with ethanol, i.e., displacement of the air in the nanopockets to create a Cassie state against air, leads to a superaerophobic surface in a process that can be fully reversed by drying. Ultimately, applying this fabrication process to a porous sheet enabled the gated permeation of air bubbles when the nanopockets were filled with air and the break-through pressure was thus sufficiently lowered, while the blocking of airflow was realized when the sheet was pretreated with ethanol.

Though control over gas transport is a challenge in itself considering their inherent unfavorable size, reversible gas separation poses a true challenge in permeation due to the minimal size differences between gaseous molecules and their reduced membrane interactions. Tailoring the desired reversible changes at the membrane-air interface requires a level of synergy that is not often achieved, albeit Cao et al. managed to do so through an azobenzene-containing liquid crystal polymer network.\[116\] The application of liquid crystal polymer networks as polymer membranes brings forth the benefit of tunable isotropic and cholesteric morphologies and the opportunity to disturb the packing parameter by incorporating stimuli-responsive units, such as azobenzenes (Figure 5). Interestingly, the morphology of the liquid crystal polymer networks alone had a striking effect on both their thermally as well as photochemically induced gas permeation. The isotropic membrane

![Figure 5](image-url)
exhibited a 6% increase in N₂ flux upon surpassing its glass transition temperature, whereas the cholesteric membrane showed an 8% decrease (Figure 5B). Furthermore, a rigid response in the isotropic membranes was observed upon irradiation at 365 or 455 nm, while in the ordered cholesteric membranes upon irradiation at 365 nm a decrease of 9% in N₂ permeation was observed that was reversible thermally over 10 h, as well as within 10 min by irradiation at 455 nm (Figure 5C,D). The authors attribute the counterintuitive response in permeation to a decrease in the packing parameter of the liquid crystal polymers as a result of the occupying of ordered voids present in the initial high order cholesteric phase, either through the rubbery state above the glass transition temperature or the distortion in packing upon E- to Z-isomerization of the azobenzenes. The possibility to tune gas permeation by facile external stimuli such as temperature and photoirradiation, makes the use of liquid crystal polymers to form responsive membranes a promising approach for further advances in tunable gas transport and permeation.

4. Responsive Adhesion

Per definition, adhesives are nonmetallic substances that, when applied between two surfaces, prevent their separation. In the history of mankind, the earliest examples of adhering materials are presumably older than 200 000 years, as tar-hafted stone tools originating from this time have been found. Until the development of synthetic plastics, adhesives were solely fabricated from naturally occurring resources like casein, animal hides, or natural rubber to name only a few. In our everyday life we are dependent on glues in many different areas. Fixed dental brackets need to be glued to the teeth or in the fabrication of cars in automobile industry adhesives are indispensable. In many applications, not simply the strongest possible adhesion between two materials, but rather the control over the adhering properties is of prime interest, so that components in complex devices can be easily recycled simply by deactivating the adhesive. Materials that are capable of self-healing (such as supramolecular hydrogels) are one interesting approach toward responsive adhesion, since the self-healing nature allows for repeatable gluing events after breakage. Interestingly, the majority of responsive glues is based on host–guest interactions or dynamic covalent bonds. Some of the most appealing contributions from the past few years are discussed in this section. Note that we do not cover the extensive literature on responsive interfaces for cell-material adhesion.

Host–guest interactions as reversible supramolecular bonds have widely been used in the development of responsive adhesives. One of the most famous classes of host compounds are cucurbit[n]urils (CB[n]), which are cyclic oligoglycolurils connected by CH₂ groups. The most suitable guests for CB[n] are hydrophobic cations which bind in aqueous media through hydrophobic interactions with the CB cavity and cation dipole interactions with the CB carbonyl portal. High affinity binding with $K_a = 10^{9–10^{17}} M^{-1}$[110] make CB[n] outstanding components in the development of supramolecular adhesives. Ahn et al. demonstrated the fabrication of a “supramolecular velcro” by combining a surface grafted with a CB[7] polymer and a surface grafted with a complementary ferrocene (Fc) polymer.[121] Under water, this system shows strong and reversible adhesion because of the formation of multiple host–guest complexes between CB[7] and Fc, which dissociate upon oxidation of Fc.

The strong supramolecular interactions between CBs and guest molecules were also exploited in the development of different dynamic hydrogel networks. Liu et al. used a copolymer consisting of acrylamide and 1-benzyl-3-vinylimidazolium bromide mixed with CB[8] for the adhesion of various porous and nonporous substrates, such as glass, metals, wood and bone.[122] The acrylamide side chains act as anchoring points toward the substrates surface, while the benzylimidazolium bromide is known to form a ternary 2:1 host–guest complex with CB[8] consisting of two guest molecules and one CB[8] host. This leads to a supramolecular connection of multiple polymer strands and in consequence to an adhesion of the two joined substrates. Notably, because of the dynamic and noncovalent nature of the polymer network, when put under shear stress the host–guest complexes act as sacrificial bonds that can break and reform, leading to a strong interfacial adhesion attributed to the energy dissipation.

Another versatile class of supramolecular hosts are cyclodextrins (CDs), which are cyclic oligosaccharides consisting of α-1,4 linked glucose subunits. The most prominent CDs are α-, β-, and γ-CD (6, 7, and 8 glucose units, respectively). CDs form cup-like macrocycles with a hydrophilic exterior and a hydrophobic interior, which makes them good host for hydrophobic guest molecules in aqueous media. The driving force is of entropic nature because during the binding event high energy water from the cavity is replaced by the guest molecule. Individual complexes were measured to have rupture forces of 61 ± 10 pN.[123] Similar to CB[n], also CDs can form redox-responsive host–guest complexes with Fc.[124] By switching the oxidation state of Fc, reversible adhering velcro-based on poly(ionic liquid) membranes were fabricated.[125] Our group reported on responsive surface adhesion based on host guest chemistry of β-CD and a light switchable aryloxyrazole (AAP).[126] Compared to azobenzenes, AAPs are characterized by their improved photostationary states and their increased Z-isomer half-life. Similar to azobenzenes, the E-isomer tends to form inclusion complexes with CDs while the bent Z-isomer only shows weaker binding constants due to an increased polarity and a higher steric demand. Glass-surfaces were functionalized with copolymers containing either AAP-PAAPA-PHEA or β-CD-moieties (PCDA-PHEA) in their side chains via surface-initiated atom transfer radical polymerization (SI-ATRP). Three different systems were investigated. Either two surfaces both functionalized with PAAPA-PHEA were glued together with a solution of a β-CD-polymer (SysI) or the complementary case (PCDA-PHEA surfaces glued together with an AAP polymer, SysII) was tested. In both cases good adhering properties could be observed with 2.17 kg cm⁻² for SysI and 1.77 kg cm⁻² for SysII. Because of the dynamic nature of the host–guest bond the surfaces could be readdressed after breakage, but with less strength which can be attributed to a certain amount of rupture of the polymer brushes. The third system consisted of one PAAPA-PHEA and one PCDA-PHEA surface (Figure 6A). In this case no additional polymer for cross-linking purposes is necessary. We emphasize that in this
case also the highest weight could be attached (3.27 kg cm\(^{-2}\), Figure 6B,C). Also, SysIII is water-resistant, meaning when immersed into water the adhering supramolecular forces were still present, while SysI and SysII were not water resistant likely due diffusion of the cross-linking polymers into the solution. Although a light-switchable adhesion would have been desirable, the adhering force could not be weakened via photoinduced \( E \rightarrow Z \) isomerization using UV-light. This phenomenon is likely to be explained by an incomplete photoisomerization of the AAP in the host–guest complex in a “dry” environment. Nevertheless, the surfaces could be inactivated by UV irradiation during the gluing process.

Besides host–guest interactions, many other covalent and noncovalent interactions have been exploited for responsive surface adhesion. Some adhesives respond to changes in temperature due to the incorporation of poly(N-isopropylacrylamide) (PNIPAM) or other thermoresponsive side chains into a polymer network. This is caused by phase separation that occurs when the characteristic LCST is exceeded. Among others, this was accomplished in a polyelectrolyte system. PNIPAM side chains were grafted from poly(acrylic acid) (PAA-g-PNIPAM) and poly(dimethylaminopropylacrylamide) (PDMAPAA-g-PNIPAM). When mixed, below the LCST the system is a fluid complex coacervate, that transitions into a nonflowing hydrogel when the temperature exceeds the LCST. This system is fully reversible and has potential applications in the bonding of biological tissues due to its underwater adhesive properties. Another example using PNIPAM in
thermosresponsive adhesives makes use of the adhesive properties of catechols. A copolymer containing adhesive catechol groups and adamantane guest moieties was deposited on a surface. Afterward, the surface was dip coated in a solution of a thermoresponsive PNIPAM copolymer containing CD host moieties. At room temperature (below LCST) the PNIPAM copolymer is in a swollen state and thus shielding the interfacial interaction of adhesive catechol groups. Above LCST, the PNIPAM copolymer agglomerates which exposes adhesive catechol groups. This results in an increased interfacial adhesion.

Our group also developed an adhesive based on dynamic covalent chemistry of phenylboronic acids (PBA) and catechols. Catechols, similar to other 1,2 and 1,3-diols, bind reversibly to boronic acids wherein the equilibrium constant is determined by factors as the \( pK_a \) of the PBA, the geometry of the diol or the \( \text{pH} \) of the solution. Phenylboronic acid acrylate, as well as catecholacrylamide were copolymerized with HEA (PPBAA-PHEA and PCAA-PHEA respectively) on glass (Figure 6D). When these surfaces were brought into contact, a strong adhesion of 2.38 kg cm\(^{-2}\) was obtained (Figure 6F). Additionally, the adhesion shows good water-stability and a decent reusability. Due to the dynamic nature of the underlying reaction, submerging the system in a fructose solution as a competitive binder to the phenylboronic acid shifted the equilibrium to the unbound state and thus to a loosening of the surfaces. This behavior could only be observed when patterned surfaces were employed and pressed together orthogonally (Figure 6E). It is likely that the patterning results in nanochannels at the interface of the two surfaces, which favor the penetration of the fructose solution into the material.

Kim et al. implemented photoresponsivity into an adhesive by introducing 2-nitro-1,3-benzenedimethanol dimethacrylate (NBDM) as a photolabile cross-linker into an acrylate-based polymer (Figure 7A). The utilized polymer poly(N-methacryloyl-3,4-dihydroxyl-l-phenylalanine-co-sulfobetaine methacrylate-co-2-nitro-1,3-benzenedimethanol dimethacrylate), poly(MDOPA-co-SBMA-co-NBDM) had a composition of MDOPA:SBMA:NBDM = 10:87:3. DOPA was used for its adhesion-enhancing properties and the main compound SBMA was implied for its potential in biomedical applications. The cross-linking NBDM moiety can effectively be cleaved via irradiation at 352 nm resulting in shorter polymer strands and thus weakening the whole polymer network (Figure 7B,C). Polyesters films that were bonded with this adhesive showed adhesion strengths of 341 kPa, which could be decreased by 33% after illumination at this wavelength for only 30 min (Figure 7D). Control polymers that did not contain NBDM showed no response to UV light. Other responsive adhesives rapidly depolymerize upon exposure to fluoride.
5. Response through Patterning

In the previous sections, the majority of functional interfaces could be achieved with substrates homogeneously functionalized with responsive molecular components. In contrast to this, patterning of responsive molecules can induce a new dimension to generate responsive function. For example, patterns can be written on stimuli responsive surfaces and afterward be erased and rewritten. This can be achieved by various chemistries and stimuli. For example, patterns can be created, erased and rewritten by photodynamic disulfide exchange,\cite{31} light switchable molecules can spatially be switched using photomasks,\cite{132} but also (de)protonated by electrical writing\cite{133} or reversibly patterned by “transclick” reactions at elevated temperatures.\cite{134} This section covers examples of several applications, including the previously discussed responsive wettability and permeation, but with a strong focus on patterning as key element for function. Other applications addressed in this section are actuators, shape memory, and orthogonally switchable surfaces. For a clearer overview, this section is divided into subsections dealing with patterned for responsive wettability and permeability and a subsection dealing with actuators and shape memory materials since the type of patterning is quite different in these active materials.

Responsive wettability can strongly benefit from surface patterning. In the majority of published papers, surfaces are switched from hydrophobic to hydrophilic or vice versa, but the resulting wetting of the surface is mostly isotropic (see Section 2).\cite{135–137} Patterning has proved to be useful to introduce a new dimension of functionality at interfaces. For example, Ge et al. reported pH-responsive surfaces that could differentiate between basic and acidic aqueous solutions and show an inverse anisotropic wetting behavior (Figure 8a–f).\cite{138} Key elements are Janus silicon cylinder arrays (Si-CAs). The cylinders were fabricated by dry etching of a silicon wafer using hexagonally assembled polystyrene microspheres as mask. The substrates were functionalized with an ATRP initiator and polymerized with poly(2-(dimethylamino)ethyl methacrylate) (PDMEMA). Afterward, the “Janus” aspect was introduced via 45° oblique thermal Au evaporation, yielding cylinders with a 20 nm Au layer on one side only. These silicon substrates were incubated in a solution of 11-mercaptoundecanoic acid (MUA) and 1-dodecanethiol (DDT). At this point the cylinders had amino groups on one side (from PDMEMA) and carboxyl groups on the other side (from MUA) (Figure 8a). Applying acidic solutions below pH 4 resulted in a protonation of amino groups and thus an increase in hydrophilicity on the PDMEMA side of the cylinders. The acidic water droplet migrates in that direction (Figure 8c,f, left). Likewise, basic solutions above pH 10 deprotonate the carboxyl groups and result in increasing hydrophilicity on the opposing (MUA) side of the cylinders. The basic droplet migrates in the opposite direction than the acidic one (Figure 8e,f, right).

Jiang et al. combined actuating microstructures and responsive wettability to create a system whose wetting properties could be switched due to the movement of these microstructures.\cite{139} Similar to the previous example they used Janus microstructures, in this case PDMS microplates with a high aspect ratio, as structural element (Figure 8g–k). Carbonyl iron particles were embedded in the microplates to make them responsive to an external magnetic field. Upon applying a strong magnet, the microplates bent in such a way that only one side was exposed to the surrounding media and thus was responsible for the surface properties. The anisotropic Janus character was introduced by first treating both sides with a superhydrophobic spray and successive magnetic bending and laser scanning to remove the hydrophobic paint from the top side. Inverting the magnetic field switched the surface properties between superhydrophobic and hydrophilic (arising from carbonyl iron particles). In the superhydrophobic state a water contact angle of 158° was measured with air pockets being present indicating Cassie state, while in the hydrophilic state the contact angle decreased down to ~40°. This system was also used to mimic the assimilatory coloration of chameleons (red/green dyed side of microplates) and to fabricate a magnetically responsive optical shutter by mimicking the light blocking function of venetian blinds where light is transmitted in the unbent and blocked in the bent state (Figure 8k).

As explained in Section 3, liquid–gas separation is very challenging. Principle applications in the area of crude oil processing to exclude corrosive gases from pipes are conceivable. In recent years, many examples have been published that impressively demonstrate how structured membranes can offer added value over unstructured ones. The employed materials varied from metals such as copper mesh that was structured by chemical etching\cite{141,142} and aluminum foils\cite{143} to nonmetallic ones such as PDMS.\cite{144} They all have in common that gas bubbles are unidirectionally transported either with or against the buoyancy direction through microstructured pores. These pores have a Janus character, which is characterized by different aerophilic properties on opposing sides of the pore. In principle, gas transport always takes place from the more aerophilic to the more aerophobic side. An important example making use of microhole arrays (MHA) fabricated by femtosecond laser drilling on PDMS was recently published by Chen et al.\cite{144} Depending on the number of laser pulses, pores of different sizes could be obtained. More importantly, the pore diameters and the overall roughness on opposing sides of the PDMS was also different and can be considered as a Janus system (larger pore surface, LHS; smaller pore surface, SPS). As can be seen in Figure 9f,g, with smaller pulse numbers (and smaller holes) the SPS is more hydrophilic (and aerophobic, AB) and with increasing pulse numbers the SPS tends to be the more hydrophobic one (super-aerophilic, SAL) with a crossing point at intermediate pulse numbers of around 150. Therefore, the gas penetration direction could be switched from SPS → LPS (Figure 9i) to LPS → SPS (Figure 9j) just by tuning the pore sizes. The transport speed increased from 764 ms at small pore sized (SPS → LPS) to an ultrashort period of 81 ms at larger pore sizes (LPS → SPS). At intermediate pulse numbers gas could penetrate in both directions. Moreover, the samples showed unidirectional underwater antibuoyancy transport of air bubbles with the direction also tunable via the pore sizes.

In contrast to the previously mentioned examples covering wettability and permeability where the patterning ultimately generated spatially resolved differences in hydrophilicity or hydrophobicity, actuators and shape memory materials can be fabricated by patterning out of equilibrium materials that relax when a certain stimulus is applied. Actuators are materials that
Figure 8. a–f) Responsive wettability through Janus silicon cylinder arrays. a) Schematic representation of Janus cylinders. b,d) SEM images of top (b) and side (d) view of the cylinders. c) EDX mapping of Au. e) Ratio of travelled distance in preferred ($D_{\text{easy}}$) and unfavored ($D_{\text{difficult}}$) direction depending on the pH. f) Photographs of droplets at pH values between 0.98 and 13.05. Adapted with permission.[138] Copyright 2018, Wiley-VCH.

g–k) Responsive wettability, coloration and optical shutter through microplates. g) Bending behavior of microplates in orthogonal magnetic fields. h) Schematic fabrication procedure of Janus HAR-MMA. i) Reversible switching between superhydrophobic and hydrophilic state. j) Reversible switch of coloration between red and green. k) Reversible switching of optical shutter between transmitting and blocking state. Adapted with permission.[139] Copyright 2019, Wiley-VCH.
display a macroscopic movement after being exposed to a stimulus such as light, humidity, heat or others. The actuation derives from released stress that was build up inside the material. Many systems rely on liquid crystalline networks (LCN) as they combine the elasticity of polymeric materials and the anisotropy of liquid crystals. LCNs also are capable to transduce energy from different stimuli such as light, temperature, electric field, humidity or magnetic field. Often the actuation mode is predefined by a spatial treatment of the material with light to program the stress that leads to the movement when released. Other examples do not rely on a spatially resolved stimulus, but on patterned surface itself that is responsible for the macroscopic behavior of the material. One simple yet powerful example was recently published by Zhang et al. where they used micropatterned graphene oxide (GO) films for humidity driven actuation. To this end, an aqueous GO solution was casted onto a patterned PDMS stamp with stripe features, dried and peeled off. The resulting GO films exhibited a patterned side with stripe patterns in different periodicities and a flat unpatterned side. Key element is the area ratio of the patterned and unpatterned side. GO is known for “quantum confined superfluidics” (QSF) which enables ultrafast adsorption and transmission of water molecules along channels between GO sheets. Due to the adsorption of water the distance between the GO sheets increases and the material swells. The area ratio leads to a more pronounced swelling on the patterned side and a subsequent bending of the film toward the unpatterned side. As expected, a higher area ratio resulted in a higher maximum curvature. Depending on the cross-angle at which the stripes are oriented to the GO film, the shape of the film can be adjusted to helixes with different twists (see Figure 10a–i). These asymmetrically structured films can be mirror inverted to each other, whereby also the rotation of the helix inverts. The authors fabricated an artificial bug (“smart centipede”) with as described asymmetrically patterned films as legs, which can crawl at a speed of 0.98 mm s⁻¹ when alternatingly exposed to humid and dry air (twisting and untwisting, Figure 10k,l). This example shows impressively how the type of patterning affects the properties of the macroscopic system. Actuators have much in common with shape memory materials, for example the materials in both cases are often based on polymeric structures which change their shape through an external stimulus. Both types of materials are pushed out of equilibrium and by applying the stimulus they relax back to it. Shape memory materials have also been engineered using patterned substrates. For example honeycomb patterns of an azobenzene containing deblock copolymers could be reversibly stretched or compressed along different axes depending on the polarization of the incident light, leading to either rhombic or rectangular shaped micropores. The honeycomb pattern was achieved using the breath figure process. Light that was either polarized parallel (V direction) or perpendicular (S direction) to the honeycomb walls was used to switch the azobenzene moieties. Before irradiation, the azobenzene moieties are randomly distributed in the polymer network, but they align when irradiated with linear polarized light, which results in directional mass migration of polymer. Depending on the polarization, either the honeycomb walls parallel to the polarized light (V direction) expand, leading to round rectangular shaped pores. On the other hand, light polarized in S direction resulted in the contraction of the perpendicular honeycomb wall and ultimately in round rhombic pores.

6. Conclusions and Outlook
As illustrated in this progress report, many approaches have been developed to impart active functionality at interfaces using...
responsive molecular components. Along with the chemical toolbox of molecular switches that is currently available, this has provided the opportunity to modify surfaces with a wide range of responsive units, allowing the fabrication of functional interfaces suitable for (future) use in various fields of application. In particular, the enhanced interfacial properties and property changes achieved by tailoring the interface structure to synergistically amplify the properties of the molecular components open up opportunities that are greater than the sum of the two parts. Furthermore, the increased understanding of the molecular structure–property relations at interfaces has allowed for implementation of multiresponsive functionality, generating active interfaces that can be tuned with various noninvasive stimuli. Increasingly, various responsive interfaces find applications in our everyday life. For example, materials showing responsive wettability can be used in cars and buildings to achieve self-cleaning surfaces. Responsive permeability has enormous potential in applications such as water and air purification. Responsive adhesives obviously will be used where a precise control over the adhesive strength of components in complex devices is needed. Responsive adhesives could also be beneficial in a variety of medical applications (e.g., fixing dental brackets). Actuators and shape memory materials on the other hand can be used in smart robotics. However, although the highlighted approaches show great promise, we foresee that the following issues and developments should be addressed before the full potential of interactive interfaces will be unlocked:

1. The durability of the interfaces should be enhanced, both intrinsically as well as the nanoscale switching process itself. Though many examples show impressive repeatability under controlled conditions, outliers to the testing conditions as well as conditions that exceed the scope of the study (but not that of the application) may irreversibly alter the interface. In particular, though the synergy between molecular components and surface structure yields impressive functionality changes, surpassing the threshold for wetting/delubrication of the interstructural space often results in irreversible property changes.

2. The selected stimuli should be practical and tailored to the application, where autonomous and self-regulating functionality is preferred but remains essentially unexplored. Additionally, although the potential use of multiple stimuli can be highly beneficial, care should be taken that these are cross-compatible, as well as that singly responsive interfaces
do not experience interference upon their practical application. For example, photoswitchable interfaces often have an inherent incompatibility with heat, as the barrier for thermal switching is finite, and at electrode interfaces the application of excessive potentials can in addition lower the local pH by solvent oxidation.

3. The large number of recent publications in the area of stimuli-responsive adhesives shows that there is a huge demand for such systems. In many applications, “gluing is preferred to screwing” and responsive adhesives would allow the easy exchange, repair and recycling of components in complex devices. We assume that this trend will continue and ultimately results in multiresponsive adhesives that offer even better and faster response, with substantial differences between addressable states being the optimal case. However, we believe that a distinct on/off switch between very strong adhesion and zero adhesion, specifically, will remain a challenge for the next few years.

4. Considering the high number of patterned systems in almost all applications covered, the increasing importance of the combination of responsive molecules and patterned interfaces is pertinent, i.e., moving from 2D to 3D structures. Moreover, by further downsizing the features greater responses could be achieved because of the increased surface area. Impressively, resolution can already be attained but creating responsive structure at the sub 10 nm range is still a challenging task. Here we see a prominent role for programmed assembly using DNA since a clever combination of DNA origami (including responsive units) and surface modification could lead to active interfaces (2D) and materials (3D) with molecular precision.

5. The active interfaces covered in this progress report are exclusively solid surfaces modified with immobilized responsive molecular components. This implies that responsive supramolecular rearrangements at the interface are limited, since the lateral mobility of the molecules at the interface is restricted. We expect that by taking inspiration from biological membranes, in which molecular components are continuously distributed, clustered and rearranged at various time scales, truly active interfaces, in which not only the local environment but also the cooperative behavior of molecular components is regulated, can be achieved. Needless to say, an optimal compromise of dynamic supramolecular assembly and interface stability will be a key challenge also in this approach.

Nevertheless, the scientific community has come a long way in closing the gap between principle and practice in the development of responsive surfaces. Using toolbox that is currently available, many highly interesting systems can and could be generated, limited only by the creativity and imagination of scientists. Furthermore, we believe that with ongoing research and development of new responsive molecular components, new and previously unimaginable applications can be realized.

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Conflict of Interest
The authors declare no conflict of interest.

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