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Supramolecular Velcro for Reversible Underwater Adhesion**

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Underwater adhesion is a challenging task for most synthetic adhesives. Efforts to overcome this challenge have largely focused on modifying natural molecules produced by marine organisms such as mussels, sandcastle worms, barnacles, and sea urchins.[1–4] In particular, the adhesive 3,4-dihydroxy-L-phenylalanine (DOPA) residue found in proteins secreted by mussels has been a popular inspiration for several synthetic underwater adhesives.[5–7] Although such biomimetic approaches can be powerful, synthetic materials that are able to achieve a similar function using orthogonal methods could be valuable alternatives. For example, most DOPA-based adhesives require curing agents that irreversibly cross-link the residues to the surfaces.[8,9] Efforts to achieve reversibility have largely been limited to the microscopic level.[10] We thus decided to investigate whether a synthetic system entirely unrelated to DOPA could achieve underwater adhesion and potentially overcome limitations, such as the lack of reversibility at the macroscopic level.

A major challenge in adhesion in an aqueous environment is how to repel the water molecules between the adhesive and adherend surfaces. The presence of water prevents direct chemical contact between them, and diminishes the surface energy of the adherend that provides the driving force for adhesion.[11] Because molecular recognition in aqueous media between a water-soluble host with a hydrophobic cavity and a guest molecule involves disposal of the water molecules to form a supramolecular complex,[12] we reasoned that supramolecular host–guest chemistry may be an ideal strategy for achieving underwater adhesion. However, most macrocyclic hosts exhibit only modest binding in water, as typified by cyclodextrins (CDs; association constant, $K_a \approx 10^6$).[13] To increase the binding strength, multivalent host–guest chemistry has thus been employed in developing functional materials.[14] Recently, specific and stimuli-responsive macroscopic recognition between CD-functionalized and guest-functionalized hydrogels has also been demonstrated.[15] However, strong underwater adhesion has never been explored with multivalent macrocylic host–guest chemistry owing, at least in part, to the relatively weak nature of the interaction. We presumed that a macrocyclic host–guest pair with much higher affinity would exhibit robust underwater adhesion based on multivalent interactions.

We and others recently discovered that cucurbit[7]uril (CB[7]), a member of the cucurbit[*n*]uril (CB[*n*], $n = 5$–8, 10) macrocycle family[16] with a hydrophobic cavity and two identical carbonyl-fringed portals, forms exceptionally stable host–guest complexes with aminomethylferrocene (Fc) and 1,1′-bis(trimethylammoniomethyl)ferrocene (BFc) in water, and their binding strength ($K_a \approx 10^{12}$ and $10^{15}\,\text{M}^{-1}$, respectively) is on par with that of a biotin-avidin complex.[17–20] We envisaged that multivalent interactions between a large number of host (CB[7]) and guest (Fc) molecules, microscopic supramolecular events en masse, may be used to achieve underwater adhesion, a macroscopic property. Furthermore, Fc is known to undergo oxidation and the resultant Fc^+ has much weaker binding affinity toward CB[7],[21] which can be exploited for chemically or electrochemically switchable adhesion.

Herein, we report the synthesis of supramolecular "velcro"—a new approach for achieving strong and reversible underwater adhesion based on the ultrahigh-affinity host–guest binding pair. Our strategy, using a velcro or "hook-and-loop fastener" type mechanism, involves functionalizing two separate silicon surfaces ([Si]): a "loop" surface functionalized with CB[7] hosts and a "hook" surface with Fc guests (Figure 1). The CB[7] loops and Fc hooks form a supramolecular velcro, which adheres in water without any need of curing agents. Our velcro exhibits excellent holding power and lap shear adhesion strength, which can be tuned by controlling the density of Fc hooks. Remarkably, our strategy offers both

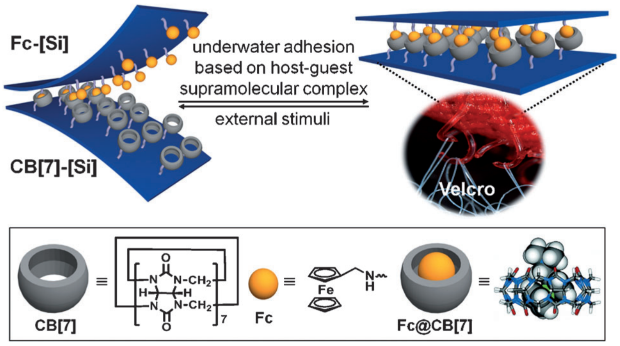

Figure 1. Supramolecular velcro or hook-and-loop strategy for underwater adhesion based on CB[7]- and Fc-modified surfaces. In an aqueous environment, the surfaces strongly adhere with each other through ultra-high affinity host–guest interactions, which is similar to commercial Velcro or hook-and-loop fastener (optical microscope image of commercial Velcro). The supramolecular velcro can be unfastened by mechanical and chemical means and fastened again.

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mechanical reversibility and chemical switchability at the macroscopic level.

We prepared the host- and guest-molecule anchored loop and hook surfaces of the supramolecular velcro by conjugating the CB[7] and Fc moieties, respectively, to the polymer grafted silicon surface [Si] (Figure 2). To begin with, hydroxy terminated silicon wafers were reacted with 3-glycidoxypropyltrimethoxysilane (3-GPTS) to obtain epoxy-functionalized surfaces (EP-[Si]). Subsequently, branched polyethyleneimine (bPEI) was allowed to react with EP-[Si] to impart multiple amine groups on the surface. Successful grafting of bPEI was evidenced by the appearance of new peaks at 400 eV corresponding to nitrogen (N 1s) using X-ray photoelectron spectroscopy (XPS; Supporting Information, Figure S1 a,b). From the bPEI-grafted surface (PEI-[Si]), the hook surface (Fc-[Si]) was prepared through an amine-aldehyde condensation reaction between ferrocenecarboxaldehyde and the primary amine groups of bPEI, followed by $NaBH_4$ reduction of the newly formed imine bonds. The conjugation of ferrocene was confirmed by XPS showing the $Fe2p_{2/3}$, $Fe2p_{1/2}$ peaks at 706 eV and 720 eV, respectively (Supporting Information, Figure S1 c,e). The loop surface (CB[7]-[Si]) was obtained in two steps from PEI-[Si]. Initially, the amine groups were allowed to react with ethylene sulfide to become thiol functionalized PEISH-[Si]. Subsequently, a thiol–ene click reaction was carried out with PEISH-[Si] and newly synthesized alkene-functionalized monoallyloxy-CB[7] ($(allyloxy)_1CB[7]$) (Supporting Information, Scheme S1) resulting in CB[7]-[Si]. In the XPS spectra, an intense N 1s peak appeared at 400 eV and two characteristic C 1s peaks at 288.2 eV and 289.6 eV, which correspond to the carbonyl group (N−C=O) and methylene bridge (N−C−N) of CB[7], respectively (Supporting Information, Figure S1 d,f).

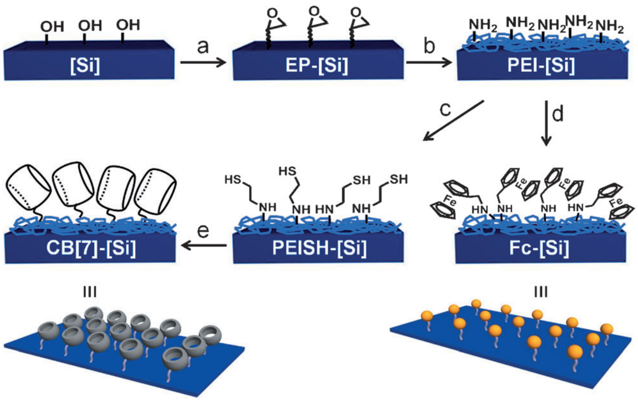

Figure 2. Preparation of CB[7]- and Fc-functionalized silicon surfaces. a) Incubation of hydroxy terminated [Si] in 3-glycidoxypropyltrimethoxysilane (3-GPTS) solution to give epoxy termini in EP-[Si]. b) Epoxide ring opening with branched-polyethyleneimine to give amine functionalized PEI-[Si]. c) Reaction with ethylene sulfide resulting in thiol-functionalized PEISH-[Si]. d) Anchoring of Fc groups by condensation with ferrocenecarboxaldehyde followed by reduction with $NaBH_4$, resulting in Fc-[Si]. e) Thiol–ene “click” reaction between $(allyloxy)_1CB[7]$ and PEISH-[Si] to give CB[7]-[Si]. Note that the schematic drawings of CB[7]-[Si] and Fc-[Si] are highly simplified and the actual structures of the PEI layers, wherein CB[7] and Fc anchored, are highly complex.

The newly fabricated surfaces were further characterized by various techniques. The thickness of the polymer adlayer of PEI-[Si] was approximately 2.2 nm, as measured by ellipsometry (Supporting Information, Figure S2). In Fc-[Si] and CB[7]-[Si], the thicknesses of the adlayer increased to 3.0 and 6.3 nm, respectively, approximately in proportion to their molecular sizes (0.49 nm for ferrocene and 1.6 nm for CB[7]). AFM analysis revealed that the surfaces of CB[7]-[Si] and Fc-[Si] are smooth (Supporting Information, Figure S3). Contact-angle measurements confirmed the wettability of the modified surfaces (Supporting Information, Figure S2). For a water droplet, CB[7]-[Si] and Fc-[Si] showed contact angles of 32(±1)° and 53(±1)°, respectively. The contact angle for CB[7]-[Si] may be attributed to the hydrophilic carbonyl groups of CB[7] attached on the surface. The amount of Fc in Fc-[Si] was found to be approximately $4.0\times10^{-9}\,mol\,cm^{-2}$, as analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). To quantify CB[7] on the surface of CB[7]-[Si], it was titrated with (ferrocenylmethyl)trimethylammonium iodide (FcA), which is known to form a tight host–guest complex with CB[7]. Subsequent ICP-AES analysis of the FcA-bound CB[7]-[Si] suggested that the amount of accessible CB[7] in CB[7]-[Si] was $0.83\times10^{-9}\,mol\,cm^{-2}$, approximately five times less than that of Fc molecules in Fc-[Si], which may be attributed to the large molecular volume of CB[7].

After the two surfaces were characterized, we proceeded to perform underwater adhesion experiments. Unlike most synthetic adhesives where water or moisture acts as a surface contaminant, our CB[7]-[Si] and Fc-[Si] surfaces in fact require an aqueous environment for adhesion because the expulsion of water is the driving force that induces the Fc hook molecules to be included into the loop of CB[7] by way of host–guest interactions. The two surfaces were immersed in water (pH 7.4), without any additional curing agents, and mechanically pressed together using fingers with a contact area of $1\times1\,cm^2$, which resulted in strong adhesion even under turbulent environments (Figure 3 a,b, also see the Supporting Information, Movie S1). The adhesion was enough to support a two kilogram weight plate attached to the supramolecular velcro (Figure 3 c) in water. The adhesion strength increased significantly upon air drying for 12 hours and the resulting velcro was able to withstand a four kilogram weight plate (Figure 3 d). The hanging power of our supramolecular velcro is far superior to that of typical commercial dry adhesives. We stuck together three pairs of silicon surfaces with different commercial adhesives and checked their holding power in the air. The resultant silicon surfaces adhered with commercial Velcro (3M #H&L), a double-sided foam tape (3M #2120), and a double-sided tape (3M #138) withstood only 0.2, 0.7, and 2.0 kg of weight plates, respectively (Supporting Information, Figure S4). We prepared six control experiments: 1) host- and guest-free surfaces (PEI-[Si]/PEI-[Si]) (Figure 3 e, also see Supporting Information, Movie S1), 2) either host or guest surface and an inert surface (CB[7]-[Si]/PEI-[Si], Fc-[Si]/PEISH-[Si]), 3) two host surfaces (CB[7]-[Si]/CB[7]-[Si]), 4) two guest surfaces (Fc-

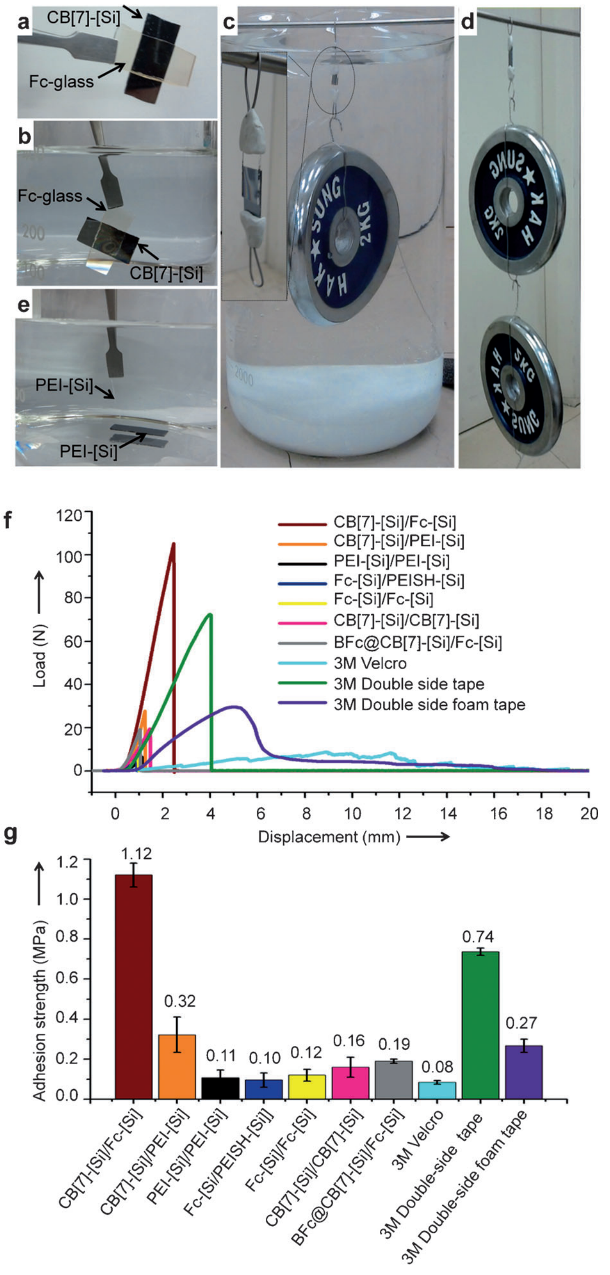

Figure 3. Characterization details of adhesion properties of the supramolecular velcro. a) Underwater adhesion of supramolecular velcro and b) its robust adhesion in a turbulent aqueous solution (see Movie S1). Holding power of supramolecular velcro c) in water and d) in the air after drying. e) Failure of adhesion in PEI-[Si]/PEI-[Si] that has no CB[7] or Fc components. f) Loading curves for supramolecular velcro (CB[7]-[Si]/Fc-[Si]), control experiment surface pairs, and commercial adhesives. g) Lap shear adhesion strengths of supramolecular velcro, control experiment surface pairs, and representative commercial adhesives. The experiments were repeated at least four times, and the error bars denote the standard deviations.

[Si]/Fc-[Si]), and 5) a host surface wherein most of the cavities of CB[7] are occupied with guest molecules (BFc) that have higher affinity than Fc and a guest surface (BFc@CB[7]-[Si]/Fc-[Si]). They all failed to adhere under water readily.

To precisely quantify the adhesion strength of the supramolecular velcro (CB[7]-[Si]/Fc-[Si]), we performed lap shear adhesion experiments. We prepared the samples of the supramolecular velcro (CB[7]-[Si]/Fc-[Si]) and pairs of control surface-modified substrates in the following sequence for the analysis: 1) immersing the substrates in water (pH 7.4) to become well hydrated, 2) pressing them (1×1 cm^2) under water with a clamp (approximately 2 N), 3) removing the clamp after one hour adhesion time, and 4) drying them at room temperature for 12 hours. We carefully clamped the samples in a machine to test tensile strength and measured the force to pull apart the sample pair at the rate of 1 mm s^{-1} in a lap shear mode (Figure 3 f), and the adhesion strengths were obtained by dividing the maximum load at the failure point by overlap area (Figure 3 g). The maximum lap shear strength of the supramolecular velcro was 1.12 ± 0.06 MPa, which is in the realm of high-adhesion strength,[22,23] whereas the control experiment surface pairs showed much weaker adhesion strength (Figure 3 g). The significant difference in lap shear adhesion strength between the supramolecular velcro and all six control experiment surface pairs clearly confirmed that the strong underwater adhesion of the former is mainly due to specific multivalent host–guest binding between CB[7] and Fc from their respective surfaces. The superiority of the supramolecular velcro (CB[7]-[Si]/Fc-[Si]) in comparison with commercial dry velcros was reflected in lap shear adhesion strength as well: silicon surfaces adhered with the commercial Velcro, double-sided foam tape, and double-sided tape (see above) exhibited lap shear adhesion strength of 0.08 ± 0.01, 0.27 ± 0.03 and 0.74 ± 0.02 MPa, respectively.

Although it is difficult to directly compare with other adhesives owing to the many variables involved in each adhesive system, the adhesion strength of supramolecular velcro is on par with other biomimetic adhesive polymers. For example, mussel-mimetic adhesives such as poly(lysine-DOPA) ($M_n \approx 98\,000$)[24] and poly[(3,4-dihydroxystyrene)-*co*-styrene] ($M_n \approx 16\,000$)[23] showed adhesion strengths of 1.5 and 1.2 MPa, respectively, comparable to the strength of our synthetic adhesion pair. Similarly, under wet conditions, the supramolecular velcro exhibited a lap shear adhesion strength of 0.34 ± 0.25 MPa without drying, which is comparable to 0.29 MPa[1] of mussel adhesive plaques and 0.40 and 0.77 MPa of mussel-mimetic materials.[25,26] Importantly, though, these biomimetic adhesives require further oxidizing agents, which are cytotoxic for biomedical applications, under wet conditions, which our adhesive surfaces do not.

Having established the high adhesion strength of the supramolecular velcro, we reasoned that if the multivalent host–guest interactions between CB[7] and Fc are responsible for the adhesion strength, it may be possible to tune this property by varying the amount of hooks relative to the loops. To test this hypothesis, we assembled different supramolecular velcros with a varying concentrations of Fc on the Fc-[Si]; we prepared a series of Fc-[Si] surfaces by immersing five different PEI-[Si] surfaces into twofold serially diluted ferrocenecarboxaldehyde solutions (2.5 mM to 0.125 mM), followed by ICP-AES analyses to confirm the Fc content of each modified Fc-[Si] surface. The amount of Fc attached to Fc-[Si], which varied from 0.3×10^{-9} to 4.0×10^{-9} mol cm^{-2}, was in a direct correlation with the concentration of ferrocencecarboxaldehyde in the solution (Supporting Information, Figure S5). Subsequently, the newly prepared Fc-[Si] surfaces were adhered to CB[7]-[Si] prepared with the same concentration (0.83×10^{-9} mol cm^{-2}), independently. The resultant lap shear adhesion strengths, after drying, are in proportion to the amount of Fc in the Fc-[Si] (Figure 4 a). This result not only confirmed that the adhesion strength is tunable, but also proved that multivalent supramolecular interactions are indeed responsible for the underwater adhesion.

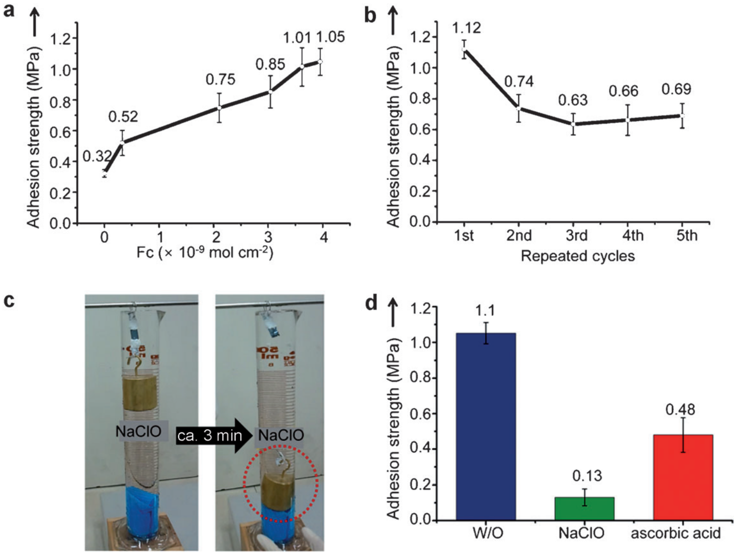

Figure 4. Characterization details of the tunable and reversible adhesion properties of the supramolecular velcro. a) Tunability of the adhesion strength by varying the amount of the Fc moiety attached on the surface. The amount of CB[7] in all CB[7]-[Si] surfaces was 0.83×10^{-9} mol cm^{-2}. b) Reversibility of supramolecular velcro by mechanical means and c) the detachability of supramolecular velcro with an oxidizing reagent (NaClO, 10 mM). d) The reversibility of supramolecular velcro by chemical means (W/O = without any additional reagents).

Finally, we decided to investigate the reversibility of our supramolecular velcro. The first type of reversibility we considered was mechanical reversibility or reusability; that is, how robust our adhesives are to repeated fastening and unfastening. Such reversibility is one of the critical traits of a velcro being considered for applications requiring the reversible binding of components. Our experiments confirmed that the supramolecular velcro can be unfastened by mechanical means with a tensile force, refastened readily under water, and the cycle can be repeated over several times. The lap shear adhesion strength of the refastened velcro was approximately 70 % of that of the freshly adhered velcro. Even though some loss of adhesion strength occurred after the first cycle, the adherence was retained in subsequent cycles (Figure 4 b). The reason for the reduction in adhesion strength is not known at present, but may be attributed to some structural changes or deformation of the grafted polymer layer, which may alter the surface roughness.

In addition to mechanical reversibility (robustness to fastening and unfastening), our adhesive pair demonstrates chemical switchability; by taking advantage of the redox-active behavior of Fc we can fasten and unfasten the velcro by chemical means. Such switchable adhesion is a noteworthy function, which can offer control over the stickiness on demand. When a supramolecular velcro (CB[7]-[Si]/Fc-[Si]) assembled under aqueous condition was immersed in an NaClO (10 mM) solution with a 0.5 kg weight, the two surfaces came apart in a few minutes. This was due to the oxidation of Fc into Fc$^+$, with which CB[7] has much lower binding affinity (Figure 4 c). To demonstrate the reversibility, the Fc$^+$-[Si] was reduced back to Fc-[Si] by immersing the surface in ascorbic acid (20 mM) for one hour and the retention of adhesion in water was examined by adhering it with CB[7]-[Si]; the supramolecular velcro held the 0.5 kg or even 1.0 kg for at least one hour. This was further confirmed with lap shear adhesion experiments between Fc$^+$-[Si]. When a Fc-[Si] immersed in aqueous NaClO (10 mM) was adhered to CB[7]-[Si] in water and subsequently dried for 12 hours, the shear strength was measured to be 0.13 ± 0.05 MPa. Once the Fc-[Si] surface was reduced back from Fc$^+$-[Si], the resulting adhesive pair with CB[7]-[Si] gave a shear strength of 0.48 ± 0.10 MPa (Figure 4 d). The incomplete recovery of adhesion strength (44 %) in comparison with that of virgin Fc-[Si] may be attributed to decomposition of Fc$^+$ or adsorption of a minute amount of contaminants from the added chemical reagents. If so, an electrical field might offer a more efficient alternative to a chemical redox agent for switchable underwater adhesion.

Our supramolecular velcro based on the host–guest interactions between CB[7]-[Si] and Fc-[Si] offers a new strategy for achieving mechanically reversible and chemically switchable macroscale underwater adhesion. Unlike mussel-mimetic adhesives, it does not rely on any external curing agents, apart from water, for underwater adhesion. The non-cytotoxic nature of CB[7][27] and Fc[28] permits potential biological applications. In addition, the redox-active nature of the Fc moiety is promising for the development of electroactive adhesive materials. As a corollary, we believe that replacing Fc with aminoadamantane derivatives, which also have similar ultrahigh affinity with CB[7],[18] would offer yet another alternative underwater adhesive system, robust enough to withstand strong oxidizing agents. We believe that the general versatility of our design will make our strategy potentially useful for a wide range of applications that require controllable adhesion in aqueous environments.

Experimental Section

Preparation of modified surfaces, Fc-[Si]: The PEI-[Si] (see Supporting Information) surface was reacted with ferrocenecarboxaldehyde (5.3 mg, 25 μmol) in ethanol (10 mL) at 60 °C for 6 h. The surface was then washed with ethanol and isopropyl alcohol (IPA) and immersed in a solution of sodium borohydride (0.1 mM) in methanol for 1 h. Subsequently, the newly obtained Fc-[Si] was washed with methanol, water, and IPA several times, and air dried at room temperature. Preparation of CB[7]-[Si]: The PEISH-[Si] (see Supporting Information) surface was placed in a water/acetonitrile (80:20, 4 mL) solution of (allyloxy)$_1$CB[7] (1.5 mg, 1.2 μmol) and tris(2-carboxyethyl)phosphine (2.5 mg, 10 μmol) in a quartz tube. The tube was closed with a rubber septum, degassed with Ar and irradiated in a photoreaction chamber for 3 h. Subsequently, the surface was washed with deionized water to obtain CB[7]-[Si].

Measurement of lap shear adhesion strengths: Adhesion strengths were determined using the tensile mode of a texture analyzer, TA-XT2i (Stable Micro System Ltd.), equipped with a 250 N load cell. The crosshead speed was set to 1 mm s^{-1} in tensile mode to obtain the load-displacement curves (Figure 3 f). The adhesion strength, in pascals (Pa = N m^{-2}), was determined by dividing the load (N) corresponding to the breaking points by an adhesion area (m^2).

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