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Fusing Catechol-Driven Surface Anchoring with Rapid Hetero Diels–Alder Ligation

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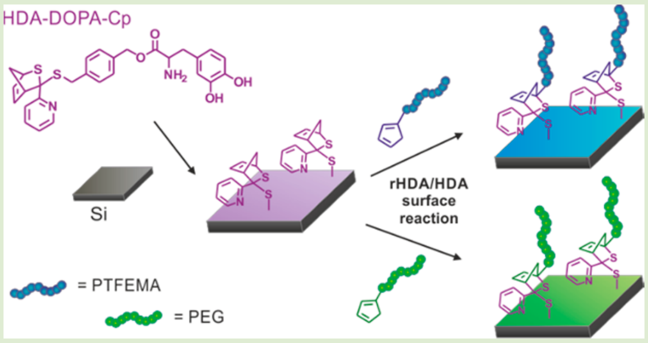
Supporting Information

ABSTRACT: We fuse the surface anchoring abilities of catechols with the rapid ligating nature of thiocarbonyl thio-based hetero-Diels–Alder (HDA) reactions via the synthesis of a new small molecule (HDA-DOPA-Cp) combining a HDA moiety with a catechol. Inspired by the mechanism of strong adhesion of marine mussels, we employed catechols as anchors to attach HDA ligation points to silicon wafers. The latter was exploited to generate a base for the HDA reactions on the surface employing α-cyclopentadiene (Cp) functional polymers such as poly(ethylene glycol)-Cp (PEG-Cp) and poly(trifluoro ethyl methacrylate)-Cp (PTFEMA-Cp) as dienes. By utilizing the fast and efficient HDA chemistry in combination with catechol anchoring groups, a new method for creating functional surfaces was developed.



To cope with the need for novel functional materials for information technology, material science, biomaterials, electronics, nanotechnology, biosensing, life sciences, and medicine, an enormous amount of synthetic methods have been developed.[1−4] The function of (bio)materials is typically endowed by precisely engineered modifications of its surface. These modifications are dictated by its intended application. Typically, a film of a few nanometers can radically change the properties of the material and its applicability.[5] Thus, techniques able to control modifications at the nanoscale emerged. Typical examples include self-assembling monolayers of silanes on oxides or alkanethiols on gold, chemical vapor deposition (in its different variants), growth of polymer brushes as well as various lithographic techniques, such as colloidal lithography.[6] The range of techniques available for the material chemist allows the modification of even more complex surfaces or substrates such as cellulose fibers. By mimicking the adhesive protein of some bivalves, a new type of surface coating enabled to access the modification of even substrates with low surface energy and non-amenable to functionalization.[7−14] The latter technique exploited the ability of dopamine to self-polymerize in slightly alkaline solution to generate continuous films able to adhere to virtually any surface.[15] Thus, this unmatched ability later merged with advanced polymer chemistry and ligation techniques to provide excellent tools to tailor surfaces' properties.[16−19] The surface modification with desired polymer strands can be either performed via a "grafting-from" or a "grafting-to" approach.[20] In the former, the polymers are grown from surface-bound initiators (or chain transfer agents) by controlled polymerization techniques such as ring-opening polymerization (ROP),[21,22] atom transfer radical polymerization (ATRP),[8−10,13] reversible addition-fragmentation chain transfer (RAFT) polymerization,[23,24] and single electron transfer living radical polymerization (SET-LRP) among others.[25,26] In the grafting-to approach, the previously prepared polymer chains are attached to the surfaces via various methods.[14,27−29] Grafting-to offers a series of advantages in the control of the surface modification. The chains to be tethered can be characterized in detail via variable techniques before grafting.[20] Typically, more narrow distributions of molecular weight can be achieved in solution polymerization and these chains can be subsequently grafted to surfaces.

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Conventional anchoring molecules are based either on functional silanes (for silicon and other oxide surfaces) or thiols that attach to metals such as Au and Ag.[30] The use of silanes has been widely applied; however, recent studies have called into question their stability.[31,32] Klok and co-workers have shown that when long polymer chains tethered to the surface are placed in a good thermodynamic solvent, the imposed osmotic pressure is able to cleave the chains from the surface. This is also in agreement with previous studies evidencing that silane layers could be unstable when forming multilayers.[33−35] Thiol-based chemistry, on the other hand, is highly specific (only Au and Ag) and yields surfaces, which are not stable at temperatures higher than 60 °C nor in the presence of other functional thiols, which can perform ligand exchange.[36] These findings have driven the attention toward more versatile linkers. Arguably, catechols stand as one of the most versatile linkers to provide strong anchors to a large number of substrates.[10,16]

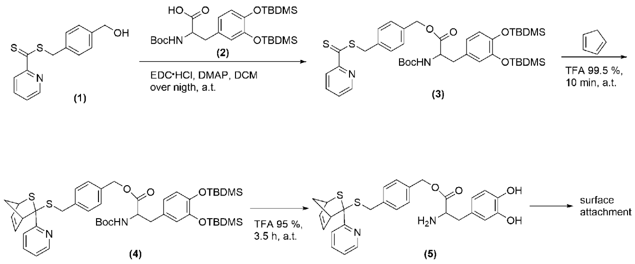
Due to their naturally rough environment, marine mussels possess the extraordinary ability to adhere to a wide variety of materials such as rocks, wood, ship coatings, or metals and remain there even under harsh conditions.[37,38] These strong adhesion properties are linked to the presence of 3,4-dihydroxy phenylalanine (DOPA) units presented in at least six adhesive peptide subtypes, the *Mytilus edulis* foot protein 1-6 (Mefp 1-6).[16,39] The highest concentration of DOPA units was found in Mefp-3 (20 mol %) and Mefp-5 (30 mol %), which are located in the plaque at the mussels distal ends near the plaque-substrate interface.[16,39,40] The finding and understanding of the strong adhesion properties of the adhesive produced by these mussels turned the attention of several researchers to employ the catechol units of DOPA, or dopamine (the decarboxylated derivative of DOPA), as anchor molecules on either inorganic substrates, organic substrates, and even in inorganic nanoparticles.[11,12,16]

Our research group recently published several approaches featuring ligation techniques on surfaces employing DOPA and dopamine derivatives that carry a suitable moiety to perform either thermal- or photoinitiated (photoenol) Diels−Alder conjugation with cyclopentadiene- or maleimide-carrying polymer strands, respectively.[17,18] In the present study, we fuse rapid Diels−Alder ligation protocols with catechol driven surface attachment.

However, the ability to bind to a particular surface is only one of the steps to engineer a surface. Equally important is the ability to design the architecture of the molecules at the surface by starting from well-defined building blocks. In this regard, we adopted the rapid, facile and reversible hetero-Diels−Alder (HDA) ligation abilities of specially activated dithioester moieties, for our novel surface modification method. The concept of HDA ligation was introduced by Barner-Kowollik and Stenzel in 2008 in the context of RAFT-HDA conjugation.[41] RAFT-HDA has proven to be a powerful tool as it combines the excellent control and pseudolivingness achievable by RAFT with an inherent ligation technique.[41−44] While RAFT accounts for the preparation of narrowly disperse polymers, HDA chemistry accounts for a facile and reversible way to link polymers and build complex architectures. The concept of thiocarbonyl thio HDA chemistry is based on the fast conjugation of activated C═S double bonds (that are also present in specifically designed RAFT chain transfer agents) with dienes such as cyclopentadienes (Cp) or 1,3-butadienes.[41−44] The degree of activation of such a C═S double bond in a dithioester moiety, which is responsible for the HOMO−LUMO interaction, depends strongly on the electron withdrawing character of the group attached to the carbon at the C═S bond (referred to as Z-group). Frequently employed Z-groups for the improvement of HOMO−LUMO interaction in HDA conjugations are phosphoryl- or pyridinyl-moieties, which are activated by Lewis acids, such as zinc chloride ($ZnCl_2$), or Brønsted acids, such as trifluoroacetic acid (TFA).[41] Remarkably, this ligation technique has been recently demonstrated even in aqueous media.[45]

Herein, we introduce a novel strategy to reversibly decorate surfaces with precisely designed polymer strands by fusing fast HDA ligation with catecholic anchor surface attachment, inspired by the strong adhesion abilities of marine mussel byssus, to generate a new surface functionalization that operates (i) fast and (ii) efficient. For this purpose, a new HDA capable agent that carries a DOPA-unit (namely, HDA-DOPA-Cp (**5**)) and exhibits a Cp-protected dithioester-moiety to avoid nucleophilic attack within the surface attachment step, was designed. By employing the catechol group, the HDA-DOPA-Cp (**5**) was attached to silicon wafers and underwent a one-pot retro-HDA (rHDA)/HDA cycle to tether polymer chains bearing a Cp functionality at the α-end (Scheme 2). In a second step, α-cyclopentadienyl-poly(ethylene glycol) (PEG-Cp) and α-cyclopentadienyl-poly(trifluoro ethyl methacrylate) (PTFE-MA-Cp) were grafted to the surface. The rate of the conjugation was assessed by model studies in solution using UV/vis spectroscopy. The optimized conditions were subsequently utilized for the surface modification. The success of the conjugation was monitored by X-ray photoelectron spectroscopy (XPS) and ellipsometry. In addition, it was found that the newly designed RAFT agent (protected, HDA-DOPA-TBDMS$_2$-Boc (**3**)) could enable controlled RAFT polymerization as evidenced by a linear evolution of M_n with conversion (refer to the Supporting Information section).

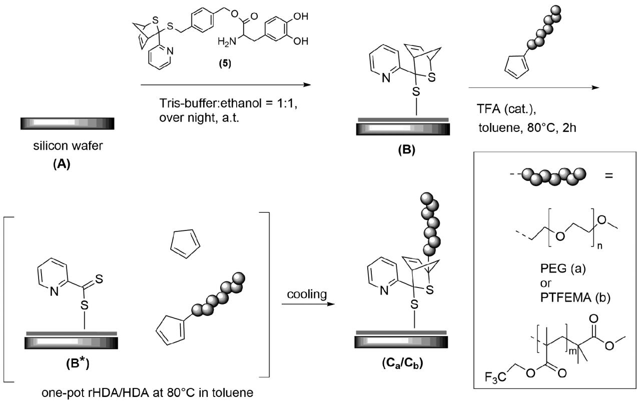
Scheme 1. Reaction Sequence for the Synthesis of HDA-DOPA-Cp (5)[a]



[a]HDA-DOPA-TBDMS$_2$-Boc (**3**) was synthesized by EDC-coupling of Dithio−OH (**1**) and DOPA-TBDMS$_2$-Boc (**2**) at ambient temperature. Subsequently, the dithioester moiety of (**3**) was protected employing HDA ligation with cyclopentadiene (Cp) and TFA catalysis. Next, the −OH and −NH_2 moieties were deprotected by exposing (**4**) to TFA (95%) for 3.5 h to achieve HDA-DOPA-Cp (**5**), which was attached to plasma cleaned Si wafers immediately.

To create a surface technique that combines the strong adhesion properties of catechol anchors of DOPA and HDA ligation, we developed a new molecule that exhibits both functionalities. The full reaction sequence of the synthesis of HDA-DOPA-Cp (**5**) is depicted in Scheme 1. A Dithio−OH (**1**), capable of performing HDA ligation at ambient temperature was employed in an EDC-coupling reaction with

Scheme 2. Detailed Schematic Representation of the Surface Attachment of HDA-DOPA-Cp (5) on a Silicon Wafer (A) and the following retro-HDA/HDA One-Pot Reactions (B*) to Form Surfaces that carry different Polymers (C_a/C_b)[a]



[a]The Cp polymers employed are poly(ethylene glycol)-Cp (PEG-Cp) (M_n = 2200 g·mol^{-1}) (a) and poly(trifluoro ethyl methacrylate)-Cp (PTFEMA-Cp) (M_n = 5200 g·mol^{-1}) (b).

protected DOPA (DOPA-TBDMS$_2$-Boc (**2**)) to achieve HDA-DOPA-TBDMS$_2$-Boc (**3**). The new molecule (**3**) was characterized by ^{1}H and ^{13}C NMR spectroscopy (Figures S1 and S2), ESI-MS evidencing the expected mass (m/z [M-Na$^+$]$_{exp}$ = 805.42; Figure S5), and UV/vis spectroscopy with an absorption maximum at λ_{max} = 348 nm (Figure 1). The observed pink color of (**3**) is common for such pyridinyl-dithioesters and originates from the C═S double bond.

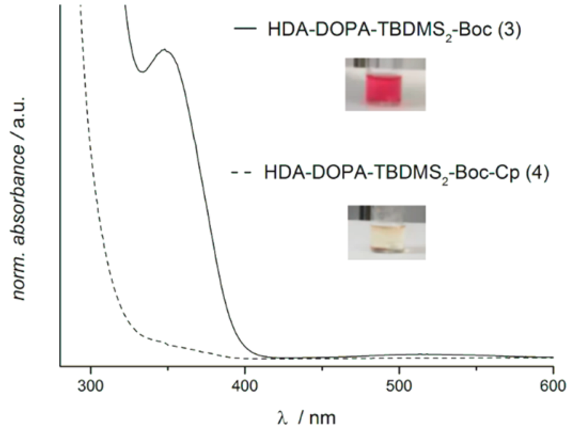


Figure 1. UV/vis spectra of HDA-DOPA-TBDMS$_2$-Boc (**3**) and HDA-DOPA-TBDMS$_2$-Boc-Cp (**4**). HDA-DOPA-TBDMS$_2$-Boc (**3**) depicts a maximum at λ_{max} = 348 nm (C═S double bond), whereas HDA-DOPA-TBDMS$_2$-Boc-Cp (**4**) does not show any extinction due to the protection of the C═S double bond. The color change from pink (**3**) to colorless (**4**) is also depicted.

In the following HDA reaction, which was performed to protect the C═S double bond from a nucleophilic attack during the subsequent surface attachment, (**3**) was conjugated with Cp under TFA catalysis to obtain HDA-DOPA-TBDMS$_2$-Boc-Cp (**4**). The reaction occurred within seconds. The rapid nature of this reaction can be readily observed by the loss of the pink color of the solution (Figure 1 and Video 1). Accordingly, the absorption maximum of (**3**) at λ_{max} = 348 nm in the UV/vis spectrum was not detectable for (**4**) and is, thus, additional evidence for the successful HDA ligation. The shift in the ^{13}C NMR of the carbon atom in the dithioester-moiety −S−C═S from 226.02 ppm (Figure S2) to 75.75 ppm (Figure S4) after the HDA reaction (−S−C−S−) further underlines the findings as well as the ESI-MS results (m/z [M-Na$^+$]$_{exp}$ = 871.08; for detailed spectra refer to the SI).

In preparation for the HDA ligation reactions with polymers on the surfaces, we performed a UV/vis absorption versus time experiment in solution, depicting the fast conjugation of (**3**) with a Cp-carrying polymer, namely, PEG-Cp (Figure 2). The absorbance decreases rapidly within the first 2 min. The reaction was finished within 10 min.

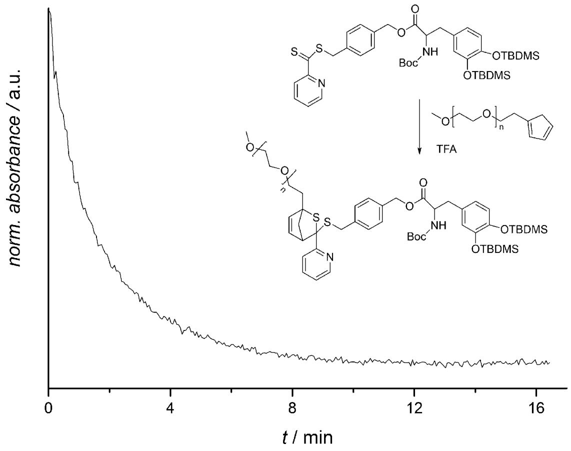


Figure 2. Absorption (at λ_{max} = 348 nm) vs time UV/vis spectrum of the HDA ligation reaction between HDA-DOPA-TBDMS$_2$-Boc (**3**) and PEG-Cp. Full conversion is achieved within 10 min.

After optimizing the conditions in solution, the ligation strategy was transferred to the surface of the silicon wafers as depicted in Scheme 2. First, the Boc- and TBDMS-moieties of (**4**) were removed in 95% TFA in 3.5 h to provide HDA-DOPA-Cp (**5**) to allow its immobilization to silicon surfaces. In the ESI-MS spectrum, the corresponding masses were detected at m/z [M-Na$^+$]$_{exp}$ = 543.00 and m/z [M-H$^+$]$_{exp}$ = 521.00.

HDA-DOPA-Cp (**5**) was subsequently attached to plasma-cleaned silicon wafers (A) in a mixture of ethanol:Tris-buffer =1:1 at ambient temperature. The surfaces (B) were further employed in a one-pot rHDA/HDA reaction with PEG-Cp (M_n = 2200 g·mol^{-1}; a) or PTFEMA-Cp (M_n = 5200 g·mol^{-1}; b), respectively. The substrates (B) were placed in a Schlenk tube, containing the appropriate Cp-polymer in toluene and a catalytic amount of TFA, and heated to 80 °C. At this temperature, the rHDA reaction occurs, freeing the Cp and regenerating the C═S double bond (B*) able to conjugate Cp-containing polymers upon cooling. We recorded a video to demonstrate the rDA reaction in solution, monitoring the color change that occurs when the C═S double bond is freed, which operates within 1 min after heating to 80 °C (see SI and Video 2). The temperature was maintained at 80 °C for 2 h to ensure the complete evaporation of the Cp (bp 40 °C) and prevent competing reactions between the freed Cp and the Cp-polymers in the HDA reaction during the cooling down cycle. After the HDA conjugation, the surfaces (C_a; PEG) and (C_b; PTFEMA) were characterized via XPS and ellipsometry. In order to confirm that the surface attachment was performed via HDA ligation and not simply by adsorption, we also employed non-Cp-carrying polymers as control samples, namely, PEG(-OMe)$_2$ and PTFEMA-Br, which underwent the same conditions also in the presence of a substrate (B).

The C 1s XPS spectrum of the resulting surface after PEG-Cp attachment (C_a) via HDA conjugation onto the HDA-DOPA-Cp surface (B) depicts a strong signal at 286.6 eV, which can be clearly assigned to the C−O bond of the additional PEG units that were attached (Figure 3).[17]

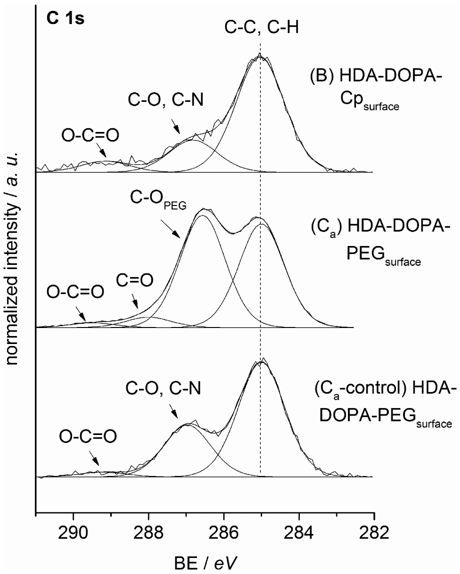


Figure 3. C 1s XPS spectrum of the surface before (B) and after a HDA conjugation with PEG-Cp (C_a). The intense peak assigned to the C−O bonds of PEG at 286.6 eV confirms the attachment.[17] The spectrum of the substrate from the control sample experiment (C_a-control) evidences that the HDA ligation only occurs in the presence of Cp-carrying polymers.

Furthermore, the control experiment (C_a-control) underlines that no adsorption occurred as there was no PEG detected. These findings were also confirmed by ellipsometry measurements, which show an increase of close to 9 nm of thickness on (C_a) compared to (B) and (C_a-control).

In order to confirm the HDA conjugation of PTFEMA-Cp with dithioester groups attached to the substrate (B), the C 1s and the F 1s spectra of (C_b) were compared to (B) and the corresponding control experiment (C_b-control; Figure 4). The C 1s spectrum of (C_b) shows the appearance of an additional peak at 293.2 eV that can be assigned to the $-CF_3$ moiety in the polymer backbone of PTFEMA.[14] In addition, the F 1s spectrum of (C_b) also depicts a signal at 688.8 eV which further confirms the attachment.[14] Furthermore, the ratio of the amount of carbon of the $-CF_3$ moiety in the C 1s and the amount of fluorine in the F 1s was found to equal 1:3 (1 × C: 3 × F) and, therefore, underlines the previous results. The spectra (C 1s and F 1s) of the control experiment (C_b-control) show no attachment of PTFEMA. It is worth noting that the ellipsometry measurements showed an increase in thickness of (C_b) compared to (B) and (C_b-blind), but not as strong as for the PEG-chains, which is most likely caused by steric hindrance in the PTFEMA backbone.

As noted, HDA-DOPA-TBDMS$_2$-Boc (**3**) possesses an additional feature, in particular its ability to control RAFT polymerizations. In a kinetic study, we employed (**3**) in bulk polymerizations with either styrene or *iso*-bornyl acrylate at 60 °C using AIBN as initiator. The controlled character of the styrene RAFT polymerization was verified by the linear evolution of M_n (SEC) with conversion (Figure S8). For figures and experimental data refer to the SI.

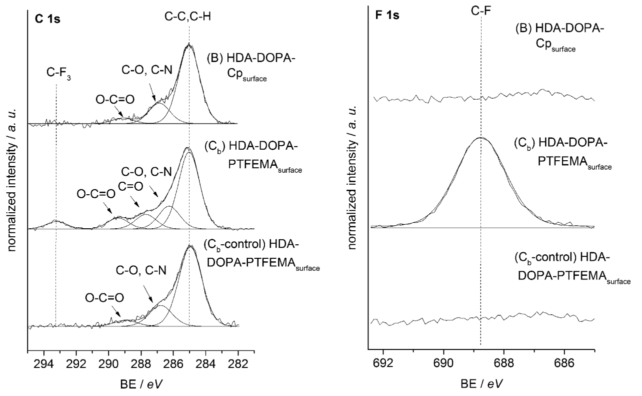


Figure 4. C 1s (left) and F 1s (right) XPS spectra of the surface before (B) and after HDA conjugation with PTFEMA-Cp (C_b). The appearance of the signal assigned to the $-CF_3$ group in the C 1s spectrum at 293.2 eV, as well as in the F 1s spectrum at 688.8 eV verifies the successful HDA conjugation. The spectrum of the substrate of the control sample experiment (C_b-control) approves that the HDA ligation only occurs with Cp-carrying polymers.

In summary, we fuse the ease of catechol anchoring on surfaces with rapid HDA ligation chemistry via a catechol functional activated dithioester moiety capable of performing fast conjugation in solution and on surfaces. As the attachment of the HDA-DOPA-Cp molecule functions under mild conditions—at ambient temperature and in an ethanol—water mixture, and as the HDA conjugation is feasible at ambient temperature, this modular ligation method in combination with the strong adhesion properties can be envisioned as a promising route for fields where versatile surface modifications are required.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

All syntheses, experimental characterization methods, and instrument data, the spectra that where referred to in the main text and the details of the chemical reactions of the videos. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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