Supporting Information for:

Biofunctionalization of a “Clickable” Organic Layer Photochemically Grafted on Titanium Substrates

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Content

1. Control experiments for the photochemical grafting of TMG-C10 on TiO_2

In this control experiment, we attempt to test whether alkyne will attach to the TiO_2/Ti substrate via UV-irradiation, and more importantly, to prove that the TMG group offers a strong protection for the terminal alkyne.

Two compounds (**S1** and **S2**) were employed, and their synthetic protocol was demonstrated in Scheme S1. As for the modification of Ti substrate, both of the reactants were subjected to the same conditions (including rinsing) as described for **TMG-C10** in the main body of paper. Figure S1a shows a freshly cleaned Ti sample. A weak and broad C 1s signal was observed, which was attributed to the traces of contamination or “adventitious carbon”. Figure S1b shows a sample that was in contact with liquid **S1** and illuminated with 254 nm UV light for 4 h. It clearly indicates a significantly increase of C 1s area and a slightly reduction of the Ti 2p peak. On the other hand, the photografting of **S2,** in which both of alkyne termini were protected by TMG, yielded a surface with the carbon and titanium contents very close to the pristine Ti substrate (Figure S1c). Moreover, there was no detectable feature for Ge 3d signal on the substrate. Consequently, we conclude that unprotected triple bond can readily attach on the Ti substrate and TMG group offers a strong protection for the alkyne functionality.

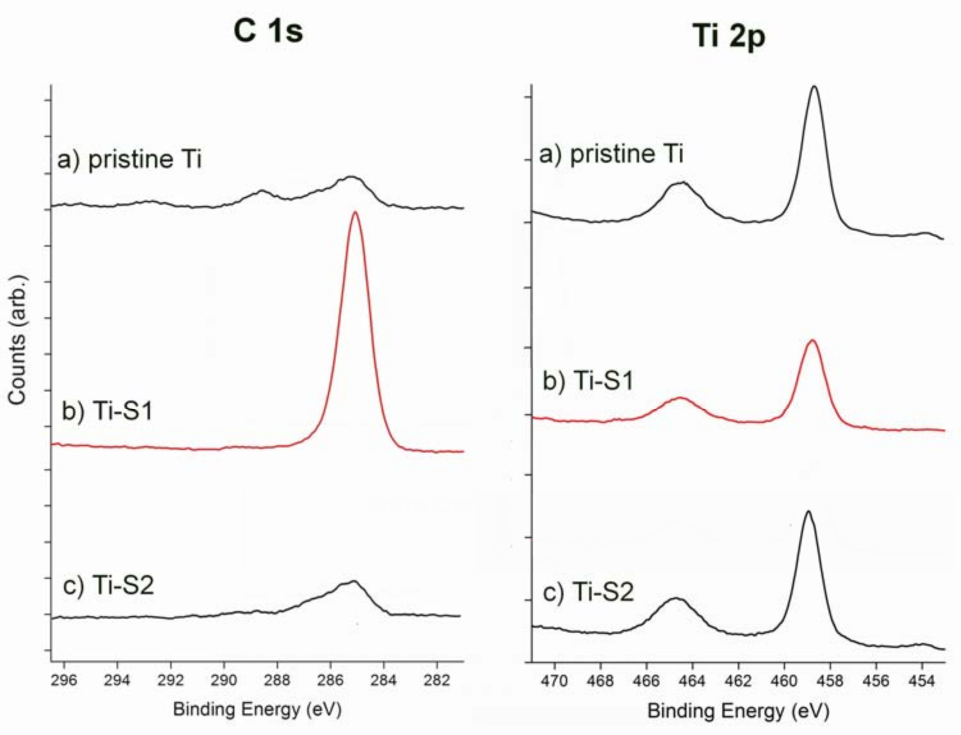
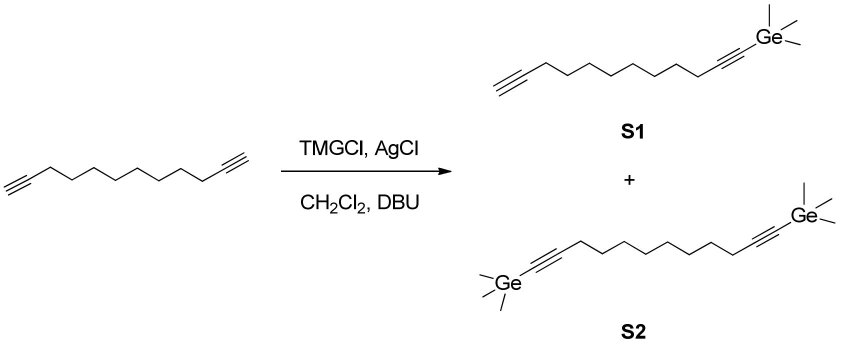


Figure S1. C 1s and Ti 2p XPS spectra of the control samples: a) pristine Ti substrate, b) Ti substrate exposed to **S1**, and c) Ti substrate exposed to **S2**. All samples were illuminated with UV light for 4 h and were rinsed as described in the main body of the paper.

2. Synthetic protocols for the TMG-protected alkynes (S1 and S2)



Scheme S1. Synthetic protocols for the TMG-protected alkynes.

S1

DBU (360 μL, 2.4 mmol) was gradually added to a solution of 1,11-dodecadiyne (345.1 mg, 2 mmol) and AgCl (57 mg, 0.4 mmol) in anhydrous CH_2Cl_2 (10 mL). After the mixture was stirred for 2 h at room temperature, TMGCl (288 μL, 2.4 mmol) was added dropwise. The resulting solution was stirred for another 24 h at room temperature before evaporated under vacuum. The residue was dissolved in hexane (10 mL) and extracted with brine twice. The organic layer was dried over anhydrous $MgSO_4$, and purified by silica gel column (eluent: hexane) to afford **S2** (205 mg) as colorless oil. Yield: 37%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.31 (s, 9 H), 1.24-1.42 (m, 8 H), 1.44-1.56 (m, 4 H), 1.93 (t, 1 H, *J*=2.1 Hz), 2.14-2.22 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 0.07, 18.48, 19.92, 28.54, 28.77, 28.90, 29.04, 68.17, 83.97, 84.85, 106.25; EI-MS: *m/z* 265 [M-CH_3], 159 [M-$Ge(CH_3)_3$].

S2

The synthetic protocol of **S2** is similiar to that of **S1**, except 2.5 equivalent of TMGCl was used in the reaction. Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.31 (s, 18 H), 1.21-1.40 (br. s, 8 H), 1.49-1.52 (m, 4 H), 2.22 (t, 4 H, *J*=7.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 0.07, 19.86, 28.52-29.07 (m), 68.17, 84.17, 106.31.

3. Density estimation for the click immobilized OEG component via SAM formation on Au(111) as a reference

Taking advantage of a CF_3-terminated SAM on Au substrate, the surface density of compound **2a** ($D_{CF3\text{-}Ti}$) introduced via the one-pot click coupling can be calculated by the following equation:

$$D_{CF3\text{-}Ti} = D_{CF3\text{-}Au}\, A_{F\text{-}Ti} / A_{F\text{-}Au} \qquad (1)$$

where $D_{CF3\text{-}Au}$ is the density of **CF_3-C13-SH** absorbed on the Au (111) substrate (4.63×10^{14} molecules/cm^2 for the well-defined self-assembly monolayer[1]).

$A_{F\text{-}Ti}$ and $A_{F\text{-}Au}$ is the integrated area of F 1s peak obtained from XPS measurements for modified Ti surface and the reference Au (111) substrate, respectively. The two samples (TiO_2/Ti and Au substrates) were placed side by side on a single sample holder to ensure identical XPS alignment. The F atoms were assumed on top of the organic layers for both substrates, and no inelastic scattering effect was considered in the calculation.

After 4hrs CuAAC reaction between the TMG-acetylene functionalized surface and compound **1a**, the ratio of $A_{F\text{-}Ti}$ to $A_{F\text{-}Au}$ equals to 0.49, thus $D_{CF3\text{-}Ti}$ is estimated to be 2.27×10^{14} molecules/cm^2,

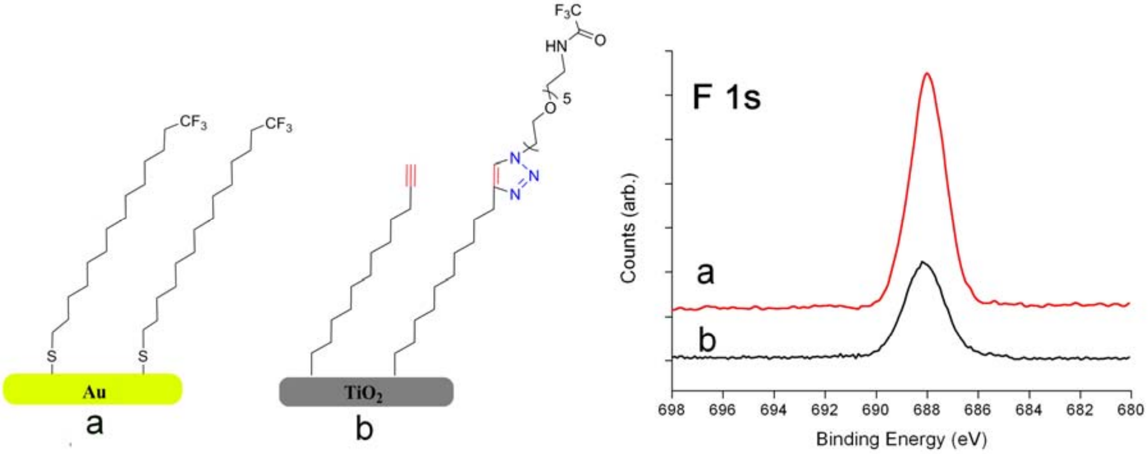


Figure S2. High-resolution F 1s spectra of the (a) **CF_3-C13-SH** derived self-assembled monolayer on Au and b) click immobilized CF_3-tagged azide derivative on Ti substrate.

4. Removal of the copper residue after click immobilization

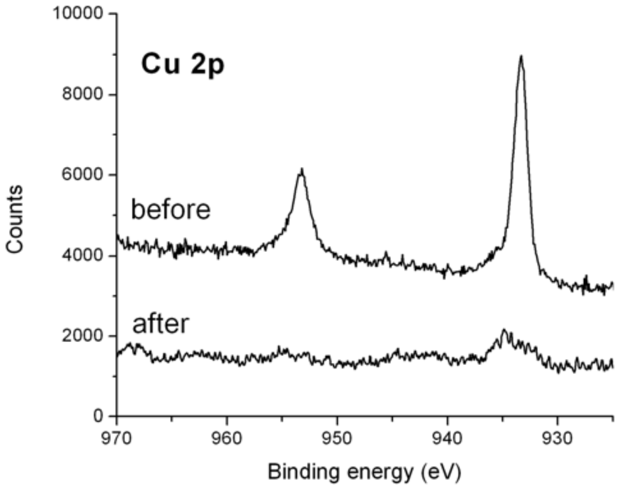


Figure S3. XPS narrow scan for Cu 2p region of surface **C** before (upper line) and after 10 minute ultrasonic sonication in EDTA (0.15%) solution (bottom line).

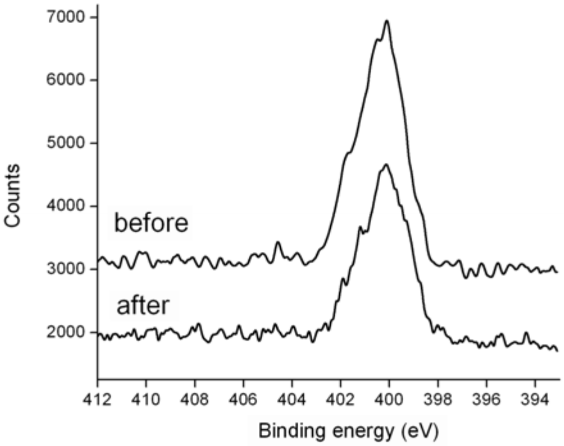


Figure S4. XPS narrow scan for N 1s region of surface **C** before (upper line) and after ultrasonic clean in EDTA solution (bottom line). The slight decrease (~5%) of the N 1s intensity was probably attributed to the simultaneous remove of contamination (e.g., Cu(I)-ligand) on the surface during the sonication clean.

Reference:

1. Wallart, X.; de Villeneuve, C. H.; Allongue, P. *J. Am. Chem. Soc.* **2005**, *127*, 7871-7878.