Supporting Information

Disulfide-yne Reaction: Controlling the Reactivity of a Surface by Light

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Experimental

Materials

4-Pentynoic acid, dibutyl disulfide (DBD), 2-hydroxyethyl disulfide (HED), 2-Carboxyethyl disulfide (CED), 3-mercaptopropiolic acid (MPA) 2,2-Dimethoxy-2-phenylacetophenone (DMPAP), fluorescein isothiocyanate isomer I (FITC), N, N'-Diisopropylcarbodiimide (DIC), cystamine dihydrochloride, 2-hydroxyethyl methacrylate, ethylene glycol dimethacrylate were obtained from Sigma-Aldrich (Germany). 4-(Dimethylamino) pyridine (DMAP), ethanol, dichloromethane (DCM), dimethyl sulfoxide (DMSO), acetone, dimethylformamide (DMF) and other solvents were obtained from Merck KGaA (Germany). The glass plates used in the experiment were Nexterion B glass from Schott AG (Germany). An OAI model 30 deep-UV collimated light source (San Jose, CA, USA) fitted with a 500 W HgXe lamp was used for UV irradiation. The lamp was calibrated to 7.5 mW/cm² at 260 nm with the OAI 306 UV power meter. The microscopy images were obtained by a BIOREVO BZ-9000 microscope (Keyence GmbH, Germany).

FITC-disulfide was synthesized as follows: Cystamine dihydrochloride (4 mg) and triethylamine (8 μL) were mixed in 2 mL DCM, and vortexed until cystamine dihydrochloride was dissolved. FITC (13 mg) was dissolved in 1 mL DMSO. Cystamine solution was added into FITC solution, followed by the addition of 12 mg DMAP and stirred for 16 hrs to obtain FITC-disulfide. FITC-disulfide solution was evaporated by Biotage V10 to remove DCM, and diluted with DMSO to the concentration of 10 mg/mL.

Disulfide-yne reaction in small molecular level

The disulfide-yne reactions in small molecular level were carried out in 20 mL glass vials. 49 mg 4-pentynoic acid was added into a glass vial containing 2 mL THF, followed by the addition of different eq of DBD and 7 mg DMPAP. After purged by argon for 1 min, the vial
was placed under UV and irradiated for 15 min. A sample with BT: alkyne =1:1 eq was also prepared. The samples were then diluted and tested by mass spectroscopy.

In addition, the small molecular level vinyl disulfide structure was reacted with hydroxyl, carboxyl and amino groups, respectively. In the vinyl disulfide product obtained above, 4 eq of butanol, acetic acid and octylamine were added respectively. After purging with argon for 1 h, the vial was placed under UV and irradiated for 1 hour. The sample is then diluted and tested by mass spectrometry.

Formation of alkyne surface

The alkyne surface was formed by esterification of 4-pentynoic acid on HEMA-EDMA surface. 110 mg 4-pentynoic acid was added into a 50 mL Falcon tube containing 45 mL DCM, followed by the addition of 176.5 μL DIC. Then porous HEMA-EDMA surface was placed into the tube, and the solution was stirred with a small magnetic stirrer overnight after the addition of 56 mg DMAP. The HEMA-EDMA surface was then washed with ethanol and acetone and dried by N2.

Disulfide-yne modification on alkyne surface

Few drops of disulfide solution (DBD, CED or HED, 20% wt in DMF, containing 1% wt DMPAP as photoinitiator) was added on alkyne surface, then the surface was covered by a quartz glass and irradiated under UV for 5 min. After washed with acetone and dried by N2.

Kinetics of disulfide-yne chemistry on surface modification

In order to study the kinetics of the disulfide-yne photo chemistry on alkyne surface, few drops of dibutyl disulfide (DBD) was added on alkyne surface, and the surface was then covered by a quartz glass followed by irradiation under UV for 15s, 30s, 60s, 120s, 180s, 300s, respectively. The WCA of each sample was measured and the kinetics of the modification could be acquired by comparing the WCA of each time points. Same experiment was done by using CED as the disulfide.

Photo patterning on alkyne surface by disulfide-yne chemistry

Few drops of disulfide solution (20% wt in DMF with 1% wt DMPAP, for FITC-disulfide is 10 mg/mL in DMSO containing 0.5 mg/mL DMPAP) was added on the alkyne surface, then the surface was covered by quartz glass and irradiated under UV for 3 min with photomask (for FITC-disulfide, 5 min). The surface was then washed with acetone and dried by N2.
Reactivity test on thiol modified and disulfide modified alkyl surface

Porous alkyne surface was used in the test. The alkyne surface was first modified with DBD solution for 3 min, then CED solution was added on the surface, followed by cover the surface with a quartz glass and irradiated for 10 min under UV. Afterwards the surface was modified by DBD solution again (10 min), WCA of the surface after each modification was recorded. The modification of CED solution on ethyl dithioether surface was also done as control experiment. To test the reaction between vinyl dithioether surface and thiol, the surface after DBD modification was modified by MPA solution for 10 min, followed by the modification of DBD solution for 10 min, WCA of the surface after each modification was tested.

Combination of thiol-yne chemistry and disulfide-yne chemistry

The alkyne surface was first modified with mercapto ethanol solution for 30 s under UV with a photomask, followed by flood irradiation with HED solution for 2 min. This leads to a hydrophilic surface with a hidden pattern. Afterwards the surface was flood irradiated with DBD solution for 2 min, to turn the HED modified area hydrophobic and led to a hydrophilic-hydrophobic pattern.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) measurement

Images were obtained with TOF-SIMS machine (ION-TOF GmbH, Münster, Germany). The analysis chamber was held at $\sim 8 \times 10^{-9}$ mbar during the experiment. A pulsed of 25 keV Bi$_{1+}$ primary ion beam was used for all image and spectral data acquisition. All data were collected in high mass resolution bunched mode. Care was taken to use a new sample area for each analysis.
Fig. S1. NMR result of the purified 4,5-bis(butylthio)-4-pentenoic acid.
Fig. S2. Mass spectrometry analysis of the disulfide-yne reaction mixture. (a) Reaction between 4-pentyne acid (PA) and bis(carboxyethyl) disulfide. (b) Reaction between PA and hydroxyethyl disulfide. (c) Reaction between PA and diphenyl disulfide. Vinyl dithioether structures were obtained in all cases, and no peak could be found for further addition products.
Fig. S3. Disulfide-yne reaction in different solvents. (a) Reaction between PA and DBD in ethanol. (b) Reaction between PA and HED in water. (c) Reaction between PA and DBD in toluene.
Fig. S4. Dynamic addition-fragmentation chain transfer (AFCT) reaction of allyl disulfide group. The double bond on the structure is kept during the reversible addition process, leading to the possible exchange of sulfide groups on the molecules.
Fig. S5. (a) Mass spectrometry (ESI negative) analysis of the reaction between vinyl dithiolether group and hydroxyl group. (b) Mass spectrometry (ESI negative) analysis of the reaction between vinyl dithiolether group and carboxyl group. (c) Mass spectrometry (ESI+ .m) analysis of the reaction vinyl dithiolether group and amine group. It's clear that no addition or exchange products can be found.
Fig. S6. Structure of alkyne surface and the m/e value of relating fragments after thiol-yne or disulfide-yne modification.
**Fig. S7.** Kinetics of the disulfide-yne functionalization on surface, measured by the WCA change of the surface. Red: alkyne-CED, black: alkyne-DBD.
Fig. S8. Patterning fluorescence molecules on alkyne surface by disulfide-yne reaction. (a) Chemical structure of the used fluorescence disulfide. (b) The resolution of the pattern can reach 25 μm.
Fig. S9. Formation of patterned surface with combination of thiol-yne and disulfide-yne reaction.

Reference
1 W. Feng, L. Li, E. Ueda, J. Li, S. Heißler, A. Welle, O. Trapp, P. a. Levkin, Adv. Mater. Interfaces 2014, 1, 1400269.