Supporting Information

of

Photo-responsive "Smart Surface" *via* Host-Guest Interaction for Reversible Cell Adhesion

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1. Materials and Methods

undecylenic acid (UA), *N, N*-dimethylformamide (DMF), pyridine, piperidine, dichloromethane (CH_2Cl_2), triethoxysilane ($HSi(OEt)_3$), toluene, tetrahydrofuran (THF), methanol (CH_3OH), trifluoroacetic acid (TFA), acetone, 98 % (v/v) sulfuric acid, 30 % (w/v) hydrogen peroxide, 36 % (v/v) hydrochloric acid (HCl) and H_2PtCl_6 were purchased from Shanghai Reagent Chemical Co. (PR China). DMF, pyridine, toluene and acetone were purified by distillation. O-(*N*-succinimidyl)-*N,N,N',N'*-tetramethyluronium tetrafluoroborate (TSTU), sodium hydroxide (NaOH), 4-aminoazobenzene and succininc anhydride were obtained from Shanghai Reagent Chemical Co. (PR China). 3A-amino-3A-deoxy-(2AS,3AS)-α-cyclodextrin hydrate (NH_2-*α*-CD) was purchased from Tokyo Chemical Industries (TCI). *N*-Fluorenyl-9-methoxycarbonyl (Fmoc) protected L-amino acids (Fmoc-Arg(Pbf)-OH, Fmoc-Gly-OH, Fmoc-Asp(OtBu)-OH, Fmoc-Ser(tBu)-OH), 2-chlorotrityl chloride resin (100–200 mesh, loading: 0.4 mmol g^{-1}, 1 %DVB) and *o*-benzotriazole-*N*,*N*,*N*',*N*'-tetramethyluroniumhexafluorophosphate (HBTU) were purchased from GL Biochem Ltd. (Shanghai, China) and used as received. Molecular probe (Hoechst 33258) was purchased from Invitrogen (CA,USA) and Tubulin Tracker Oregon Green 488 Taxol, bis-acetate was purchased from Molecular Probes (USA). Dulbecco's Modified Eagle's Medium (DMEM), fetal bovine serum (FBS), penicillin streptomycin and Dubelcco's phosphate buffered saline (PBS) were purchased from Invitrogen Corp.

2. Synthesis of azobenzene-GRGDS and azobenzene-GDSRG

Preparation of azobenzene-COOH

4-Aminoazobene (1.97 g, 10 mmol) and succinic anhydride (1.20 g, 12 mmol) were dissolved into 25 ml distilled acetone. 0.79 g (10 mmol) anhydrous pyridine was added into the solution and the mixture was stirred for 6 h at 60 ^{o}C. The obtained suspension was filtered and after been dried at 50 ^{o}C for 48 h under vacuum drying, 2.85 g azobenzene-COOH (azo-COOH) was obtained. (yield: 96 %). Figure S1 shows the ^{1}H NMR spectrum of azo-COOH.

Preparation of azobenzene-GRGDS and azobenzene-GDSRG

GRGDS peptide was manually synthesized in 0.6 mmol scale on the 2-chlorotrityl chloride resin, employing a standard Fmoc chemistry by solid phase peptide synthesis (SPPS) method. The coupling of the first residue used 4 equiv of Fmoc-protected amino acid (Fmoc-Ser(tBu)-OH) relative to resin substitution degree with 6 equiv of DIEA in a DMF solution. Other amino acid couplings and azo-COOH were carried out with 4 equiv of Fmoc-protecting amino acid or azo-COOH, 6 equiv of DIEA and 4 equiv of HBTU for 4 h. During the synthesis, the Fmoc protecting groups were deprotected with 20 % (v/v) piperidine/ DMF twice. The cleavage of peptide was performed in a mixture of deionized water, TIS and TFA in the ratio of 2.5:2.5:95. After 2 h stirring at room temperature, the mixture was collected. The excess TFA was removed by rotary evaporation and the remaining viscous peptide solution was precipitated in the cold ether. The resulting orange product was collected and vacuum dried. The preparation of azo-GDSRG was the same as azo-GRGDS. The molecular

weight of azo-GRGDS ([M^+]) measured by ESI-MS was 768.5 (theoretical value: 768.3). Figure S2 shows ESI-MS spectrum of azo-GRGDS.

3. Pretreatment of quartz substrates

The quartz substrates were cleaned prior to alkanesilane assembly. The substrates were immersed for 2 h at 80 ^{o}C in "piranha" solution consisting of 3:7 ratio of aqueous solutions of 30 % (w/v) hydrogen peroxide and 98 % (v/v) sulfuric acid. (*Caution: this "piranha" solution has causticity and reacts violently with organic materials, so it need to be handled with extreme care*). After removal from "piranha" solution, quartz substrates were rinsed with deionized (DI) water and dried under nitrogen, then stored at room temperature.

4. Fabrication of α-CD SAMs

Preparation of compound 1 (See Scheme S1)

Undecylenic acid (UA) (1.30 g, 7.04 mmol) was dissolved in 10 ml distilled DMF and 10 ml dry pyridine was added. 1 equiv of TSTU (2.12 g, 7.04 mmol) was separately dissolved in 10 ml DMF and added slowly under stirring. The reaction flask was purged with nitrogen and reaction mixture was stirred for 5 h at room temperature. Then the solvent was evaporated and the residue was dissolved in 10 ml CH_2Cl_2. The precipitate was removed by filtration. The solution was washed with once 10 ml 5 % HCl and 10 ml DI water. CH_2Cl_2 was evaporated and compound 1 was obtained. Figure S3 shows the ^{1}H NMR spectrum of compound 1.

Fabrication of α-CD SAMs on quartz substrates (See Scheme S1)

A solution of compound 1 (1.40 g, 5.00 mmol) in 10 equivalents of triethoxysilane (8.22 g, 50.00 mmol) was heated under anhydrous conditions to 95 ^{o}C and 60 ul H_2PtCl_6 was added. The mixture was allowed to stir for further 5 h at 95 ^{o}C. Excess $HSi(OEt)_3$ was removed under vavuum and the crude product was purified by filtration over celite. Compound 2 was obtained and then it was prehydrolised in 36 ml anhydrous toluene and 40 ul 1 mol/L NaOH as a catalyst for 5 h. The pretreated quartz substrates were immersed into the silane solution for 24 h. After deposition, the substrates were gently rinsed successively with THF and DI water and were blown dry in a nitrogen stream. TSTU (0.30 g, 1 mmol) was dissolved in 19 ml distilled DMF and 1 ml dry pyridine was added. The substrates were put into this solution and shaked for 2 h at 25 ^{o}C. Then the quartz substrates were rinsed with DMF and DI water, and immersed into 15 ml 2 mg/ml NH_2-α-CD for 12 h at 25 ^{o}C. After that, the substrates were rinsed with DI water and blown dry in a nitrogen stream. The quartz substrates containing α-CD SAMs were obtained.

5. Assembling azo-GRGDS and azo-GDSRG onto α-CD SAMs

15 mg azo-GRGDS was dissolved in 1.5 ml CH_3OH and this solution was dropped into 13.5 ml DI water. The α-CD SAMs were put into this mixture and shaked gently for 24 h at room temperature. After assembly, the substrates were rinsed with DI water scrupulously and dried with a nitrogen stream. The α-CD/azo-GRGDS SAMs were obtained. The preparation of α-CD/azo-GDSRG SAMs was the same as

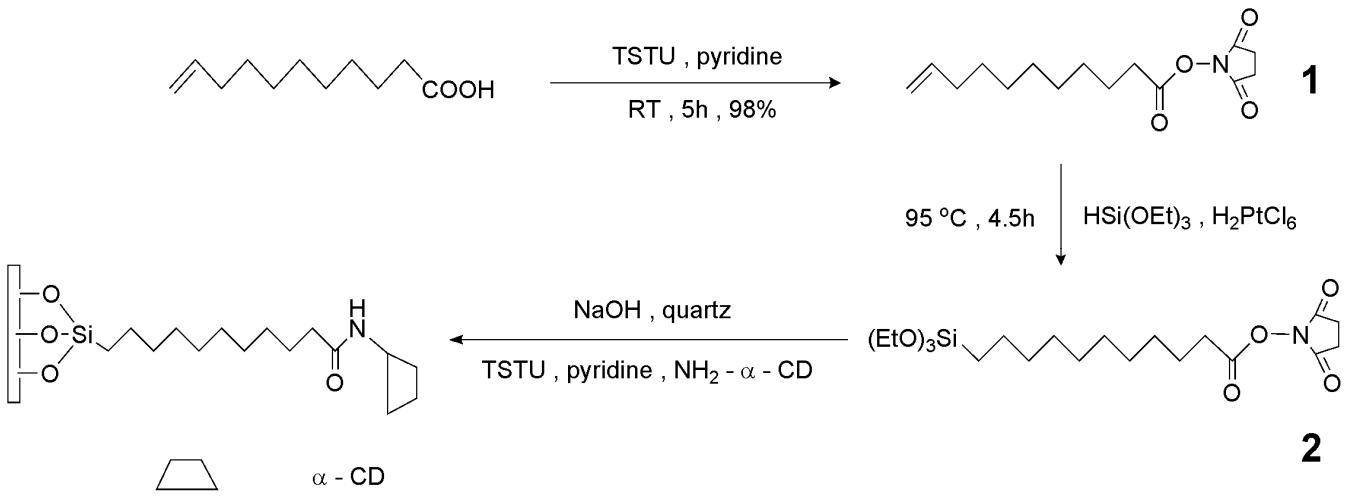
α-CD/azo-GRGDS SAMs.

6. Evaluation of cell Adhesion and proliferation on different surfaces

Human cervix carcinoma (HeLa) cells were cultured in DMEM medium with 10 % FBS and 1 % antibiotics (penicillin-streptomycin, 10000 U/mL) at 37 °C in a humidified atmosphere containing 5 % CO_2. Before seeding, all of substrates were sterilized with high temperature. 1 ml DMEM culture medium and 150 ul DMEM medium containing 2×10^5 cells/ml was added to each substrate and this culture was maintained for 24 h. Then clean quartz substrates, α-CD/azo-GRGDS SAMs and α-CD/azo-GDSRG SAMs were irradiated with UV light (365 nm, 15 W) for 10 min, the old medium was removed and new DMEM medium was added. These samples were incubated at 37 ^oC, 5 % CO_2 for 1 h. The UV irradiation process was repeated three times and then the cells were counted and recorded. The nucleus of HeLa cells was stained with 20 ul (2 ug/ul) of Hoechst 33258 for 15 min at 37 ^oC, after which the cells were further washed with PBS three times. Then 1 ml 0.5 mM Tublin Tracker Oregon Green 488 Taxol, bis-acetate solution was added into and these samples were incubated for 30 min at 37 ^oC/5 % CO_2, after that the cells were washed three times with PBS. The cells were observed with a confocal laser scanning microscope (C1-Si, Nikon, Japan) equipped with a 405 nm diode for Hoechst 33258.

Table S1. Elemental composition on modified surfaces by XPS analysis.

At%	C	O	N
α-CD	27.59	71.84	0.54
α-CD/azo-GRGDS	46.78	50.46	2.76
α-CD/azo-GRGDS(UV)	26.48	72.83	0.69



Scheme S1. Preparation of SAMs terminated with α-CD.

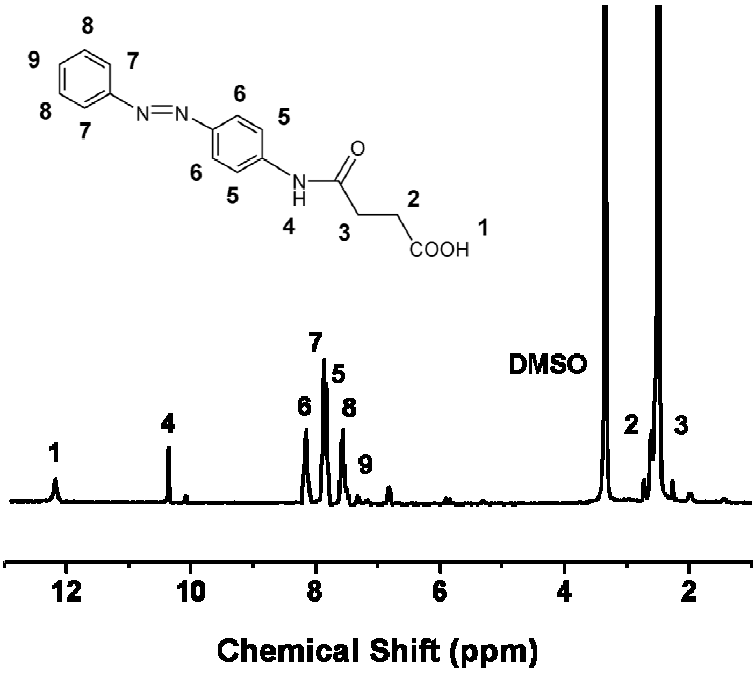


Figure S1. ^{1}H NMR spectrum of azo-COOH.

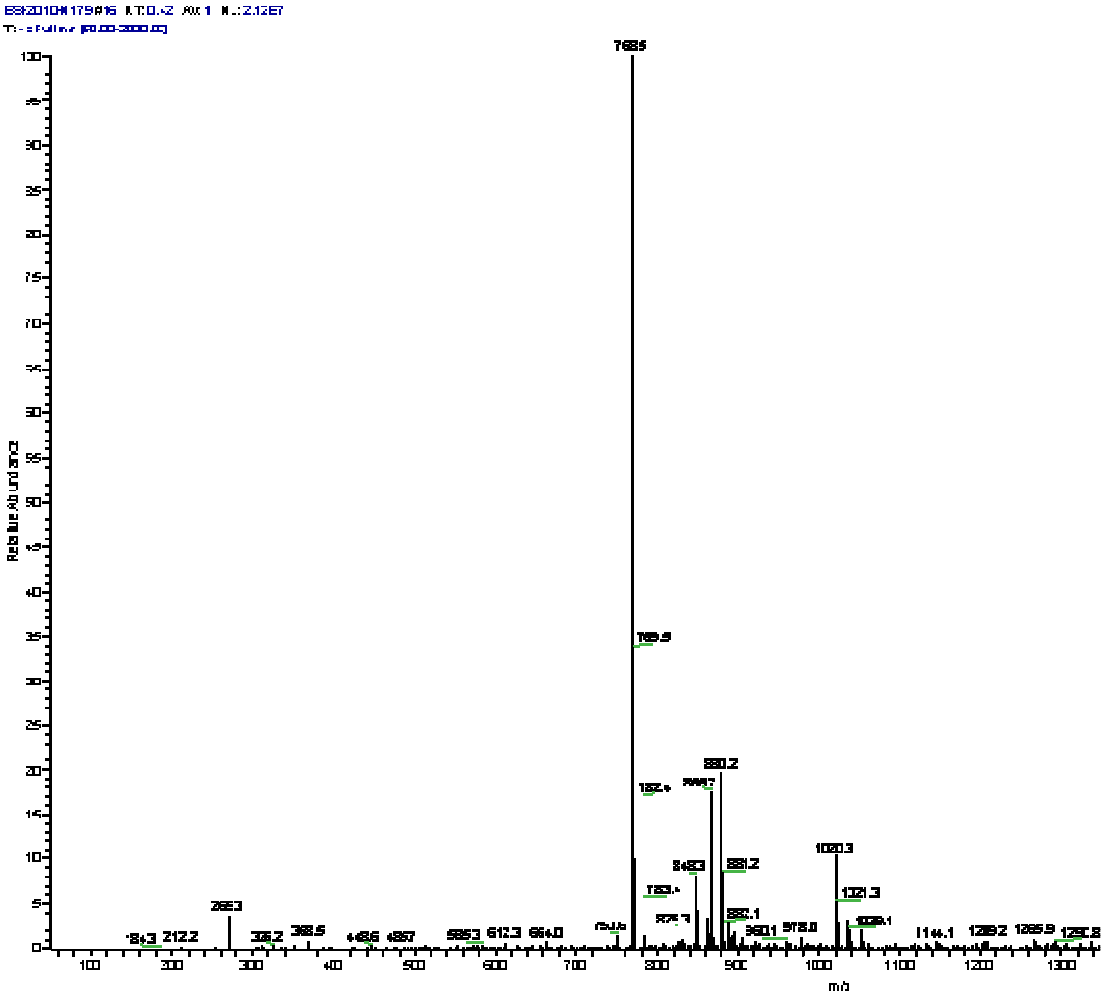


Figure S2. ESI-MS spectrum of azo-GRGDS.

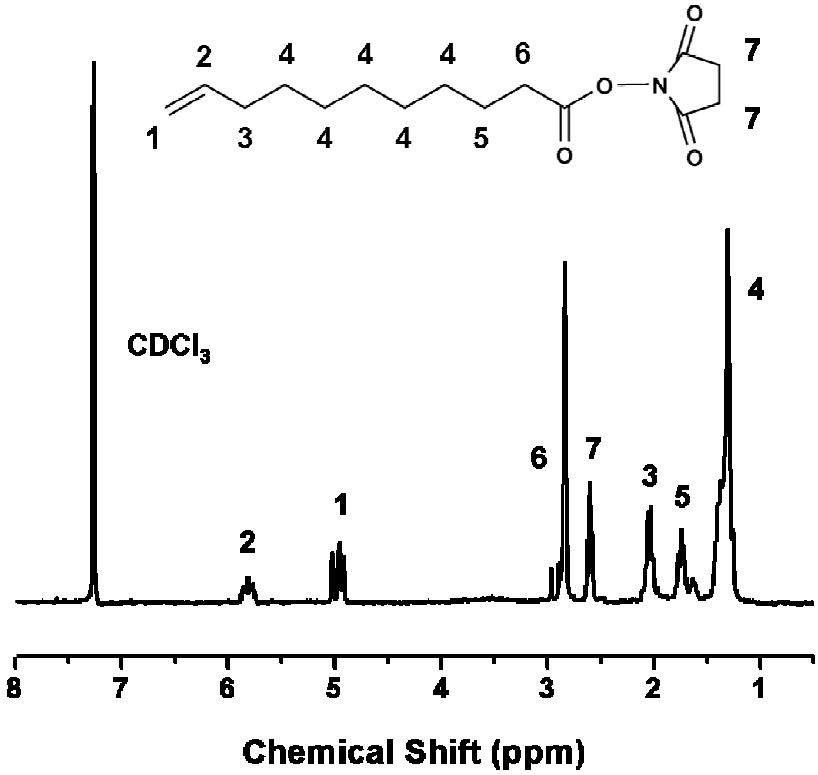


Figure S3. ^{1}H NMR spectrum of compound 1.