# Electronic Supplementary Information

## Strictly Sparse Surface Modification and Its Application for Endowing Nanoparticles with an Exact "Valency"

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### Materials and Characterization

1) Materials

2,2-Dimethylol propionic acid (Bis-MPA), 2,2-dimethoxypropane, propargyl chloride, N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), poly(ethylene glycol) (HO-PEG-OH, $M_n$ = 2000) 2-hydroxyethyldisulfide, DOWEX 50W resin (200 mesh), oleyl amine, *N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%), 2-bromoisobutyryl bromide (98%), borane tert-butylamine complex (97%), tosyl chloride, propargyl bromide, 4-ethylumbelliferone, γ-chloropropyl triethoxysilane, dithiothreitol (DTT), 1,2,3,4-tetrahydronaphthalene were purchased from Aldrich and used as received. Styrene (98%, Aldrich) was purified twice by passing the monomer through a column filled with basic alumina to remove the inhibitor. CuBr was washed with acetic acid, followed by washing with methanol to remove impurities. Triethylamine was dried with $CaH_2$ overnight and then distilled just before use. Tetraethyl orthosilicate (TEOS, 98%), sodium azide, ammonium hydroxide (25-28%), hydroquinone, tert-butanol, potassium tert-butylate, pyridine, chloroauric acid·$4H_2O$, and other commonly used reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received.

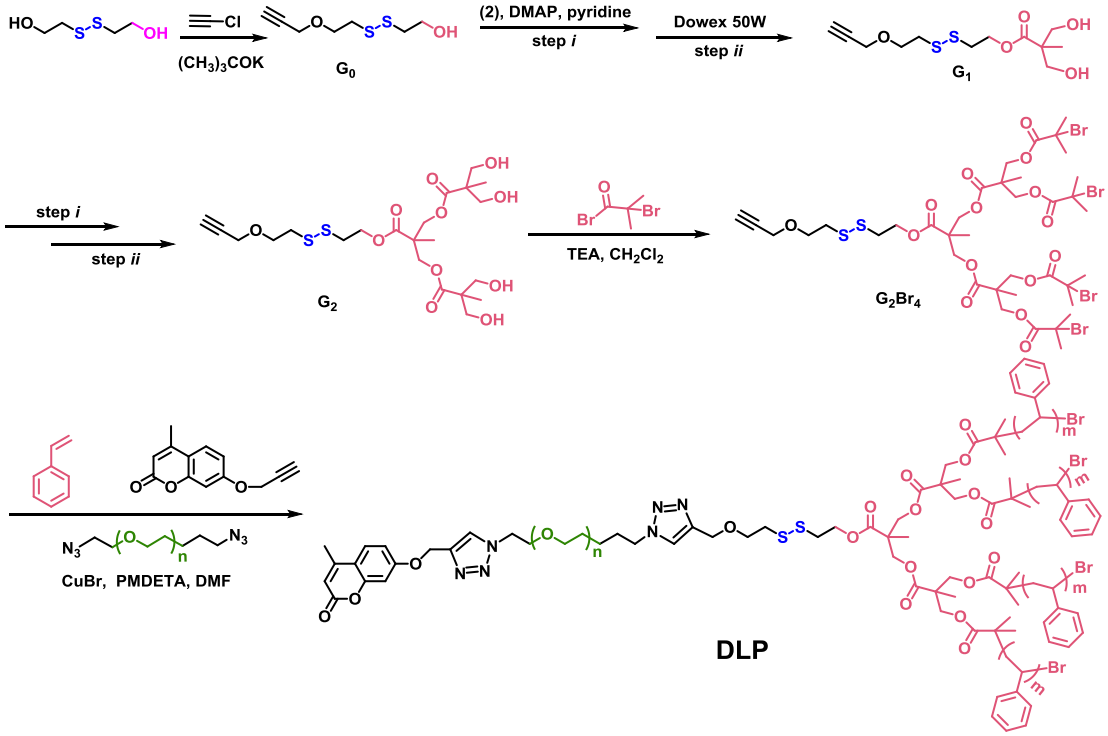
2) Characterization

$^1H$ and $^{13}C$ NMR measurements were recorded on a Bruker Advance 400 spectrometer, and the chemical shifts are reported in ppm with the signal of TMS as the internal standard. Gel permeation chromatography (GPC) analysis was carried out with a Waters Breeze 1525 GPC analysis system with two PL mix-D columns, using DMF with 0.5 M LiBr as eluent at the flow rate of 1 mL/min at 80 °C, and PEO calibration kit (purchased from TOSOH) as the calibration standard. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 FTIR spectrometer. Thermal gravimetric analyses (TGA) were conducted with a Mettler Toledo TGA. Transmission electron microscopy (TEM) experiments were carried out on a Philips CM120 microscope operated at an accelerating voltage of 80 kV. For preparing TEM specimen, 5 $\mu$L of the sample solution was deposited onto a carbon-coated copper grid, followed by drying at room temperature under vacuum. The specimens with polymer samples

were stained by $RuO_4$ for 60 min. Dynamic laser light scattering (DLS) measurements were conducted on an ALV-5000 laser light scattering spectrometer at a fixed scattering angle of 90°. Before the measurements, the samples were all filtered through 450 nm PTFE filters to remove dust. The sample solution was irradiated by UV light (25 W/cm$^2$, a wavelength of 254 nm or 365 nm) at room temperature (25 °C) using a 500W mercury lamp (CHF-XM-500W).

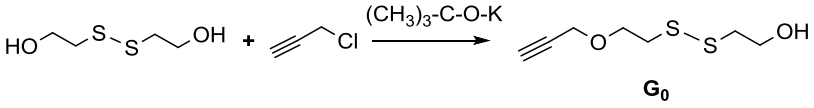
## Experimental and Methods

### S1 Synthesis of the DLP




**Scheme S1 Synthesis of the DLP.**

### Synthesis of 2-((2-(prop-2-yn-1-yloxy) ethyl) disulfanyl) ethanol ($G_0$)




A solution of 2-hydroxyethyl disulfide (9.24 g, 0.06 mol) in tert-butanol (90 mL) was slowly added to a solution of potassium tert-butoxide (6.72 g, 0.06 mol) in tert-butanol (100 mL) over 30 min at room temperature with stirring and under argon. After stirring the mixture for an additional 15 min, excess propargyl chloride (14.6 mL, 0.2 mol) was added dropwise over 30 min, and the solution was stirred at room temperature for 18 h. The solid formed in the reaction was removed via filtration, and the filtrate was concentrated using a rotary evaporator to yield a crude product of the product ($G_0$), byproduct (di-alkyne), and the unreacted diol. The crude product was redissolved in 150 mL dichloromethane and rinsed with water (30 mL) five times. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed by rotary evaporation,

yielding yellow oil. It was further purified by silica gel column chromatography with an ethyl acetate/petroleum ether (4:1 *v*/*v*) eluent to obtain a pure **G$_0$**, which was pale yellow viscous oil (5.42 g, 47% yield).

$^1$H NMR ($CDCl_3$, 400 MHz): δ 2.50 (s, H, -C***H***), 2.90-2.95 (d, 4H, -C***H***$_2$-S-),3.82 (s, 2H, -C***H***$_2$-OH), 3.92 (s, 2H, -C***H***$_2$-O-), 4.22 (s, 2H, -C-C***H***$_2$-O-).

$^{13}$C NMR ($CDCl_3$, 400 MHz): δ 38.40, 41.38, 58.23, 60.30, 68.15, 74.86, 79.31.

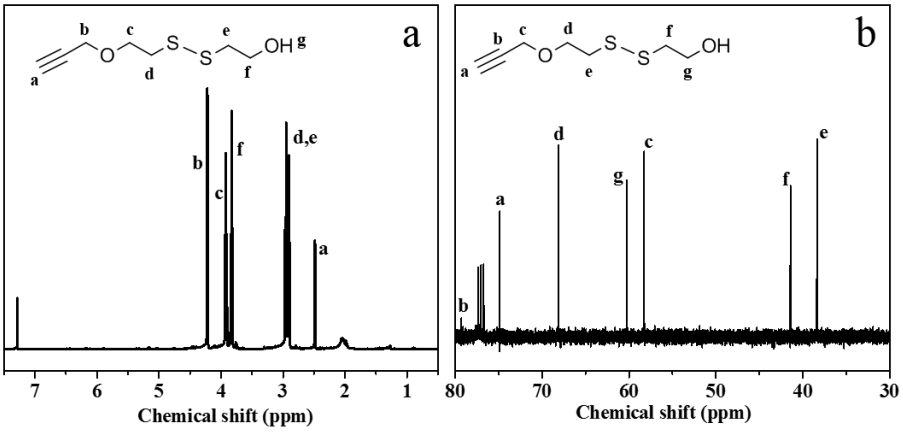
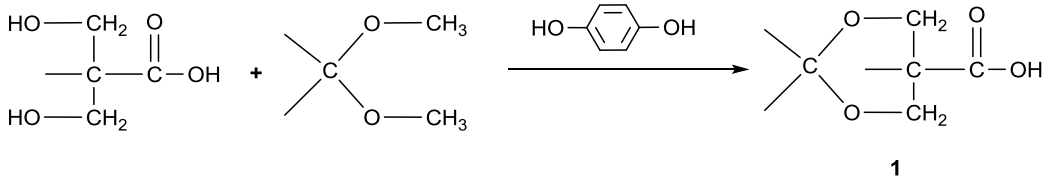



Fig. S1 $^1$H NMR (a) and $^{13}$C NMR (b) spectra of $G_0$ in $CDCl_3$.

**Synthesis of 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (1)**



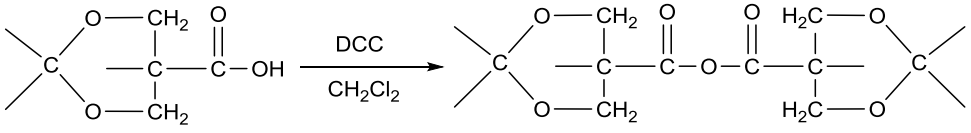
**1**

Bis-MPA (50.0 g, 0.37 mol), 2,2-dimethoxypropane (69.0 mL, 0.56 mol) and *p*-toluenesulfonic acid monohydrate (0.71 g, 0.0037 mol) were dissolved in 50 mL of acetone. The reaction mixture was stirred for 4 h at room temperature. After the catalyst was neutralized by adding approximatively 2 mL of an $NH_3$/EtOH (1:1, *v*/*v*) solution, the solvent was evaporated at room temperature. The residue was then redissolved in $CH_2Cl_2$ (1000 mL) and extracted with two portions of water (100 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated to obtain the white crystals (**1**, 51.2 g, 79% yield).

$^1$H NMR ($CDCl_3$, 400 MHz): δ 1.20 (s, 3H, -C***H***$_3$), 1.39 (s, 3H, -C***H***$_3$), 1.42 (s, 3H, -C***H***$_3$), 3.65 (d, 2H, -C***H***$_2$O), 4.18 (d, 2H, -C***H***$_2$O).

$^{13}$C NMR ($CDCl_3$, 400 MHz): δ 18.48, 22.17, 25.03, 41.78, 65.84, 98.37, 180.40.

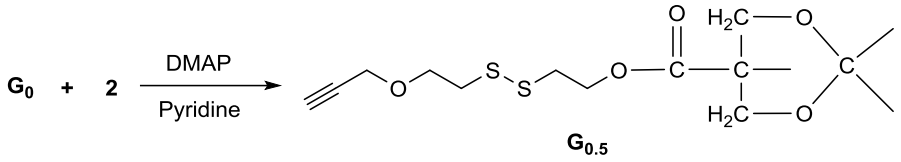
**Synthesis of acetonide-2,2-bis(methoxy)propionic anhydride (2)**




**2**

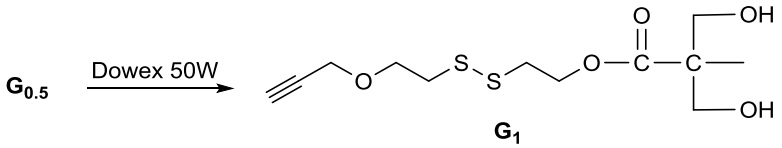
Acetonide-2,2-bis(methoxy)propionic acid (50.0 g, 0.29 mol) was added in $CH_2Cl_2$ (200 mL) with constant stirring at room temperature. Then, DCC (29.6 g, 0.15 mol) was added to the mixture and stirred for an additional 48 h at room temperature. The mixture was allowed to stir until the completion of the reaction monitored by $^{13}C$ NMR. The $^{13}C$ NMR signal of the acid carbonyl carbon at 178 ppm disappeared, while the new carbon signal of the anhydride carbonyl carbon at 169 ppm appeared. The DCC-urea was filtered off and the solvent was evaporated. The viscous residue was diluted in 1 L of hexane and stirred until a white solid formed. Thereafter, the solution was cooled to -78 °C and kept for 1 h, filtered through a fritted glass funnels, and dried under vacuum to obtain the white crystals (**2**, 26.9 g, 56% yield).
$^1H$ NMR ($CDCl_3$, 400 MHz): δ 1.21 (s, 6H, -C***H₃***), 1.36 (s, 6H, -C***H₃***), 1.41 (s, 6H, -C***H₃***), 3.66 (d, 4H, -C***H₂***O), 4.18 (d, 4H, -C***H₂***O).
$^{13}C$ NMR ($CDCl_3$, 400 MHz): δ 17.83, 21.75, 25.72, 43.83, 65.85, 98.56, 169.68.

**Synthesis of $G_{0.5}$**




**$G_0$** (3.00 g, 15.6 mmol) and DMAP (0.375 g, 3.12 mmol) were dissolved in pyridine (3.69 mL, 46.8 mmol) in a 150 mL round bottom flask, followed by the addition of 60 mL dry $CH_2Cl_2$. **2** (6.72 g, 20.3 mmol) was added slowly to the solution. The solution was stirred at room temperature for at least 12 h. The completion of the reaction was monitored by $^{13}C$ NMR and determined by the presence of the excess anhydride at ~169 ppm. The reaction was quenched with 3 mL water under vigorous stirring and followed by dilution with 100 mL of $CH_2Cl_2$. The solution was then washed with 10% $NaHSO_4$ (30 mL, 3 times), 10% $NaHCO_3$ (30 mL, 3 times) and brine (30 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel column chromatography, eluting with petroleum ether (100 mL) with gradually increasing the polarity to ethyl acetate/petroleum ether (1:4, *v*/*v*) to obtain the pale yellow oil (**$G_{0.5}$**, 3.47 g, 64% yield).
$^1H$ NMR ($CDCl_3$, 400 MHz): δ 1.22 (d, 3H, -C***H₃***), 1.39 (d, 3H, -C***H₃***), 1.43 (d, 3H, -C***H₃***), 2.48 (s, 1H, -C***H***), 2.95 (dt, 4H, -S-C***H₂***-), 3.66 (dd, 2H, -O-C***H₂***-), 3.80 (t, 2H, -O-C***H₂***-), 4.21 (m, 4H, -O-C***H₂***-C), 4.42 (t, 2H, -O-C***H₂***-C).
$^{13}C$ NMR ($CDCl_3$, 400 MHz): δ 18.65, 22.65, 24.64, 37.12, 38.65, 41.92, 58.20, 62.58, 65.95, 67.99, 74.87, 79.51, 98.08, 174.01.

**Synthesis of $G_1$**



**G1** was obtained by the general procedure for the deprotection of the acetonide group using DOWEX 50W resin. 8 g DOWEX 50W resin was added to a solution of **G0.5** (3.10 g, 8.9 mmol) in 100 mL methanol in a 250 mL round bottom flask. The mixture was stirred at 40 °C for 8 h. The deprotection was monitored by $^{13}C$ NMR and the completion of the reaction was determined by the disappearance of unique $^{13}C$ NMR signals for the acetonide group (i.e. the quaternary carbon at ~98 ppm). The resin was filtered off and the filtrate was concentrated and dried under vacuum. The pale-yellow oil was obtained (**G1**, 2.70 g, 98% yield).

$^1H$ NMR ($CDCl_3$, 400 MHz): δ 1.11 (m, 3H, -C***H*₃**), 2.48 (s, 1H, -C***H***), 2.97 (dt, 4H, -S-C***H*₂**-), 3.74 (d, 4H, -C-C***H*₂**-OH), 3.81 (t, 2H, -O-C***H*₂**-), 4.20 (t, 2H, -O-C***H*₂**-), 4.42 (t, 2H, -O-C***H*₂**-C).

$^{13}C$ NMR ($CDCl_3$, 400 MHz): δ 17.15, 37.08, 38.68, 48.57, 58.23, 62.45, 68.11, 68.41, 74.94, 80.08, 176.93.

**Synthesis of G2**

**G1** (1.85 g, 6.0 mmol), DMAP (0.288 g, 2.4 mmol), 2.84 mL of pyridine, 30 mL of $CH_2Cl_2$, and **2** (5.15 g, 15.6 mmol) were reacted according to the general esterification procedure. The residue was then purified by liquid chromatography on silica gel, eluted from petroleum ether with the increased polarity with ethyl acetate/petroleum ether (2:5, *v*/*v*) to give the pale yellow oil (**G1.5**, 1.88 g, 50.5% yield).

**G1.5** (1.86 g, 3 mmol), 5 g of DOWEX 50W, and 50 mL of methanol was allowed to react according to the general deprotection procedure to obtain the pale yellow oil (**G2**, 1.52 g, 93.8% yield).

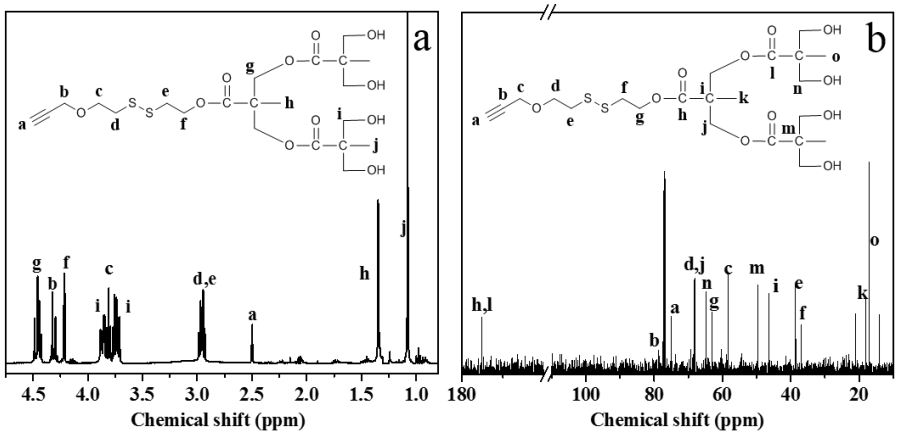



Fig. S2 $^1H$ NMR (a) and $^{13}C$ NMR (b) spectra of $G_2$ in $CDCl_3$.

**Synthesis of the 4-arm ATRP initiator G2Br4**

$G_2$ (1.08 g, 2 mmol) and triethylamine (1.39 mL, 10 mmol) were dissolved in 40 mL of $CH_2Cl_2$ in a 100 mL round bottom flask. 2-Bromoisobutyryl bromide (1.25 mL, 10 mmol) in 5 mL of $CH_2Cl_2$ was added dropwise to the above solution in an iced water bath, and the mixture was stirred at room temperature for 24 h. After the reaction, 60 mL of $CH_2Cl_2$ was added to dilute the solution. The solution was then washed with 10% of $NaHCO_3$ (30 mL, 3 times) and brine (30 mL, 2 times). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was purified by

silica gel column chromatography, eluting with ethyl acetate/petroleum ether (2:5, *v*/*v*) to obtain the pale yellow oil (**$G_2Br_4$**, 1.14 g, 50% yield).

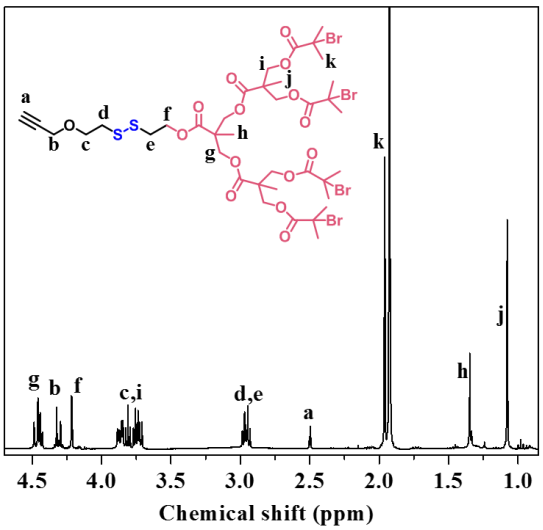
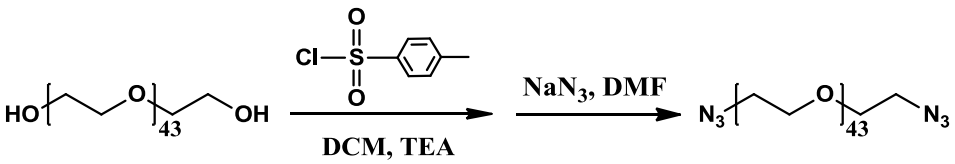



Fig. S3 $^1$H NMR spectrum of $G_2Br_4$ in $CDCl_3$

**Synthesis of bi-functional azide-terminated poly (ethylene glycol) ($N_3$-$PEG_{43}$-$N_3$).**




Both HO-$PEG_{43}$-OH (5.00 g, 2.5 mmol, $M_n$ = 2000g/mol) and toluene-4-sulfonyl chloride (9.52 g, 50 mmol) were completely dissolved in 100 mL $CH_2Cl_2$ under argon. Triethylamine (10.40 mL, 75 mmol) was added dropwise to the above solution in an iced water bath. The resulting solution was then precipitated into diethyl ether. The collected precipitant was dried in vacuum at 25 °C to give the bi-functional tosylated PEG (Ts-$PEG_{43}$-Ts, 4.85 g, 82.0% yield).

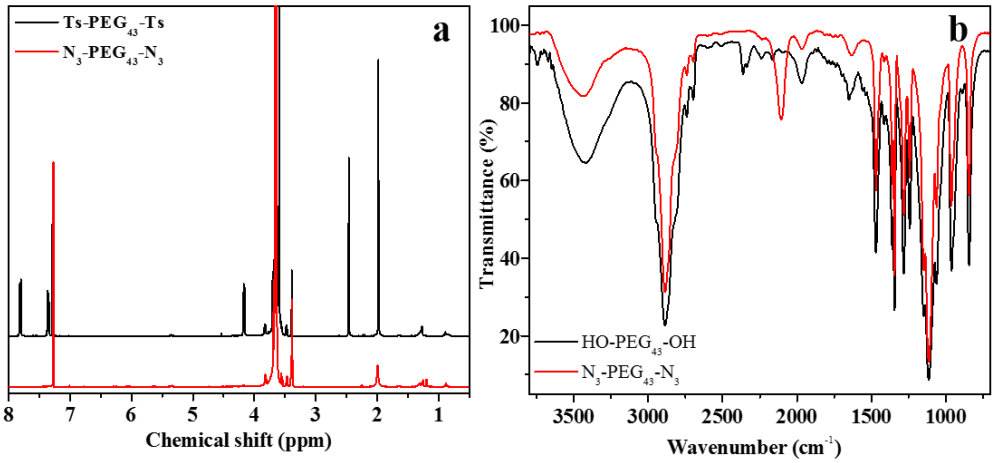
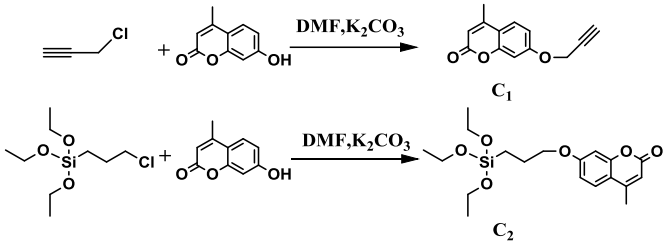



Fig. S4 (a) $^1$H NMR spectra of Ts-$PEG_{43}$-Ts (black) and $N_3$-$PEG_{43}$-$N_3$ (red) (in $CDCl_3$); (b) transmission FTIR spectra of HO-$PEG_{43}$-OH (black) and $N_3$-$PEG_{43}$-$N_3$ (red).

Sodium azide (2.60 g, 40 mmol) was added to a solution of Ts-$PEG_{43}$-Ts (2.37 g, 1 mmol) in 20 mL of dry DMF under argon, and the reaction mixture was stirred vigorously at room temperature for 24 h. DMF was removed under reduced pressure, and then the crude product was dissolved in 100 mL of $CH_2Cl_2$. The mixture was extracted sequentially with 5% NaCl solution and distilled water, dried over anhydrous $MgSO_4$, and then precipitated in diethyl ether to yield 1.69 g of bi-functional azide-terminated PEG ($N_3$-$PEG_{43}$-$N_3$, 84.5% yield).

**Synthesis of 4-methyl-7-(prop-2-yn-1-yloxy)-chromen-2-one ($C_1$) and 4-methyl-7-(3-(triethoxysilyl)propoxy)-chromen-2-one ($C_2$)**

A mixture of 7-hydroxy-4-methyl coumarin (4.41 g, 25 mmol) and $K_2CO_3$ (10.35 g, 75 mmol) was stirred in DMF (50 mL) at 60 °C for 1 h. Propargyl bromide (3.73 g, 50 mmol) was added dropwise to the mixture. The mixture was then stirred at 60 °C for an additional 24 h. The mixture was filtered and solvent (DMF) was removed under reduced pressure to yield a yellow solid. It was then purified by silica gel column chromatography eluting with ethyl acetate/petroleum ether (4:1, *v*/*v*) to yield the white solid (**$C_1$**, 2.15 g, 40.2% yield).




$C_2$ was synthesized according to the same procedure described above. The crude product was purified by silica gel column chromatograph eluting with ethyl acetate/petroleum ether (1:1, *v*/*v*) to yield the pale yellow solids (1.82 g, 19.1% yield).

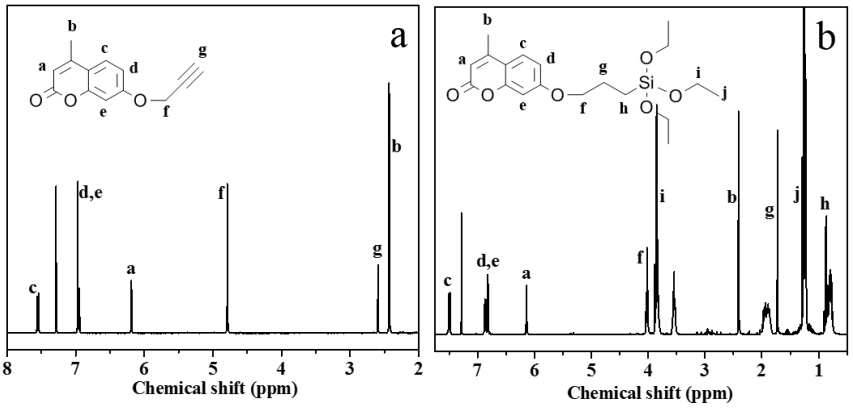



Fig. S5 $^1$H NMR spectra of alkynyl modified coumarin $C_1$ (a) and triethoxysilane modified coumarin $C_2$ (b) in $CDCl_3$.

**Synthesis and characterization of coumarin-terminated PEG-*b*-PS (DLP)**

The dendrimer-like copolymer $N_3$-PEG-*b*-PS terminated with azide group was synthesized by one-pot simultaneous ATRP and CuAAC click reaction procedure. $N_3$-$PEG_{43}$-$N_3$ (61.4 mg, 0.03 mmol), **$G_2$-$Br_4$** (11.36 mg, 0.01 mmol), PMDETA (16.6 $\mu$L, 0.08 mmol) and styrene (832 mg, 8 mmol) were dissolved in DMF (0.5 mL) in a

Schlenk flask under argon. The mixture was degassed three times by freeze-pump-thaw cycles. Then, CuBr (6.1 mg, 0.04 mmol) was added quickly into the mixture under argon. And the reaction mixture was degassed three times by freeze-pump-thaw cycles, filled with argon and placed in an oil bath at 65 °C for 24 h. The polymerization was quenched by quick cooling the reaction mixture in liquid $N_2$, exposure to air, and dilution with THF. The resulting polymer solution was passed through a neutral alumina column to remove the catalyst, copper complex. The polymer was precipitated twice from the THF solution into ethanol, filtered and dried under vacuum, to obtain the white powders ($N_3$-PEG-*b*-PS).

The degree of polymerization of PS is 520, the molecular weight of each arm is 13.5 kg/mol. Molecular weight calculated by NMR ($M_{n.NMR}$) of the obtained polymer is 58 kg/mol, and PDI measured by SEC is 1.27.

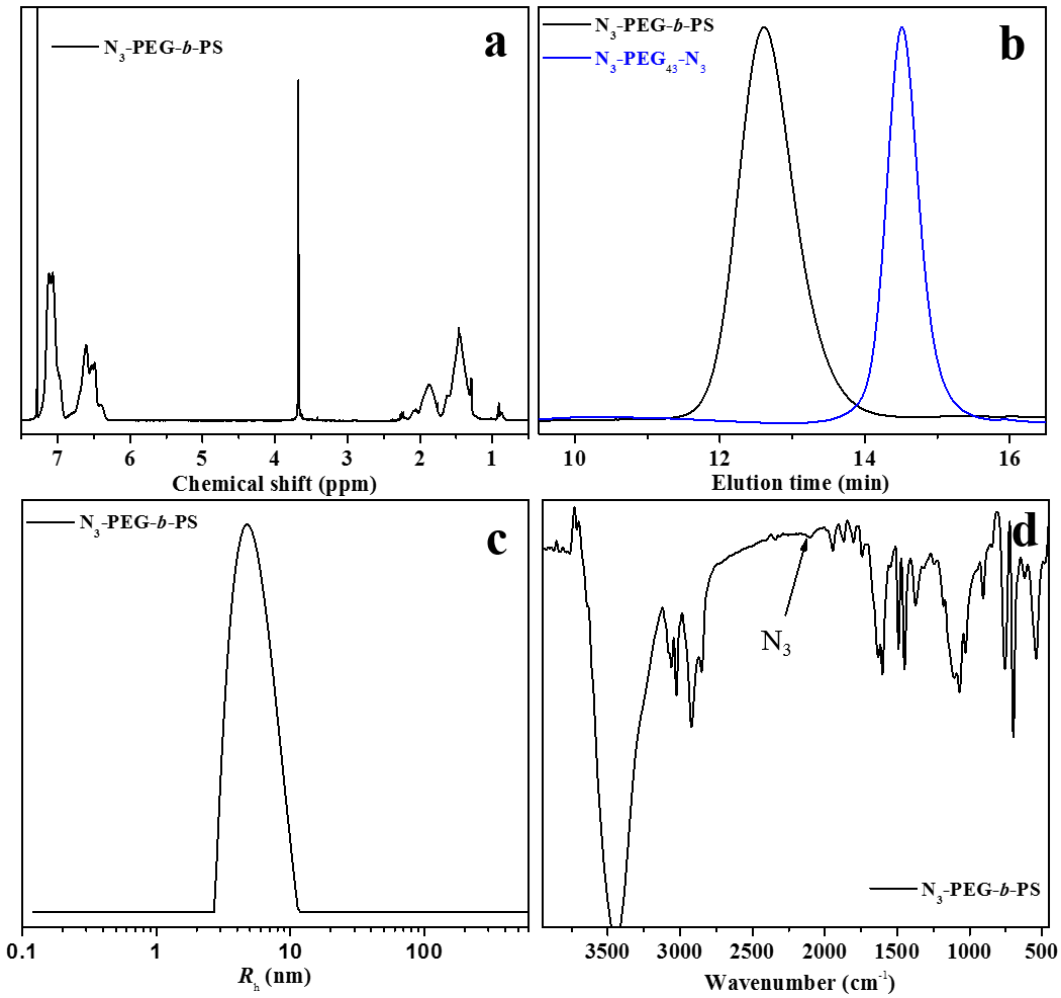



Fig. S6 Characterization of $N_3$-PEG-*b*-PS. a) $^1$H NMR spectrum of $N_3$-PEG-*b*-PS in $CDCl_3$; b) GPC curves of $N_3$-$PEG_{43}$-$N_3$ (blue line) and $N_3$-PEG-*b*-PS (black line); c) DLS curve of $N_3$-PEG-*b*-PS in THF; and d) FTIR spectra of $N_3$-PEG-*b*-PS.

The coumarin group was connected to the PEG via CuAAC click reaction. $N_3$-PEG-*b*-PS (500 mg, 0.01 mmol), **C1** (19 mg, 0.05 mmol), CuBr (2.87 mg, 0.02 mmol), and 2 mL of DMF were added to a 15 mL round bottom flask. The mixture was purged with argon for 30 min. After the solution of PMDETA (4.2 $\mu$L, 0.02 mmol) in 0.1 mL

of DMF was added, the mixture was purged with argon for an additional 30 min. The flask was sealed and placed in an oil bath at 50 °C. After reacting for 24 h, the polymer solution was exposed to air, diluted with THF, and passed through neutral alumina to remove the copper catalyst. The resulting polymer was precipitated twice from a THF solution into ethanol, and dried under vacuum for 24 h, to obtain pale yellow powders.

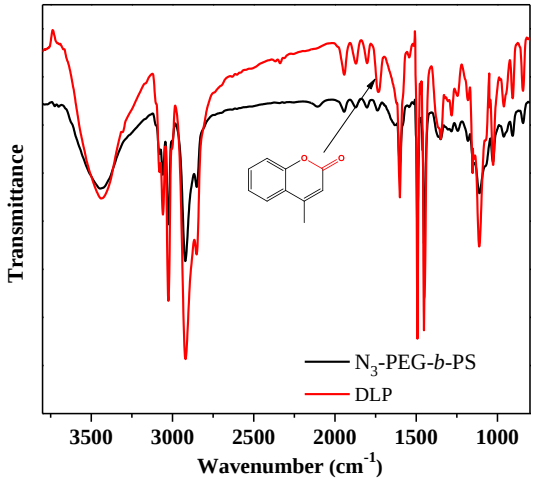



Fig. S7 FTIR spectra of (a) azide-terminated $N_3$-PEG-*b*-PS (black) and coumarin-terminated coumarin-PEG-*b*-PS (red).

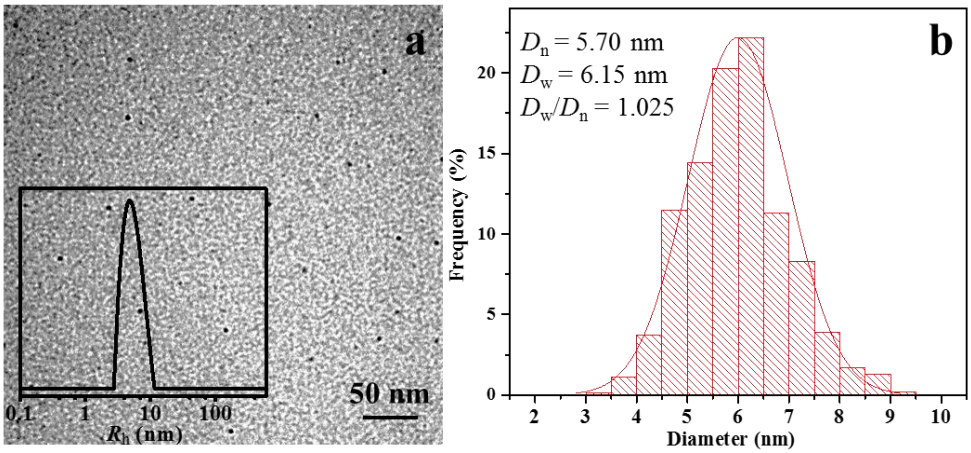



Fig. S8 (a) TEM image of the DLP stained by $RuO_4$ and DLS curves of the DLP in DMF (inset); (b) size distribution of the DLP obtained by statistics over more than 200 DLP particles in the TEM images.

## S2 Preparation of coumarin-modified silica particles

Synthesis of silica particles and surface modification with coumarin groups were conducted by the following processes. Silica particles were prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol medium in the presence of ammonium hydroxide. First, a mixture of 10 mL of ammonium hydroxide (25-28% $NH_3$ in water) and 200 mL of ethanol was prepared. 6 mL of TEOS was added dropwise into the mixture solution and the mixture was stirred for an additional 24 h. Second, **C₂** (400 $\mu$L) and methyltriethoxysilane (MTES, 400 $\mu$L) were added to the mixture and the resulting mixture was stirred for an additional 24 h. Subsequently, the mixture was

heated at reflux temperature for 1 h, and then cooled to room temperature. The mixture was then purified by washing and centrifugation cycles (washed two times with ethanol, and then five times with DMF) to give the coumarin-modified silica particles dispersed in DMF. The reactant volumes of MTES and **C₂** were kept the same to obtain stable suspension of silica particles in DMF. The concentration of silica particles in DMF was determined by the mass of the dried sample divided by the mass of a certain volume of particle suspension. According to the TEM images, the size of the coumarin-modified silica particles is about 77 nm.

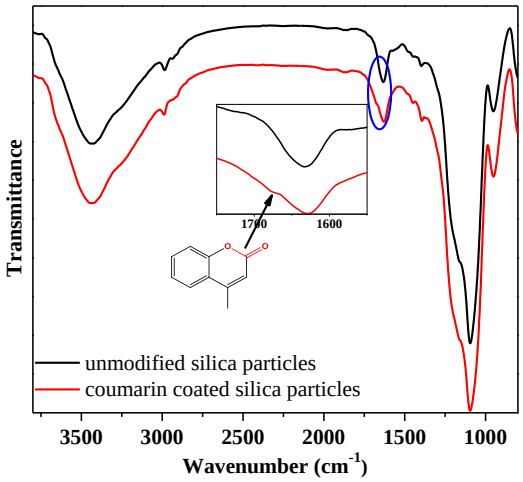



Fig. S9 FT-IR spectra of unmodified silica particles (black) and coumarin-modified silica particles (red).

**Fabrication of thiol group sparsely modified silica particles**

The DLP was grafted to the surface of the silica particles via a coupling reaction between the coumarin groups. First, 200 mg of the coumarin-modified silica particles were dispersed in 20 mL of DMF, and 20 mg of the DLP was added subsequently. The mixture was stirred and directly exposed to UV light (365 nm, 25 W/cm$^2$) using a 500 W mercury lamp (CHF-XM-500W). The irradiation was continued for 60 min under vigorous stirring to achieve sufficient coupling of the coumarin groups and avoid the sedimentation of the silica particles. The suspension was centrifuged and washed with DMF 5 times to remove the unreacted polymer completely. The unreacted polymer could be collected and reused after the UV irradiation (254 nm).

The stabilization of the S-S bond of 2-hydroxyethyl disulfide during UV irradiation was conducted and characterized by $^1$H NMR. As shown in Fig S10, the $^1$H NMR spectra of 2-hydroxyethyl disulfide remained unchanged before and after irradiation of 365 nm UV light for 60 min, which is comparable to the total time of UV irradiation applied to the sample. That is, the S-S bond is stable during the UV irradiation.

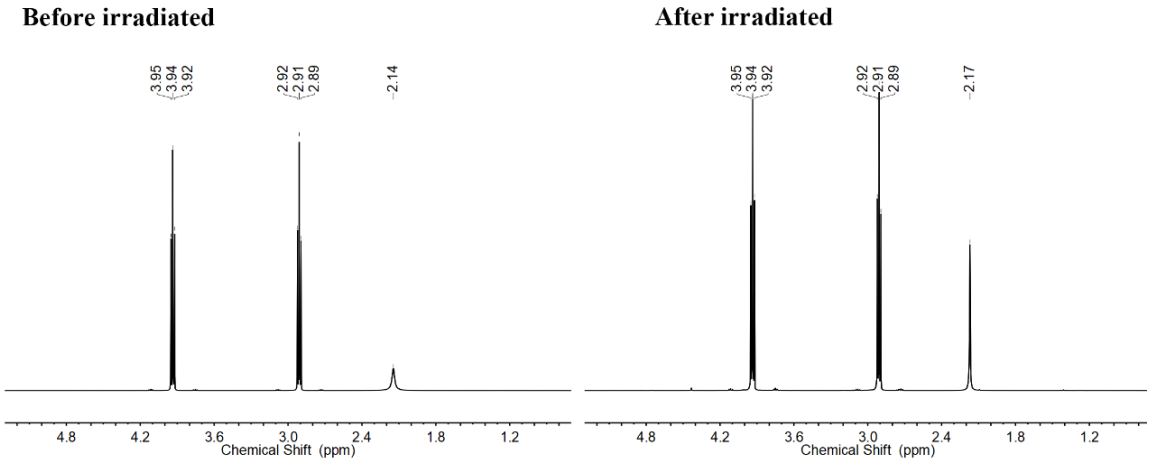



Fig S10 $^{1}$H NMR spectra of 2-hydroxyethyl disulfide before and after irradiation of 365 nm UV light for 30 min.

The thiol sparsely modified silica particles were obtained by removing PS arms of the DLP through disulfide reduction. 150 mg of DLP grafted silica particles were suspended in 15 mL of degassed DMF and placed under argon. dithiothreitol (10 $\mu$L) was added to the mixture and the mixture was stirred vigorously at 40 °C for 24 h. After the mixture was centrifuged and washed with DMF 5 times, thiol groups sparsely modified silica particles were obtained, and then re-dispersed in 10 mL of DMF and stored away from light.

**S3 Calculation of the grafting density of the DLP on the surface of silica particles.**

For the silica particles with a total weight of $m_s$ (assuming it was 100 g), the total surface area of the silica particles is:

$$6m_s/\rho D$$

where $\rho$ is the density of the silica particles (1.9 g/cm$^3$), and $D$ is the average diameter of the silica particles (77 nm).

If the grafted polymer has a total weight of $m_p$ (3.5 g), the total chain number of the grafted polymer is:

$$m_p N_A/M_{n,NMR}$$

where $N_A$ is Avogadro constant, $M_{n,NMR}$ is the molecular weight of DLP (58 kg/mol). According to the above two formulas, the average grafting density of the DLP can be calculated by:

$$6m_s M_{n,NMR}/\rho D m_p N_A$$

**S4 Determination of the reaction time for a total reduction of the disulfide bond between the PEG linker and PS arms of the DLP**

To determine the time required for the completion of the reduction reaction of the disulfide bond between PEG linker and PS arms, cleavage of the disulfide bond in DLP was conducted by the addition of DTT in the solution. Fig. S11 shows the GPC curves of the polymers obtained at different reaction time. When the reaction time reached 6

h, a new GPC peak assigned to PEG appeared, which indicated the cleavage of the disulfide bond between PEG and PS. When the reaction time was extended to 24 h, the intensity of the PEG in the GPC curve remained unchanged compared with that obtained at the reaction time of 18 h, suggesting the completion of the reduction reaction. Accordingly, the reaction time of removing the PS arms from the surface of the silica particles by the reduction reaction of the disulfide bond between the PEG linker and PS arms was determined to be 24 h.

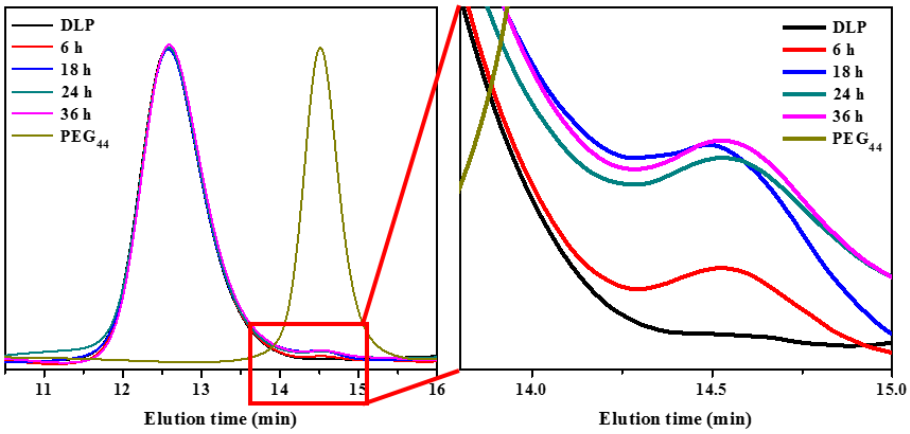



Fig. S11 GPC curves of the DTT-induced reduction of the disulfide bond in DLP at different reaction time.

**Calculation process of the cleavage degree of $PS_4$ from the surface of the silica particles.**

1) Before being grafted by DLP, the ungrafted silica particles contain both volatilizable part (VP) and non-volatilizable part (NVP). Assuming the weight of the ungrafted silica particles is $w$, because the percentage of the initial weight loss is 14.9%, the weight of VP is 0.149 $w$ and that of NVP is 0.851 $w$ (0.149 $w$/ (0.149 $w$ + 0.851 $w$) = 14.9%). 2) After the grafting, when the weight of the DLP grafted on the silica particles is denoted as $x$, the percentage of weight loss is: ($x$ + 0.149 $w$)/($x$ + $w$), which was measured by TGA to be 17.8%. $x$ is thus calculated to be 0.035 $w$. The weight ratio of DLP in the grafted silica particles is 0.035 $w$/ (0.035 $w$ + $w$) = 3.4%. 3) After the cleavage, the percentage of weight loss measured by TGA becomes 15.1%, which is contributed by volatilization of both VP and the residual polymers remained on the silica particles after the cleavage. Similarly, when the weight of the residual polymers is denoted as $y$, ($y$ + 0.149 $w$)/($y$ + $w$) = 15.1%, and the $y$ is thus calculated to be 0.0023 $w$, and the weight ratio of the residual polymers is 0.0023 $w$/1.0023 $w$ = 0.23%.

As detailed in the main text, DLP includes the $PS_4$ and the PEG short linker. As mentioned above, before the cleavage, the weight of the grafted DLP is 0.035 $w$, which is composed of 0.001225 $w$ PEG linker (0.035 $w$ * 2000/58000 = 0.001225 $w$) and 0.033775 $w$ $PS_4$ (0.035 $w$ - 0.001225 $w$). Since all the PEG linker remains after the cleavage, the abovementioned residual polymers (0.0023 $w$) contain 0.001225 $w$ PEG linker and 0.001075 $w$ $PS_4$; the small amount of $PS_4$ remains due to the incomplete cleavage. Therefore, the cleavage percentage is: (0.033775 $w$ – 0.001075 $w$)/0.033775 $w$ = 96.8%.

**S5 Fabrication of NPs with exact functionalities on the surface**

The AuNPs were prepared according to the reported Schiffrin reaction using $HAuCl_4$ and butanethiol (1:1 or 1:1.2 in molar ratio) at room temperature. The obtained AuNPs have average diameters of 3 nm of AuNPs-1 and 5 nm of AuNPs-2, which were determined by TEM (Fig. S12).

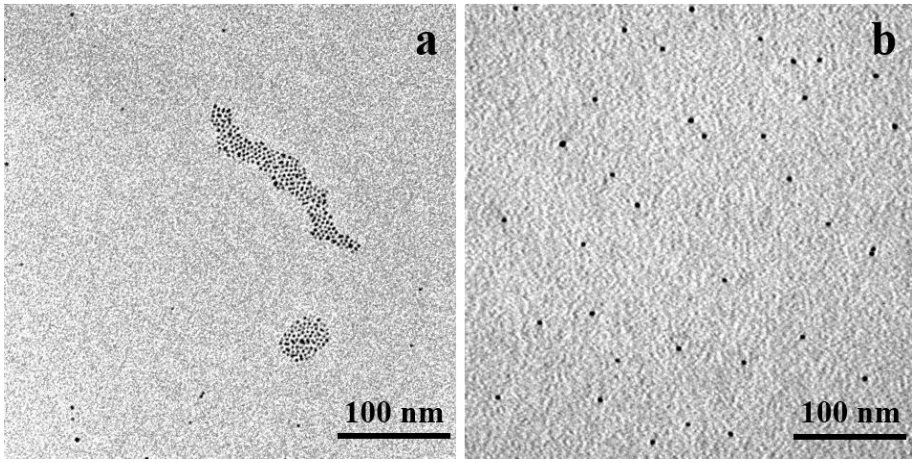



Fig. S12 TEM image of AuNPs with an average diameter of 3 nm (a, AuNPs-1) and 5 nm (b, AuNPs-2).

**(1) Preparation of "monovalent" AuNPs-1 and AuNP-1 dimer**

Step 1: 5 mg of AuNP-1 were dispersed in 2 mL of toluene. AuNPs-1 suspension was then added to the suspension of thiol sparsely modified silica particles (5 mg/mL in DMF). The ligand exchange reaction was allowed to proceed at 35 °C for 24 h with gentle shaking. The mixture was then centrifuged and the collected precipitation was redispersed in 10 mL of toluene under sonication. The centrifugation/dispersion was repeated five times to remove the unbound AuNP-1. The completion of this cycle was determined by the colorless of the supernatant after centrifugation. The resulting precipitate was then redispersed in 5 mL toluene, yielding a pale red suspension.

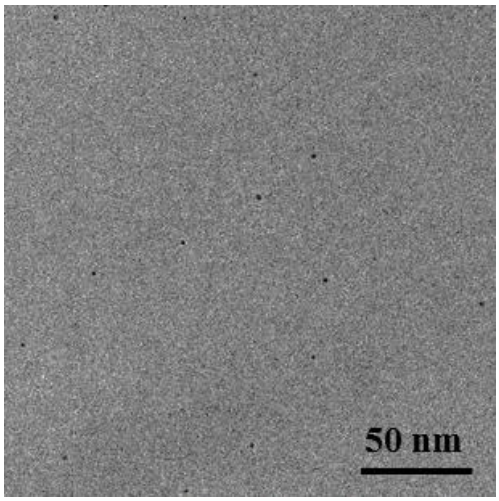



Fig. S13. TEM image of the "monovalent" AuNPs-1.

Step 2: AuNPs-1 were dissociated from the silica particles by exposing the above suspension to 254 nm UV irradiation for 90 min. Then, the mixture was centrifuged and

redispersed in toluene 3 times to obtain the pale red colored “monovalent” AuNPs-1 suspension.

AuNP-1 dimers were obtained by irradiating the “monovalent” AuNPs-1 suspension at 365 nm UV irradiation for 90 min. Each two “monovalent” AuNPs reacted with each other and formed an AuNP-1 dimer.

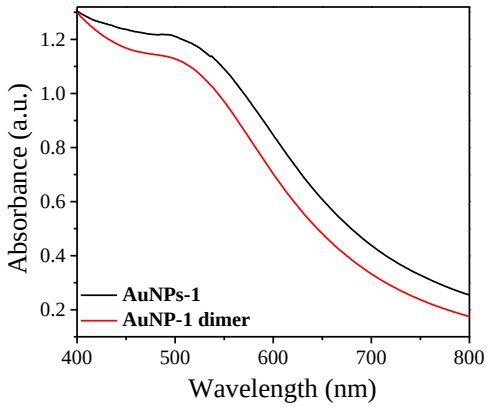



Fig. S14 UV-vis absorption spectra of AuNPs-1 (black line) and AuNP-1 dimer (red line).

**(2) Preparation of “monovalent” and “divalent” AuNPs-2**

“Monovalent” AuNPs-2 and the corresponding dimers were prepared via the same processes as described for AuNPs-1. AuNP-2 dimer was shown in Fig. S15.

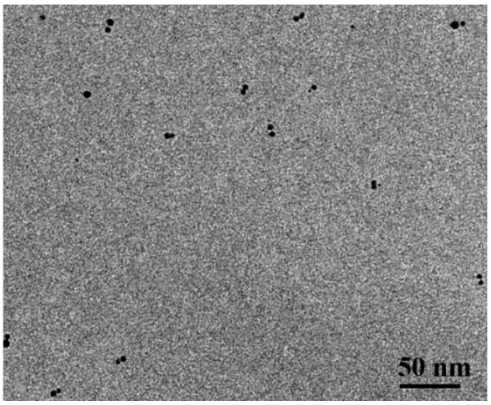



Fig. S15 TEM image of AuNP-2 dimers.

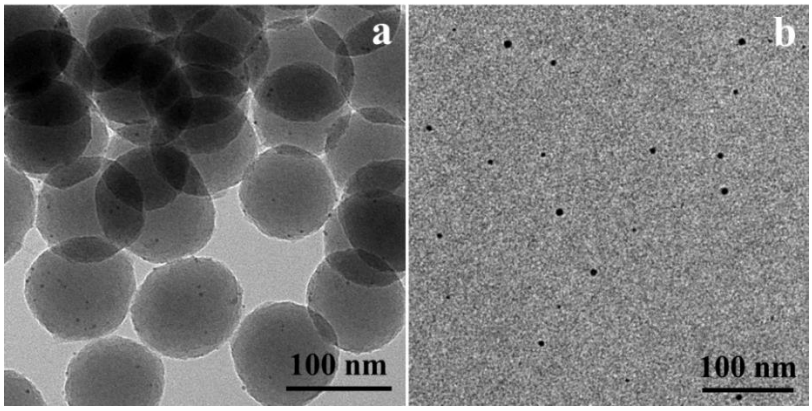



Fig. S16 TEM images of silica particles grafted with “monovalent” AuNPs-2 (a) and the “divalent” AuNPs-2 (b)