Supporting Information

Experimental Section

Synthesis and Characterization of Thioctic Acid-N-Hydroxysuccinimide (TA-NHS).



TA-NHS was synthesized as previously described.[S1] A solution of thioctic acid (2.62 mmol, 0.540 g), NHS (2.88 mmol, 0.330 g), EDC·HCl (2.88 mmol, 0.550 g) in anhydrous DMF (10 mL) was ¹⁰ stirred at room temperature for 4 h under a nitrogen atmosphere. The solution was diluted with EtOAc (50 mL) and washed with H₂O (50 mL), sat. aq. NaHCO₃ (50 mL), H₂O (50 mL x 2). The organic layer was dried over MgSO4, filtered off, and solvent were removed under vacuum. The residue was purified by flash column chromatography to yield 2.02 g of TA-NHS (75%) as a yellow solid. ¹H NMR (600 MHz, DMSO-*d*₆) δ (ppm): 3.55 (sextet, 1H, J = 4.0 Hz, S-S-CH₂-), 3.17 (sextet, 1H, J = 4.0 Hz, S-S-CH₂-), 3.11 (sextet, 1H, J = 4.0 Hz, S-S-CH-), 2.81 (d, 4H, J = 1.0 Hz, -OCH₂CH₂CO-), 2.62 (t, 2H, J= 2.0 Hz, -CH₂CO-), 2.44 (sextet, 1H, J = 6.0 Hz, S-CH₂-CH₂-), 1.90 (sextet, 1H, J = 6.0 Hz, S-CH₂-CH₂-), 1.72-1.78 (m, 2H, -CH₂-CH₂-CO-), 1.67-1.70 (m, 2H, -CH-CH₂-CH₂-), 1.52-1.56 (m, 2H, -CH-CH₂-CH₂-), ¹³C NMR (600 MHz, DMSO-*d*₆) δ (ppm):169.34, 168.62, 56.29, 40.36, 38.72, 34.62, 30.98, 28.53, 25.79, 24.56. ESI-MS: calcd. for C₁₂H₁₈NO₄S₂ (M+H)⁺: 304.0677; found: ²⁰ 304.0645.

Synthesis of Glycosylamines

The glycosylamines were synthesized by reacting the corresponding saccharides (D-lactose, Dmaltose, D-arabinose and L-arabinose for D-lactopyranosamine, D-maltopyranosamine, D-²⁵ arabpyranosamine, and L-arabpyranosamine, respectively) with ammonia as previously described.[S2] A solution of saccharide (2 mmol) with saturated NH₄HCO₃ in 16 M ammonia aqueous solution (10 mL) was allowed to stand at 42 °C for 36 h. The ammonia and NH₄HCO₃ of the mixture was removed under vacuum at 42 °C. The solution lyophilized and the brown solid was purified by flash column chromatography to yield pure glycosylamines (~85%).

Characterization of Glycosylamines.

5 Structures:

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D-lactopyranosamine (**D-Lac**): $[\alpha]_D^{20}$ +47.6 °. ¹H NMR (600 MHz, D₂O) δ (ppm): 3.54 (m, 2H), 3.58-3.98 (m, 10H), 4.43 (d, *J*=8.61 HZ, 1H, -C*H*NH₂), 4.82 (d, *J*=3.71, 1H). ¹³C NMR (600 MHz, D₂O) δ (ppm): 60.19 and 60.98 (C-6 and C-6'), 68.52, 70.93, 72.50, 73.92, 75.09, 75.31, 75.96, 78.60 (C-2, 3, 4, 5, 2', 3', 4', 5'), 84.88 (C-1), 102.87 (C-1'). ESI-MS: calcd. for C₁₂H₂₄NO₁₀ (M+H)⁺: 342.136; found: 342.139.

D-Maltopyranosamine (D-Mal): $[\alpha]_D^{20}$ +105.4 ° ¹H NMR (600 MHz, D₂O) δ 3.42 (m, 2H), 3.53-3.96 (m, 10H), 4.92 (d, *J*=3.9 HZ, 1H, -C*H*NH₂), 5.41 (d, *J*=3.89, 1H) ppm. ¹³C NMR (600 MHz, D₂O) δ 60.48 and 60.85 (C-6 and C-6'), 69.32, 69.82, 72.65, 74.14, 75.43, 76.52, 76.85, 77.06 (C-2, 3, 4, 5, 2', 3', 4', 5'), 85.02 (C-1), 99.54 (C-1') ppm. ESI-MS: calcd. for C₁₂H₂₄NO₁₀ (M+H)⁺: 342.136; found: 342.142.

D-Arabpyranosamine(D-Ara): $[\alpha]_D^{20}$ -86.7 °. ¹H NMR (600 MHz, D₂O) δ 3.41-4.02 (m, 5H), 4.86 (d, *J*=3.85, 1H, -C*H*NH₂) ppm. ¹³C NMR (600 MHz, D₂O) δ 68.21 (C-5), 70.08, 73.96, and 73.39 (C-2, 3, 4, 5), 85.28 (C-1) ppm. ESI-MS: calcd. for C₅H₁₂NO₄ (M+H)⁺: 150.072; found: 150.075.

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L-Arabpyranosamine (L-Ara): $[\alpha]_D^{20}$ +84.3 °. ¹H NMR (600 MHz, D₂O) δ 3.45-4.06 (m, 5H), 4.81 (d, *J*=3.71, 1H, -C*H*NH₂) ppm. ¹³C NMR (600 MHz, D₂O) δ 68.18 (C-5), 70.15, 74.05, and 73.48 (C-2, 3, 4, 5), 85.21 (C-1) ppm. ESI-MS: calcd. for C₅H₁₂NO₄ (M+H)⁺: 150.072; found: 150.077.

Preparation of Citrate-Stabilized Au Nanoparticles (AuNPs). All glassware used in the preparation and storage of AuNPs was cleaned with aqua regia (3:1 HCl/HNO₃), rinsed with water, and oven-dried. AuNPs were prepared according to previous reports.[S3] Briefly, a 100 mL aqueous solution of 1 mM HAuCl₄ was refluxed while stirring vigorously. Next, 10 mL of 38.8 mM citrate was quickly added, ¹⁰ refluxed for 10 min, and allowed to cool to room temperature while stirring. The resulting AuNPs had an average diameter of about 13 nm determined by TEM and an extinction maximum ($\lambda_{max} = 520$ nm).

Preparation and Characterization of Chiral and Achiral AuNPs. The chiral (D-Lac-, D-Mal-, D-Ara-, L-Ara-AuNPs) and achiral AuNPs (DA-AuNPs), were prepared by a two step method.



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First, the citrate-stabilized AuNPs were covalently modified with TA-NHS through the well-known S-Au chemistry [S4] to producing TA-NHS-AuNPs. Generally, 10 mM TA-NHS acetone solution (10 mL) with 10 nM aqueous AuNPs dispersion (10 mL) were mixed and this solution was allowed to stir in the dark for at least 16 h at 20 °C.

Second, chiral AuNPs (including D-Lac-AuNPs, D-Mal-AuNPs, D-Ara-AuNPs, and L-Ara-AuNPs) were prepared by mixing corresponding glycosylamines (10 mM) with the TA-NHS-AuNPs (10 nM) at pH 8.0 for at least 12 h at 20 °C. The NHS activated thioctic ester on the AuNPs can readily form covalent amide bond with the amino groups of the glycosylamines according to the NHS chemistry. The achiral DA-AuNPs were similarly prepared as the chiral AuNPs by replacing the glycosylamines ²⁵ (chiral diols) with dopamine (achiral diol). To avoid possible oxidization of dopamine, the AuNPs solution and all the related solvents were pre-degassed by bubbling pure N₂ for 3-3.5 h while stirring.[S5] All the AuNPs were purified for further uses through several cycles of centrifugation, decantation and redispersion. Particularly, the DA-AuNPs solutions were stocked in the presence of

0.1 wt% $Na_2S_2O_3$ to avoid oxidation of the dopamine moieties. We had also confirmed that presence of

0.1 wt% $Na_2S_2O_3$ did not interfere with subsequent sensing performance of the DA-AuNPs.

The chiral and achiral AuNPs were confirmed by FT-IR spectra (Figure S12-S16) and XPS analysis (Figure S17). The amount of surface-bound modifiers (D-Lac, D-Mal, D-Ara, L-Ara and DA) ⁵ was quantitatively estimated by XPS analysis (Figure S17, and corresponding discussions).

Chiral CE Separations. All the CE experiments were performed with a Beckman P/ACE MDQ CE system controlled by 32 Karat software V. 5.0 (Beckman, Coulter, Fullerton, CA, USA). The instrument was equipped with a UV detector set at 214 nm. Separations were carried out in fused-silica ¹⁰ capillaries of 50 µm id, 65 cm total length and 51 cm to the detector (Yongnian Optical Fiber Factory, Hebei, P. R. China).

Supporting Schemes and Figures



⁵ Scheme S1 Schematic Illustration of enantioselective ligand exchange (eLE) principle. Here, borate is act as the center ion.

The change of the plasmon resonance band of AuNPs in the UV-vis spectra with different concentration of borate ions was monitored to investigate the assembly of AuNPs. Since the aggregation of AuNPs generally resulted in significant increase in the absorbance at 700 nm (A_{700}) and decrease in the absorbance at 520 nm (A_{520}), the ratio of A_{700} to A_{520} was chosen to reflect the assembly $_{5}$ of AuNPs.[S6] A higher ratio corresponded to assembled clusters of AuNPs with blue color whereas a lower ratio referred to dispersed AuNPs with red color.

As an example of the investigations, the UV-vis spectra of D-Lac-AuNPs dispersions containing surface-bound D-Lac (0.04 mM) with different concentrations of borate ions (0-0.06 mM) were shown in Figure S1A. Briefly, at a molar ratio of borate ion to the surface-bound D-Lac = 1:2 equiv, A_{700}/A_{520} reached a peak value, suggesting spiroborate cross-linked assembly of D-Lac-AuNPs (Figure S1B) was complete.



Fig. S1 (A) UV-visible spectra of D-Lac-AuNPs dispersions containing surface-bound D-Lac (0.04 mM) with different concentration of borate ions (from 0 to 0.06 mM). (B) Absorbance ratio of D-Lac-AuNPs (containing surface-bound Lac 0.04 mM) in the presence of different concentration of borate ions (the data was derived from (A)). All the measurements were carried out in the mixture of water solutions containing 20 vol% methanol (pH 9.5, adjusted by NaOH).



Fig. S2 Change in the absorbance ratio $\Delta(A_{700}/A_{520})$ with time after the addition of borate ion at a concentration of 0.02 mM (black) and 0.01 mM (red) borate ions. The kinetic curves were fitted with the following single-exponential function: $\Delta(A_{700}/A_{520})=AI+B \exp(-t/\tau_{asm})$.[S7] Where τ_{asm} represents the characteristic assembly (asm) time of the AuNPs.



Fig. S3 (A) Absorbance ratio of different diols decorated-AuNPs (the concentration was adjusted to contain 0.04 mM surface-bound diols) in the presence of different concentration of borate ions. (B) ⁵ Effect of other common ions on the stability of AuNPs. All the cations were added to a high concentration of 10 mM. The Mg²⁺ and Ca²⁺ and Na⁺ were added as chlorides, and the K⁺ was added as KF. (C) Effect of –SH or -NH₂ group containing small molecules (10 mM) on the stability of AuNPs. All the measurements were carried out in the mixture of water solutions containing 20 vol% methanol (pH 9.5, adjusted by NaOH).

To point out, the cations $(Mg^{2+} and Ca^{2+})$ should be precipitated as hydroxides under the alkaline condition. This should also be one of the reasons that these ions have no effect on the stability of AuNPs.



Fig. S4 Dispersion of D-Lac-AuNPs assemblies (borate ion: Lac=1:2 equiv) by hydrobenzoin: UV-Vis spectra before (black) and after (red) the addition of hydrobenzoin (1 mM). All the measurements were ⁵ carried out in the mixture of water solutions containing 20 vol% methanol (pH 9.5).



Fig. S5 Enantioselective disassembly titration of D-Mal-AuNPs networks with (*R*,*R*)-hydrobenzoin or (*S*,*S*)-hydrobenzoin. [Diol]_t, concentration of the analyte (hydrobenzoin). All the measurements were carried out in the mixture of water solutions containing 20 vol% methanol (pH 9.5). All measurements ⁵ were taken at 25 °C.



Fig. S6 Enantioselective disassembly titration of D-Ara-AuNPs networks with (*R*,*R*)-hydrobenzoin and (*S*,*S*)-hydrobenzoin. [Diol]_t, concentration of the analyte (hydrobenzoin). All the measurements were ⁵ carried out in the mixture of water solutions containing 20 vol% methanol (pH 9.5). All measurements were taken at 25 $^{\circ}$ C.



Fig. S7 Enantioselective disassembly titration of L-Ara-AuNPs networks with (*R*,*R*)-hydrobenzoin and ${}_{10}$ (*S*,*S*)-hydrobenzoin. [Diol]_t, concentration of the analyte (hydrobenzoin). All the measurements were carried out in the mixture of water solutions containing 20 vol% methanol (pH 9.5). All measurements were taken at 25 °C.



Fig. S8 ¹H NMR a Bruker Avance 600 MHz NMR Spectrometer in D₂O/CD₃OD of (*R*,*R*)hydrobenzoin (blue), (*S*,*S*)-hydrobenzoin (red), and racemic hydrobenzoin (black) in the presence of D-Lac-AuNPs and borate ion (D-Lac: borate ion: hydrobenzoin=2:1:0.5 equiv). D-Lac-AuNPs solutions were 50 fold concentrated (surface-bound D-Lac 2 mM) for NMR measurements after addition of hydrobenzoin.



Fig. S9 ¹H NMR a Bruker Avance 600 MHz NMR Spectrometer in D_2O/CD_3OD of racemic hydrobenzoin (black) in the presence of D-Ara-AuNPs and borate ion (D-Ara: borate ion: hydrobenzoin=2:1:0.5 equiv). D-Lac-AuNPs solutions were 50 fold concentrated for ¹H NMR ³ measurements after addition of hydrobenzoin.

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Fig. S10 Ee correlation graph at different concentrations of hydrobenzoin.



Fig. S11 CE separation of racemic hydrobenzoin using β -cyclodextrin-borate as chiral selector. Separation conditions: fused-silica capillary, 65 cm (51.0 cm effective length)×50 µm i.d.; background s electrolytes, 200 mM borate buffer, 2.5% (*w*/*v*) β -cyclodextrin; temperature, 25 °C; applied voltage, 20 kV; UV detection at 214 nm.



Fig. S12 FTIR spectrum of D-Lac-AuNPs.



⁵ Fig. S13 FTIR spectrum of D-Mal-AuNPs.



Fig. S14 FTIR spectrum of D-Ara-AuNPs.



Fig. S15 FTIR spectrum of L-Ara-AuNPs.

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Fig. S16 FTIR spectrum of DA-AuNPs.

XPS. XPS measurements and quantitative analysis were carried out as described previously.[S8] Briefly, a 160 eV pass energy, 1 eV step size, 200 ms dwell time, and ~700 μ m x 300 μ m X-ray spot size were used for a survey scan (range = 1200 to -5 eV). Region scans (O1s, N1s, S2p, and Au4f) s exhibited typical bandwidths of 20-50 eV, 20 eV pass energies, 0.1 eV step sizes, and 1 s dwell times. All spectra were were charge-calibrated with respect to the adventitious C1s peak at 284.8 eV. The S2p peak of thioctic acid was peak fitted using the S 2p doublet with a 2:1 area ratio and an energy difference of 1.2 eV. A Shirley background was used to subtract the inelastic background from the S2p and Au4f signal. The curves were fitted using a Gaussian/Lorentzian (GL(30)) line shape. To account for differences in nanoparticle concentration in sample spots, the S 2p areas were normalized using the Au 4f area. Two areas were analyzed per sample.



²⁰ Fig. S17 XPS spectra for O 1s, N 1s, S 2p and Au 4f obtained at D-Lac-AuNPs (curve a), D-Mal-AuNPs (curve b), D-Ara-AuNPs (curve c), L-Ara-AuNPs (curve d), and DA-AuNPs (curve e).

The amount of surface-bound modifiers (D-Lac, D-Mal, D-Ara, L-Ara and DA) was quantitatively estimated by the XPS spectra according to literature [S8]. First, the S: N atomic ratio was calculated ²⁵ from the S2p and N1s peak areas using the empirical atomic sensitivity factor (SF) for them (SF=0.54 and 0.42 for S2p and N1s, respectively). Accordingly, the S: N atomic ratio for all the samples (D-Lac-AuNPs, D-Mal-AuNPs, D-Ara-AuNPs, L-Ara-AuNPs, and DA-AuNPs) was nearly 2: 1, suggesting that the carboxyl groups of TA were fully reacted with amine of the glycosylamines or dopamine. Second, the S: O atomic ratio was calculated from the S2p and O1s (SF=0.66) peak areas. ³⁰ Significantly, the S: O ratios were in accordance with the oxygen atom numbers of D-Lac, D-Mal, D-Ara, L-Ara and DA, suggesting the reliability of the results.

Atomic	D-Lac-	D-Mal-	D-Ara-AuNPs	L-Ara-AuNPs	DA-AuNPs
ratio	AuNPs	AuNPs			
S: N	1:1.89	1:2.22	1:2.14	1:1.95	1:2.47
S: O	1:5.6	1:6.3	1:3.5	1:3.2	1:1.5

Finally, the amount of surface-bound modifiers was converted from the S2p and Au4f (SF=4.95) peak areas. As pointed out by literature [S8], XPS only interrogates ca. 6 out layers of the total atomic s layers of AuNPs. For our AuNPs have an average diameter of 13 nm, they have a total atomic layers of 22. Thus, the number of Au atom of the outer six layers was calculated to be 23002. Therefore, the number of S atom per AuNPs can be calculated by the following equation:

 $N_{\rm S}/N_{\rm AuNPs} = (A_{\rm S}/A_{\rm Au}) \times (SF_{\rm Au}/SF_{\rm S}) \times 23002$

 $=1500/(79940+63230)\times 4.95/0.54\times 23002=2209$, where A_s and A_{Au} represent peak areas of ¹⁰ S2p and Au4f, respectively. The values were from the spectra of D-Lac-AuNPs. Considering each TA molecules have 2 S atoms, the density of surface-bound D-Lac could be predicted as 1104 per AuNP. Similarly, the number of surface-bound modifies per AuNPs was calculated to be 1055, 1270, 1196, and 987 for D-Mal-AuNPs, D-Ara-AuNPs, L-Ara-AuNPs, and DA-AuNPs, respectively. Such modifying densities are comparable with the results of literature [S8].

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The results indicated that the modifying densities for each modifier were almost the same. This is reasonable thanks to the AuNPs modifying procedures. As provided in foregoing, AuNPs were firstly modified with TA-NHS. The same batch of TA-NHS-AuNPs was used for further modification of every diol modifiers. Therefore, the bound amount of each modifier should be reasonably the same by mixing the TA-NHS-AuNPs with excess modifiers.

Consequently, for a 10 nM (0.074 mg/mL) AuNPs solution, the concentration of surface-bound 20 modifiers was about 10 μ M.

Supporting Tables

Chiral AuNDa	(A_{700}/A_{520})			Enantioselectivity		
	R,R	Racemic	<i>S</i> , <i>S</i>	$(A_{700}/A_{520})_{\rm SS}/(A_{700}/A_{520})_{\rm RR}$		
D-Lac-AuNPs	0.1162	0.2955	0.5547	4.77		
D-Ara-AuNPs	0.2281	0.3435	0.4656	2.04		
L-Ara-AuNPs	0.4611	0.3081	0.2197	0.48^{b}		
D-Mal-AuNPs	0.1720	0.1924	0.2275	1.32		

Table S1 Screening of the enantioselectivities of the chiral AuNPs to hydrobenzoin.^a

^a Results of the screening plate with (*R*,*R*)-hydrobenzoin (0.5 mM), racemic mixture (0.5 mM) and (S,S)-hydrobenzoin (0.5 mM). All solutions were made in the mixture of water solutions containing 20 vol% methanol (pH 9.5). All measurements were taken at 25 °C.

^b 1/0.48=2.08≈2.04 (the enantioselectivity of D-Ara-AuNPs).

Chiral AuNPs	Hydrobenzoin ^b	Diethyl tartrate ^c	1-Phenylpropane-1,2- diol ^d
D-Lac-AuNPs	4.77	2.08	2.66
D-Ara-AuNPs	2.04	2.21	1.87
L-Ara-AuNPs	0.48	0.47	0.51
D-Mal-AuNPs	1.32	2.35	1.15

¹⁰ Table S2 Enantioselectivities of the chiral AuNPs to different chiral diol enantiomers.^a

^a Structures of the enantiomers:

^b The enantioselectivity was calculated as $(A_{700}/A_{520})_{SS}/(A_{700}/A_{520})_{RR}$;

^c The enantioselectivity was calculated as $(A_{700}/A_{520})_L/(A_{700}/A_{520})_D$;

¹⁵ ^d The enantioselectivity was calculated as $(A_{700}/A_{520})_{1S2S}/(A_{700}/A_{520})_{1R2R}$.

[Diol] _t /mM			<i>ee</i> / %		
Actual	Det. ^a	Error ^b	Actual	Det. ^a	Error ^b
0.30	0.33	0.03	75.00	75.91	0.91
0.30	0.25	0.05	25.00	23.08	1.92
0.30	0.32	0.02	-25.00	-26.80	1.80
0.30	0.28	0.02	-75.00	-72.03	2.97
0.60	0.42	0.18	8.50	7.09	1.41
0.60	0.63	0.03	85.00	89.39	4.39
0.60	0.53	0.07	-8.50	-6.05	2.45
0.60	0.55	0.05	85.00	79.02	5.98

Table S3 Determination of *ee* and [Diol]_t of 8 unknown samples of hydrobenzoin.

^a Determined values. ^b Error= (actual value)-(determined value) .

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