Suppporting Information

Novel competitive fluorescence sensing platform for L-carnitine based on cationic pillar[5]arene modified gold nanoparticles

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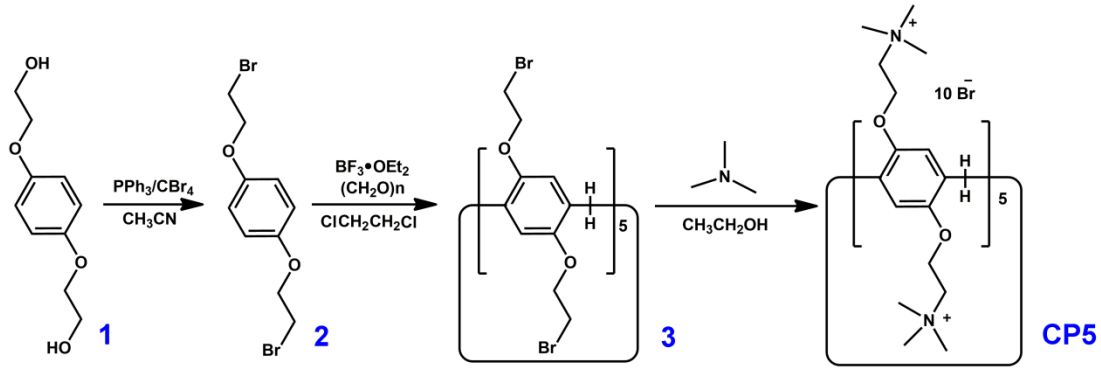
S1 Molecular Docking

The structures of CP5 and L-carnitine were constructed using AutoDockTools 1.5.6.[1] The CP5 crystal structure (ID: 4118702) was gained from Cambridge Crystallographic Data Centre (CCDC) with similar crystal structure. The AM1-BCC charges and GAFF force field were used. The optimized structures were used as starting structures. The sphgen module was applied to generate spheres surrounding the binding site. The Grid module of AutoDock 4.2.6 was employed to generate a grid file, which was used for scoring in the subsequent docking procedure. The flexible docking method was utilized to produce 1000 different conformational orientations for the guest molecule. The electrostatic interactions were calculated based on the grids. Finally, clustering analysis with an Amber14 was performed to obtain the best results.[2]

S1. Reagents and methods

1,4-Bis(2-hydroxyethoxy)benzene, dichloroethane, boron trifluoride diethyl etherate, carbon tetrabromide, triphenylphosphine, acetonitrile, paraformaldehyde, and trimethylamine were reagent grade and used as received. Solvents were either employed as purchased or dried according to procedures described in the literature. CP5 was synthesized according to the previous papers procedures.[3,4]

S2. Synthesis of cationic pillar[5]arene (CP5)



Scheme S1. Synthetic route of **CP5**.

Synthesis of 2: A solution of **1** (5.0 g, 25.0 mmol) and triphenylphosphine (16.0 g, 60 mmol) in dry acetonitrile (200 mL) was cooled with an ice bath. Under vigorous stirring, carbon tetrabromide (20.0 g, 60 mmol) was slowly added. The mixture was stirred at room temperature for 4 hours. Then cold water (150 mL) was added to the

reaction mixture to give white precipitation. The precipitate was collected, washed with methanol/water (3:2, 3 × 100 mL), recrystallized from methanol, and dried under vacuum to afford **2** as white crystals (5.9 g, 91%). The ^{1}H NMR spectrum of **2** is shown in Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, rt) δ (ppm): 6.863 (s, 4H), 4.245 (t, J = 5.6 Hz, 4H), 3.618 (t, J = 6.4 Hz, 4H). The ^{13}C NMR spectrum of **2** is shown in Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$, rt) δ (ppm): 152.81, 116.07, 68.69, 29.29.

Synthesis of 3: Boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$, 3.26 g, 23.0 mmol) was added to the mixed solution of paraformaldehyde (0.35 g, 11.5 mmol) and **2** (3.37 g, 11.5 mmol) in 1,2-dichloroethane (100 mL) under nitrogen atmosphere. Then the mixture was stirred at room temperature for 3 hour. A green solution was got. The reaction mixture was then washed with water (3 × 120 mL) and dried with excess Na_2SO_4. After the solvent was removed, the obtained solid was purified by column chromatography on silica gel with petroleum ether/dichloromethane (1:2 *v*/*v*) as the eluent to get a white powder of **3** (1.46 g, 45 %). The ^{1}H NMR spectrum of **3** is shown in Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ (ppm): 6.915 (s, 10H), 4.229 (t, J = 6.0 Hz, 20H), 3.850 (s, 10H), 3.630 (t, J = 6.0 Hz, 20H). The ^{13}C NMR spectrum of **3** is shown in Figure S4. ^{13}C NMR (125 MHz, $CDCl_3$, rt) δ (ppm): 150.05, 129.45, 116.49, 69.35, 31.06, 29.77.

Synthesis of CP5: The mixture of compound **3** (1.5 g, 1.2 mmol) and trimethylamine (33 % in ethanol, 6.43 mL, 23.8 mmol) in ethanol (50 mL) were stirred at 90 ºC for 24 h under nitrogen atmosphere. Then the solvent was removed by evaporation, deionized water (25 mL) was added. After filtration, a clear solution was got. Then the water was removed by evaporation to obtain **CP5** as a colorless solid (1.58 g, 95 %). The ^{1}H NMR spectrum of **CP5** is shown in Figure S5. ^{1}H NMR (400 MHz, D_2O, rt) δ (ppm): 6.909 (s, 10H), 4.412 (s, 20H), 3.881 (s, 10H), 3.765 (s, 20H), 3.167 (s, 90H). The ^{13}C NMR spectrum of **CP5** is shown in Figure S6. ^{13}C NMR (100 MHz, D_2O, rt) δ (ppm): 149.34, 129.89, 116.45, 64.88, 63.45, 54.04, 29.51.

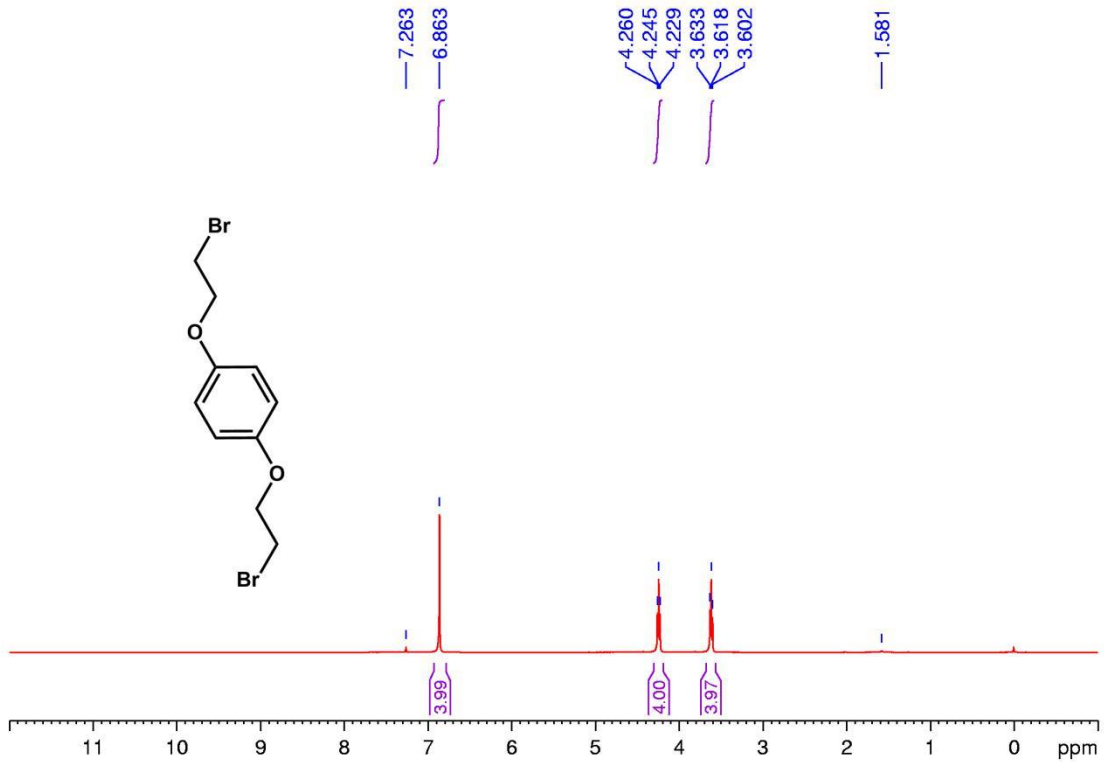


Fig. S1 ^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of **2**.

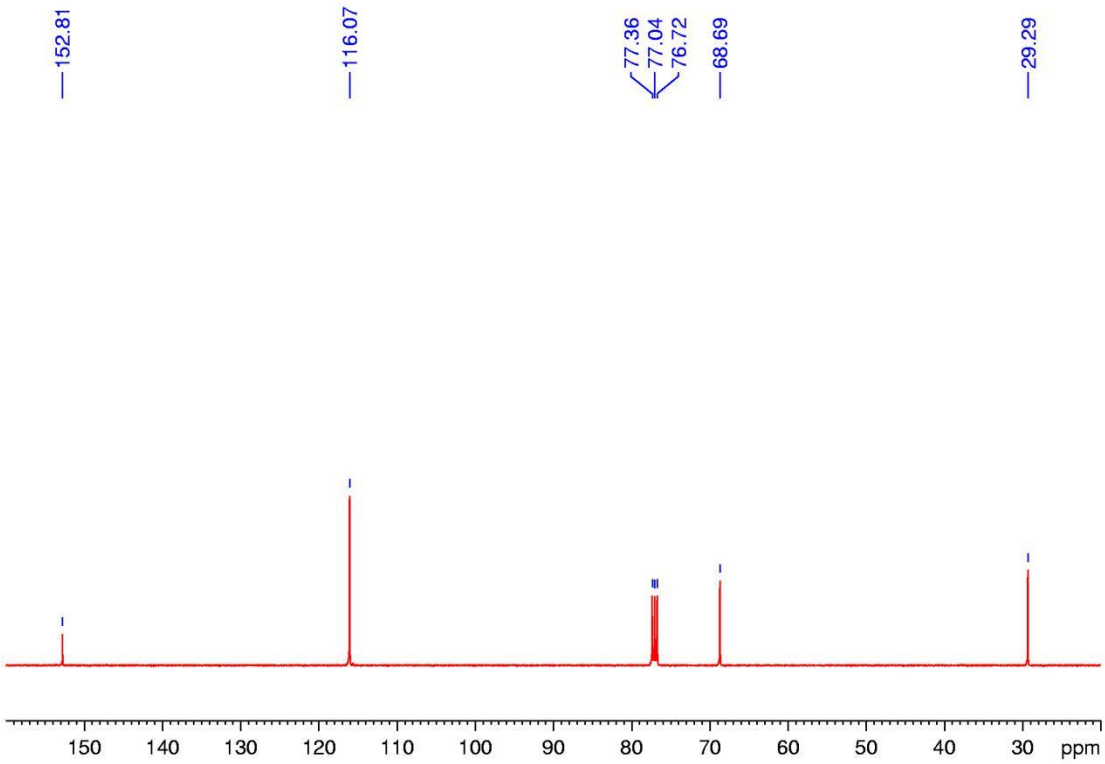


Fig. S2 ^{13}C NMR spectrum (100 MHz, D_2O, 298 K) of **2**.

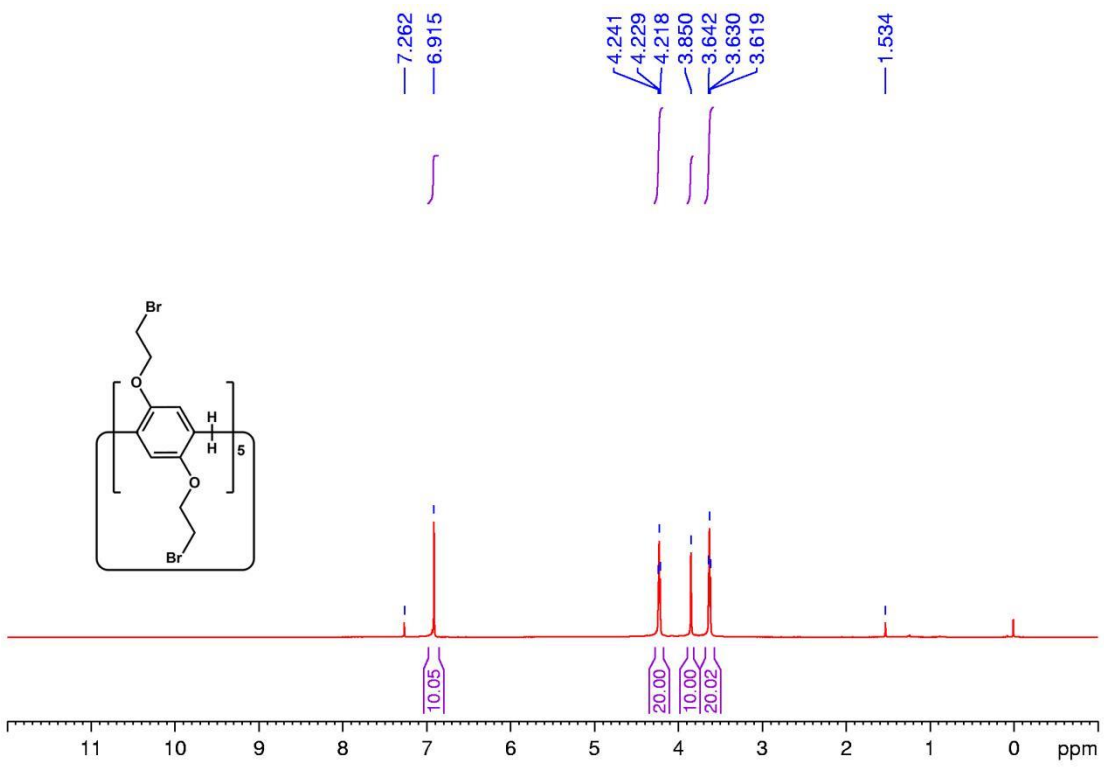


Fig. S3 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **3**.

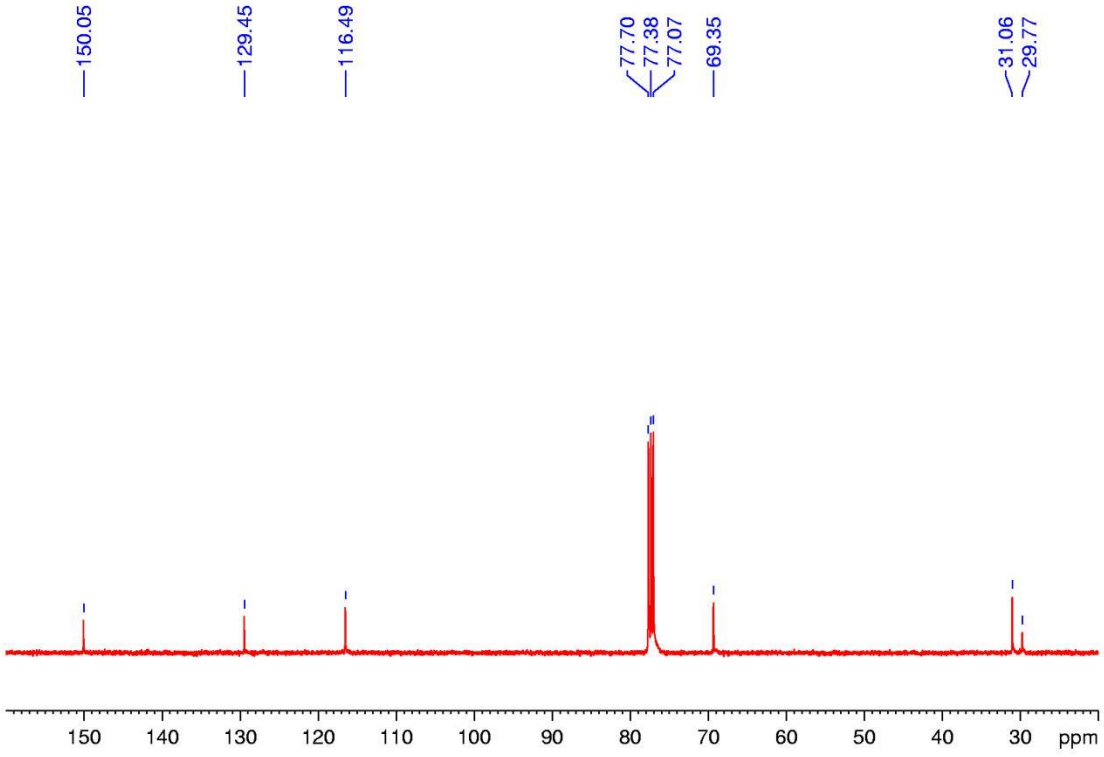


Fig. S4 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **3**.

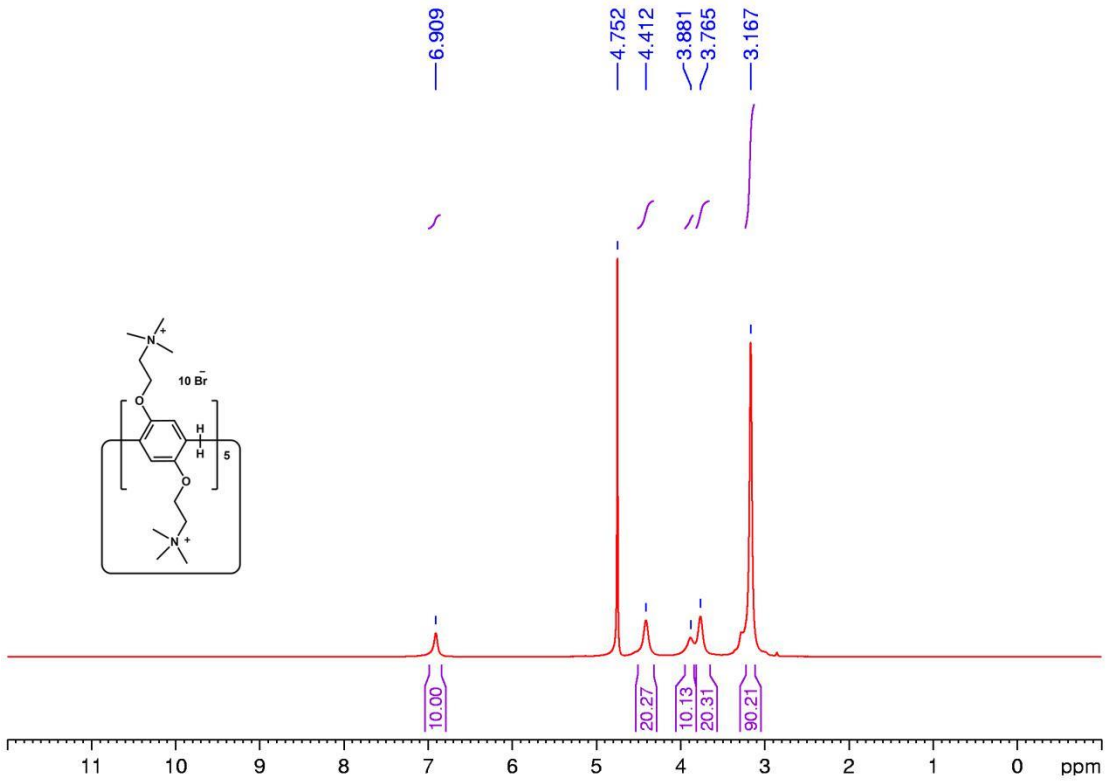


Fig. S5 ^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of **CP5**.

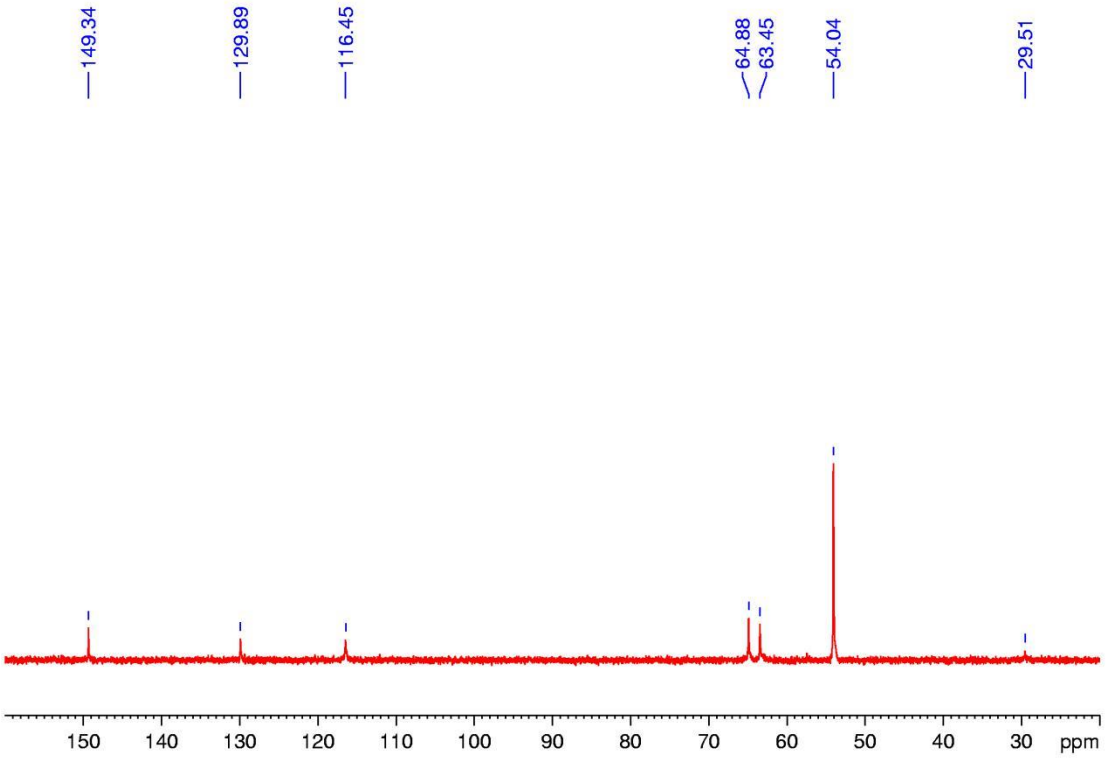


Fig. S6 ^{13}C NMR spectrum (100 MHz, D_2O, 298 K) of **CP5**.

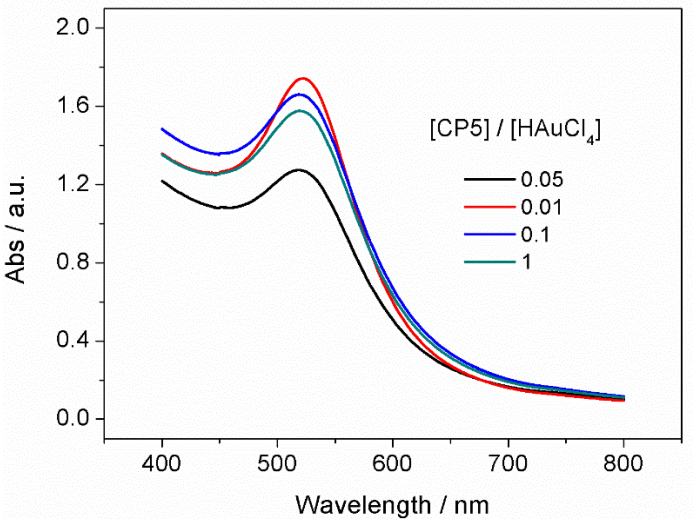


Fig. S7 Ultraviolet−visible spectra of CP5-modified Au-NPs synthesized with different [CP5]/[$HAuCl_4$] ratios.

Fig. S8 Photograph for the aqueous solution of CP5@Au-NPs.

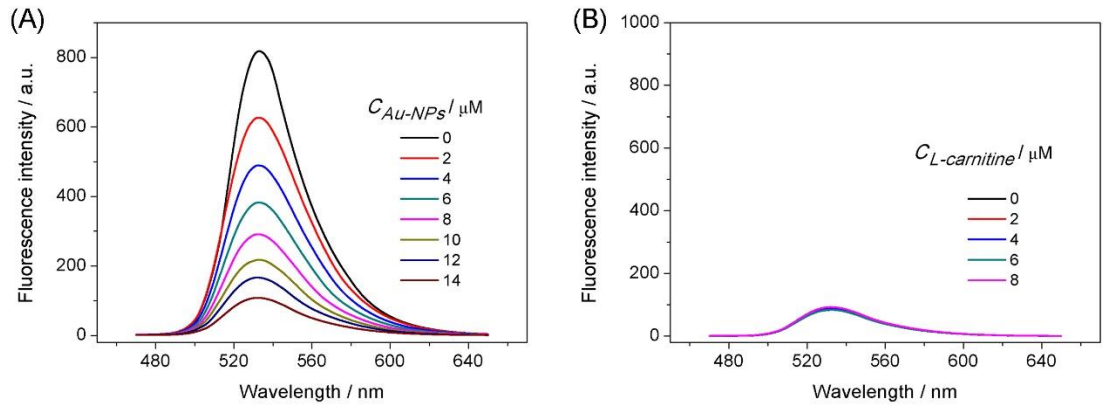


Fig. S9 The effect of increasing concentrations of Au-NPs (concentrations ranging from 0 to 14 μM) on the fluorescence intensity of 2 μM R123. (B) Fluorescence spectra of the R123@Au-NPs complex via different concentrations of L-carnitine.

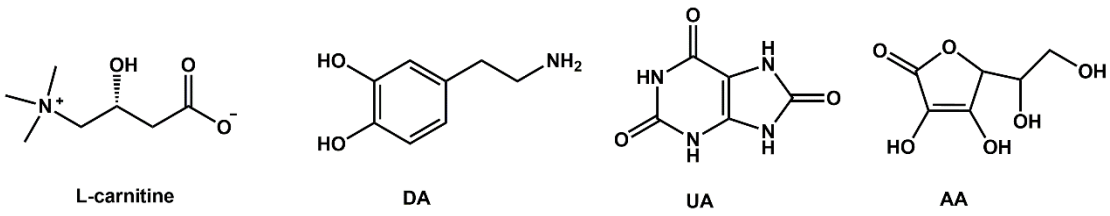


Fig. S10 Chemical structures of L-carnitine, DA, UA, and AA, respectively.

Table S1 Comparison of different methods for quantitative detection of L-carnitine.

Electrode or matrix	Method	Liner range (μM)	LOD (μM)	Ref
Ni/Cu alloy	Voltammetric	_	7.08	5
CdSe/ZnS quantum dots	Fluorescence	_	0.15	6
Cys−Au(I)	Fluorescence	1-10	0.5	7
Coenzyme A	Fluorescence	0.5-10	0.18	8
_	Capillary zone electrophoresis	9.1-200	3	9
CMG/safranine T	Fluorescence	0-534	_	10
PP5@Au-NPs	Fluorescence	0.1-25	0.067	This work

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