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Magnetic controlling migration of DNA and proteins using one-step modified gold nanoparticles†

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Experimental Section

Cetyltrimethylammonium bromide (98%, CTABr), iron trichloride (99.9%, $FeCl_3$) were purchased from Sinopharm Chemical Reagent Co. Ltd, China and used without further purification. $HAuCl_4$ was purchased from J&K Chemical LTD and $NaBH_4$ from Sinopharm Chemical Reagent Co. Ltd, China.

Herring testes double-strand DNA sodium salts were purchased from Sigma. Its molar weight was < 1200 bps as determined by agarose gel electrophoresis (AGE) and its concentration was examined through considering the DNA bases molar extinction coefficient to be 6600 mol^{-1} cm^{-1} at 260 nm. The absorbance ratio of DNA stock solution was 1.8 to 1.9 at 260 nm and 280 nm, which suggests no protein was present.

Myoglobin (Mb, from equine heart) was purchased from Sigma Aldrich. Concentrations were calculated according to the absorbance at 409 nm by considering the molar extinction coefficient of 17100 mol^{-1} cm^{-1}. Bovine serum albumin (98%, BSA) was purchased from Sigma Aldrich. Its molar weight is approximate 66 kDa.

Cetyltrimethylammonium trichloromonobromoferrate (CTAFe) was synthesized by mixing equal molar amounts of CTABr and $FeCl_3$ in methanol and stirring overnight at room temperature. The solvent was then evaporated and the product dried at reduced pressure at 80 °C for 12 h yielding brown/red solid.

The Au@CTAFe nanoparticles were synthesized as follows: mixing 5 mL desired amounts of CTAFe (Table S1) aqueous solutions with 1 mM, 5 mL $HAuCl_4$. Fresh

prepared ice-bathed $NaBH_4$ aqueous solution (0.6 mL, 3 mM) was added to this complex solution. The resulting mixtures were vigorously stirred for 2 min and kept at 25 °C.

Thrice-distilled water was used to prepare each sample solution. In all experiments, the concentration of DNA was controlled constant at 75 μmol L^{-1}, Mb and BSA concentrations were held at 10 μmol L^{-1} and 20 μmol L^{-1}, respectively. Each complex sample was prepared by adding known amounts of biomacromolecules, nanoparticles and water to a fixed volume.

The critical micelle concentration (cmc) of CTAFe was determined as 0.42 mmol L^{-1} by electrical conductivity method. A DDSJ-308A analyzer was used to perform electrical conductivity experiments. A Pyrex glass measuring cell was placed in a water bath at 25 ± 0.3 °C. The cmc was determined from the break point between the higher [dκ/d (conc)] and lower [dκ/d (conc)] linear curves. The surfactant ionic dissociation constant (β) was estimated by the ratio of the two slopes.

SQUID magnetometry shows that surfactant CTAFe is a paramagnetic compound (Figure. S1). Dried samples of surfactants were placed in sealed polypropylene tubes and mounted inside a plastic straw for measuring in a magnetometer with a superconducting quantum interference device (MPMSXL, Quantum Design, USA) and a reciprocating sample option (RSO). The data were collected at 300K.

UV spectra of DNA/nanoparticle complex solutions were examined by a U-4100 UV/visible spectrometer, using a 10 mm path length quartz cell at a wavelength range of 220-320 nm.

A JASCO J-810 spectropolarimeter was used to perform CD spectroscopy. Samples were located in 10 mm path length cells, and the scanning speed was controlled to 100 nm/min with a measuring range at 220-320 nm. Each sample was measured three times for their average value.

A BI-200SM instrument (Brookhaven) was used for the measurements of DNA/surfactant or DNA/nanoparticle complex solution samples at a constant scattering angle of 90°. All solutions were made dust-free by filtration through cellulose acetate membranes of 0.45 mm pore size.

Agarose gels (1% w/vol) were horizontally submerged in pH 7.4 TAE buffer (40 mM Tris, 2 mM $Na_2EDTA \cdot 2H_2O$, 20 mM glacial acetic acid) at 5 V/cm. DNA was visualized by ethidium bromide (0.5 µg/mL), and a standard DNA ladder of 5000 bps was utilized as a reference. This measurement was conducted in a darkroom with aluminum foil packing around the electrophoresis tank.

Supplementary Figures.

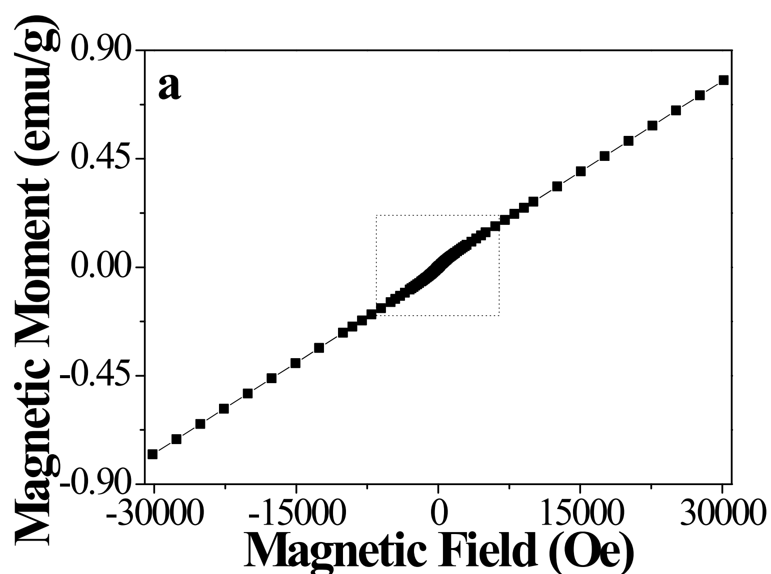

Figure S1. SQUID magnetometry results of surfactant CTAFe at 298.0 ± 0.1 K. The dotted rectangle part refers to the weak ferromagnetic signal of the surfactant.

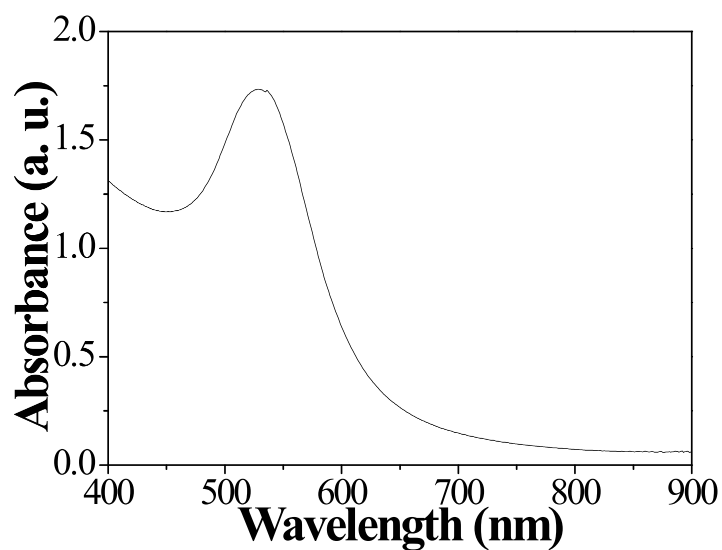

Figure S2. A UV-vis spectrum of the absorbance of the Au@CTAFe at 298.0 ± 0.1 K.

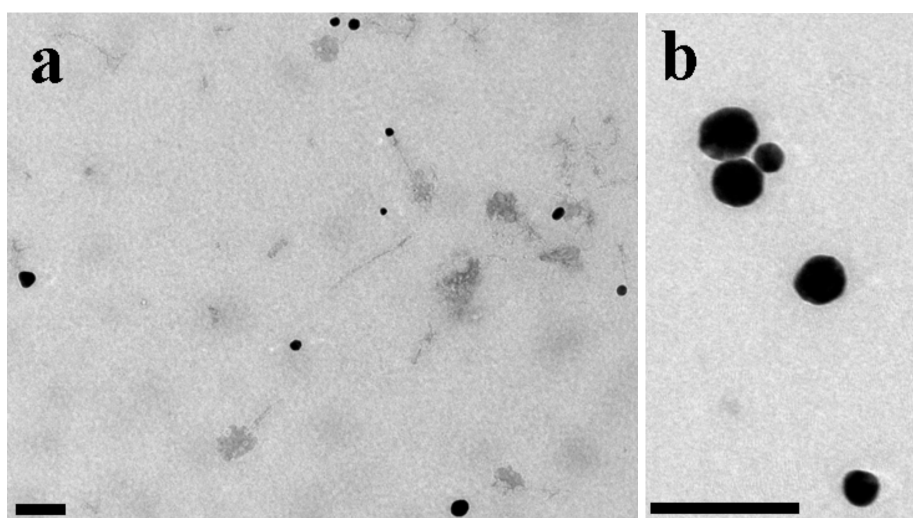

Figure S3. TEM images of the Au@CTAFe nanoparticles. Each bar is equal to 50 nm.

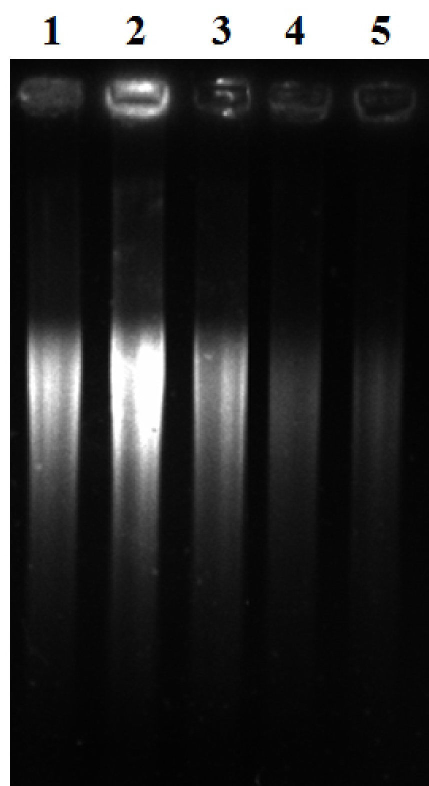

Figure S4. Aagarose gel electrophoresis results of DNA mixing with 0 μmol L^{-1} (lane 1), 1 μmol L^{-1} (lane 2), 2 μmol L^{-1} (lane 3), 4 μmol L^{-1} (lane 4) and 10 μmol L^{-1} (lane 5) Au@CTAFe, respectively.

Sample	Ratio	$2R_H$ (nm)	ξ (mV)
AuNPs/CTAFe	1:1	322.2	19.7 ± 2.16
AuNPs/CTAFe	1:2	21.1	38.81 ± 2.7
AuNPs/CTAFe	1:4	210.6	28.62 ± 1.87
AuNPs/CTAFe	1:6	57.0	41.5 ± 2.1
AuNPs/CTAFe	1:8	68.8	49.26 ± 1.7
AuNPs/CTAFe	1:10	89.4	56.33 ± 4.22

Table S1. Hydrodynamic diameters ($2R_H$) and zeta potential (ξ) values of AuNPs modified with CTAFe in different ratios at 298.0 ± 0.1 K.