Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

An anti-galvanic replacement reaction of DNA templated silver nanoclusters monitored by light-scattering technique

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Experimental Section

Materials and Measurements:

Silver nitrate ($AgNO_3$), 99.99%, and sodium borohydride ($NaBH_4$), 98%, were purchased from Alfa Aesar and used without further purification. The DNA oligonucleotides were purchased from Sangon (Shanghai, China). All other reagents were all of analytical grade. The solutions were prepared with MilliQ water (18.2 MΩ. cm) from a Millipore system. Unless otherwise noted, experiments were carried out in 10 mM Tris/HCl buffer solution (pH 7.0).

The light-scattering spectra were measured with a model LS-55 spectrofluorometer (Perkin-Elmer, USA). Fluorescence measurements were performed by a FLS-920 picosecond fluorescence lifetime spectrometer (Edinburgh Instruments, UK). UV-vis spectra were determined by an Agilent 8453 UV-vis spectrophotometer (Agilent Technologies Co. Ltd., USA). XPS measurements were implemented on a Thermo ESCALAB 250 instrument configured with a monochromated $Mg_{K\alpha}$ (1486.8 eV) 150 W X-ray source, 0.5 mm circular spot size, a flood gun to counter charging effects, and the analysis chamber base pressure $< 1 \times 10^{-9}$ mbar; data were collected with FAT = 20 eV. The takeoff angle, defined as the angle between the substrate normal and the detector, was fixed at 0°. The samples were dropped on the surface of the silicon substrate by natural evaporation. All binding energies were calibrated using either the $Au_{4f7/2}$ peak (84.0 eV) or the C_{1s} carbon peak (284.6 eV). HR-TEM images were taken with a JEM-2011 high-resolution transmission electron microscopy operating at 200 kV. The as-prepared Ag nanoclusters were dried on carbon-coated copper grids by slow natural evaporation. The fluorescence lifetimes were recorded by Fluorescence lifetime spectrometer C11367 instrument. Mass spectra were obtained on a MALDI-TOF-MS (Bruker Daltonics Inc. BIFLEX III) with a 3-HPA matrix in linear mode.

Preparation of silver nanoclusters (Ag NCs)

For the preparation of the DNA-Ag NCs, certain volume of $AgNO_3$ solution was introduced into aliquot volume of DNA solution in 10 mM Tris/HCl buffer solution (pH 7.0). The mixture was kept at 0 °C for 15 minutes. Then, the mixture was reduced by quickly adding $NaBH_4$ (must be freshly prepared before use) under vigorously shaking for 2 min.[1] Final concentrations were 15 μM in the DNA template, 90 μM in $AgNO_3$ and 90 μM in $NaBH_4$. The reaction mixture was kept

in the dark at 4 °C for another 3 hours before use.

The light-scattering spectrum of DNA-Ag NCs in the presence of Cu^{2+} ions

Certain volume of the sensor solution was added into a test tube. Then, a series of solutions of copper ions were pipetted into the test tubes by using microsyringes before light-scattering measurement. The light-scattering spectrum was then measured by scanning simultaneously the excitation and emission monochromators ($\Delta\lambda$ = 0.0 nm) from 250 to 700 nm with the excitation and emission slits 5 nm.[2-4] Based on the spectra, LS intensities were obtained at the maximum peak. Spectrum curves were made based on the data collected on the first minute after adding the solution of Cu^{2+} ions.

The fluorescence spectrum of DNA-Ag NCs in the presence of Cu^{2+} ions

A varied of solutions of copper ions were pipetted into the sensor by using microsyringes before fluorescence measurement. Fluorescence spectra were made based on the data collected on the first minute after the addition of Cu^{2+} ions.[5]

References

1 J. T. Petty, J. Zheng, N. V. Hud and R. M. Dickson, *J. Am. Chem. Soc.*, 2004, **126**, 5207-5212.

2 D. Q. Feng, G. L. Liu, W. J. Zheng, J. Liu, T. F. Chen and D. Li, *Chem. Commun.*, 2011, **47**, 8557-8559.

3 G. L. Liu, D. Q. Feng, T. F. Chen, D. Li and W. J. Zheng, *J. Mater. Chem.*, 2012, **22**, 20885-20888.

4 D. Q. Feng, G. L. Liu, W. J. Zheng, T. F. Chen and D. Li, *J. Mater. Chem. B*, 2013, **1**, 3057-3063.

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Table S1. DNA sequences of the preparation of ssDNA-Ag NCs. The sequences of all oligonulceotides are listed in the 5′ to 3′ direction.

Name (ssDNA)	Sequences (5′-3′)	DNA size (bp)
ODN1	CGCTAACGCTAACGCTAACGCTA	23
ODN2	GGCTAAGGCTAAGGCTAAGGCTA	23

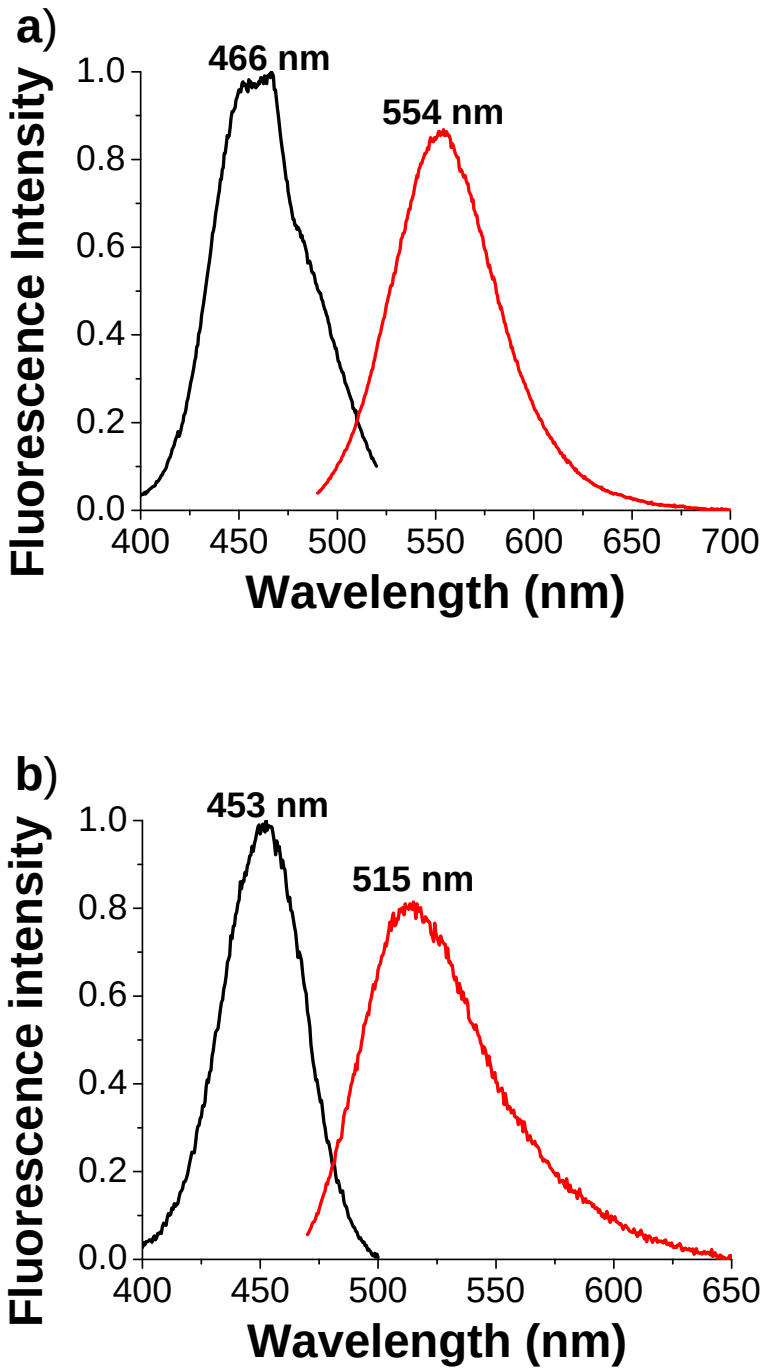


Figure S1. The excitation (black) and emission (red) spectra of ssDNA templated silver nanoclusters. The ssDNA templates are (a, ODN1) 5′-$(CGCTAA)_3$CGCTA-3′, (b, ODN2) 5′-$(GGCTAA)_3$GGCTA-3′. All DNA sequences are shown in 5′-3′.

Table S2. Optical properties of ssDNA templated silver nanoclusters.

Silver Nanoclusters	Excitation peak (nm)	Emission peak (nm)	Color
ODN1 ssDNA-Ag NCs	466	554	yellow green
ODN2 ssDNA-Ag NCs	453	515	green

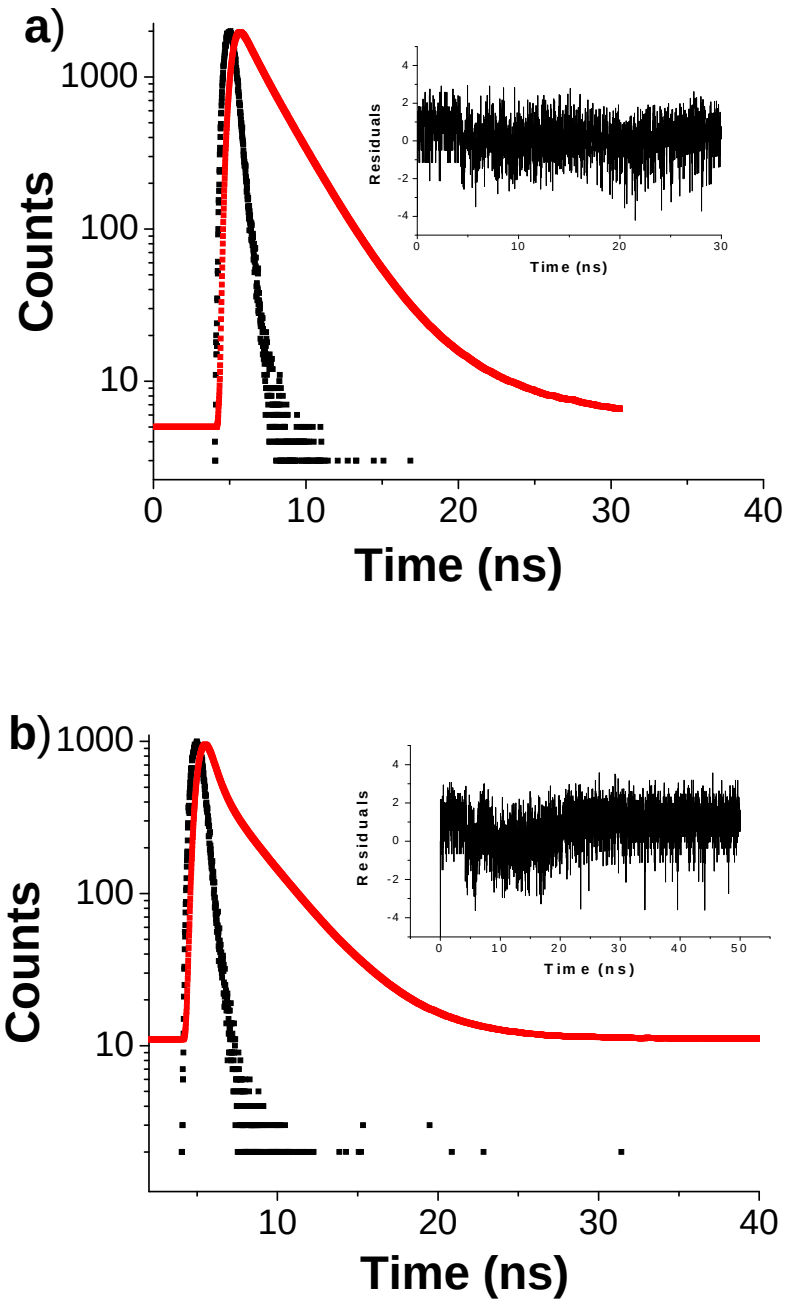


Figure S2. Fluorescence decay curves of ODN1 ssDNA-Ag NCs (a) and ODN2 ssDNA-Ag NCs (b) in Tris-HCl buffer solution (pH 7.0). The inset shows a random distribution of the weighted residuals around zero.

Table S3. Fluorescence decay parameters for ODN1 ssDNA-Ag NCs and ODN2 ssDNA-Ag NCs.

Samples	Fitting	CHI	τ (ns)
ODN1 ssDNA-Ag NCs	3rd order	1.194	2.35
ODN2 ssDNA-Ag NCs	2nd order	1.759	2.31

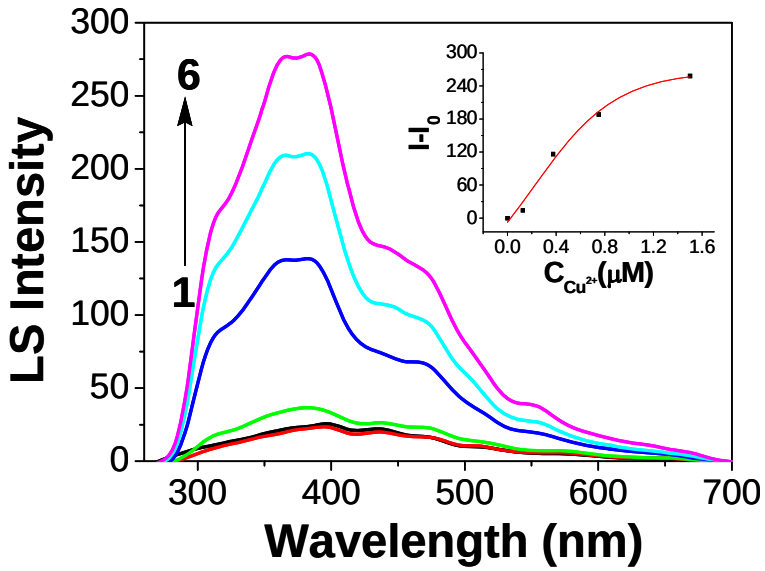


Figure S3. Light-scattering spectra of ODN2 ssDNA templated silver nanoclusters in the absence and presence of various concentrations of copper (II) ions solution at room temperature. Conditions: 1 (black), buffer solution; 2 (red), ODN2 ssDNA-Ag NCs; 3-6: 2 + Cu^{2+} ions (μM): 0.125 (green), 0.375 (blue), 0.75 (cyan), 1.5 (magenta). The inserted figure reveals the plot of the increment of the light-scattering intensity of ODN2 ssDNA-Ag NCs *versus* the concentration of copper (II) ions.

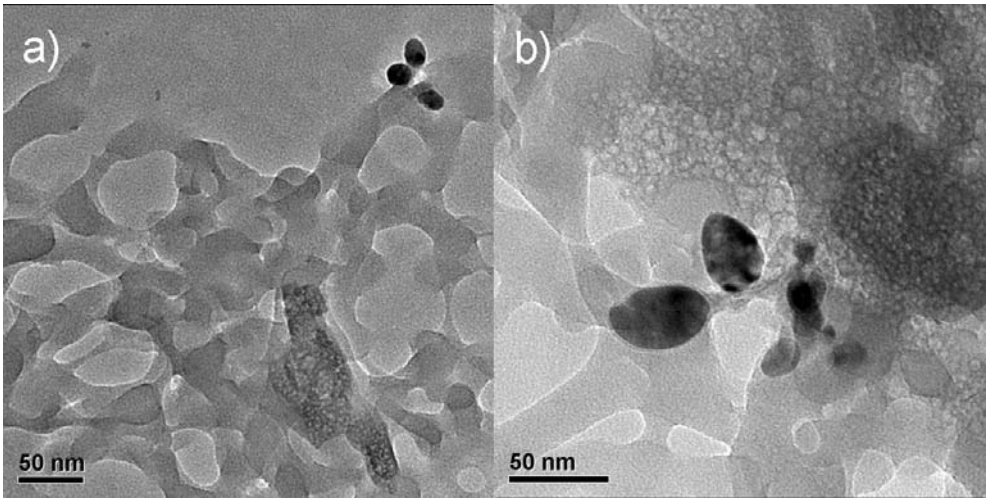


Figure S4. The TEM image of synthesized ODN1 ssDNA-Ag NCs in the presence of 1 mM Cu^{2+} ions solution at room temperature, scale bar: 50 nm.

Table S4. The parameters of the interaction between ssDNA-Ag NCs and copper ions by light-scattering spectrum.

ssDNA-Ag NCs	Stability Constant ($K_{s,}$ L/mol)	Stoichiometry (n)
ODN1 ssDNA-Ag NCs	7.7267×10^{6}	2.7195
ODN2 ssDNA-Ag NCs	5.3217×10^{6}	2.1296

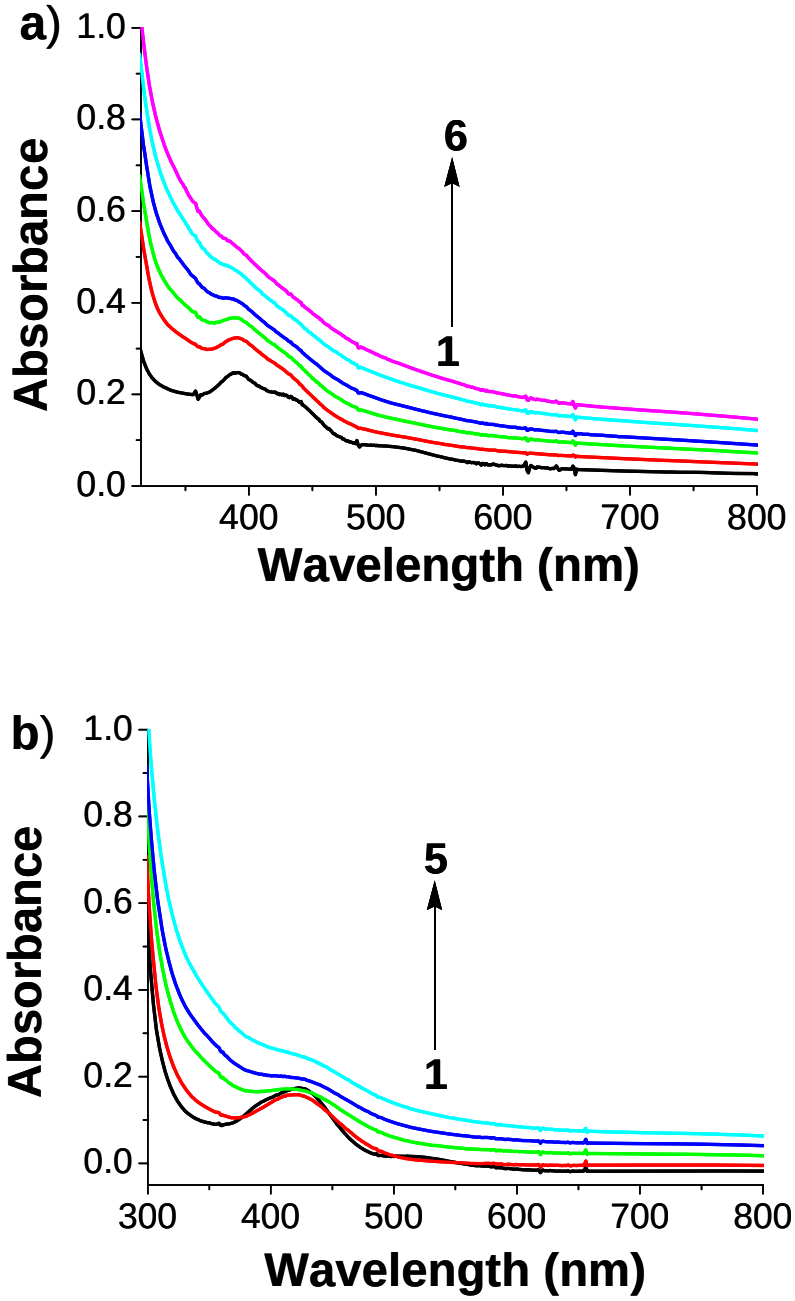


Figure S5. UV-vis spectra of the ssDNA-Ag NCs in the absence and presence of Cu^{2+} ions solution at room temperature. Conditions: (a) 1 (black), ODN1 ssDNA-Ag NCs; 2-6: 1 + Cu^{2+} ions (μM): 0.5 (red), 1 (green), 2 (blue), 3 (cyan), 4 (magenta); (b) 1 (black), ODN2 ssDNA-Ag NCs; 2-5: 1 + Cu^{2+} ions (μM): 0.5 (red), 1 (green), 2 (blue), 3 (cyan).

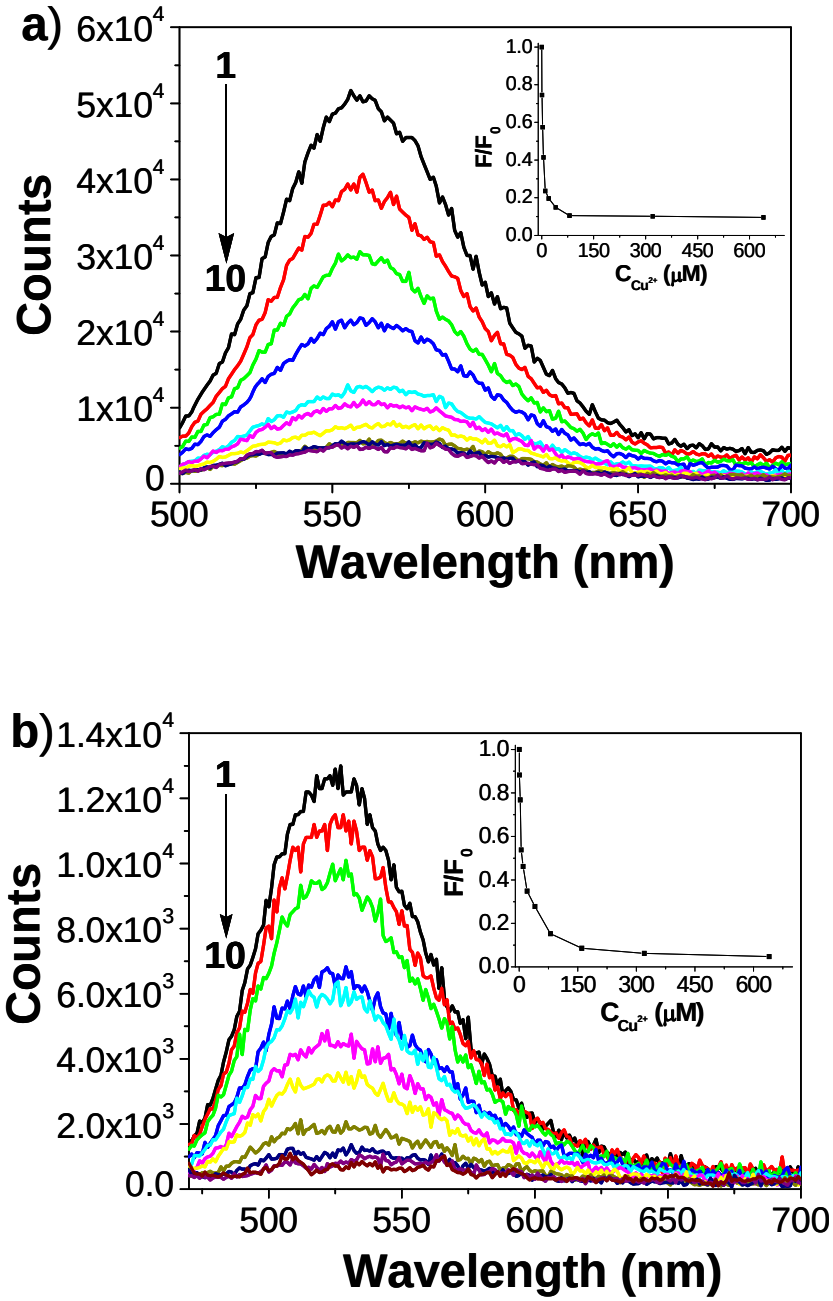
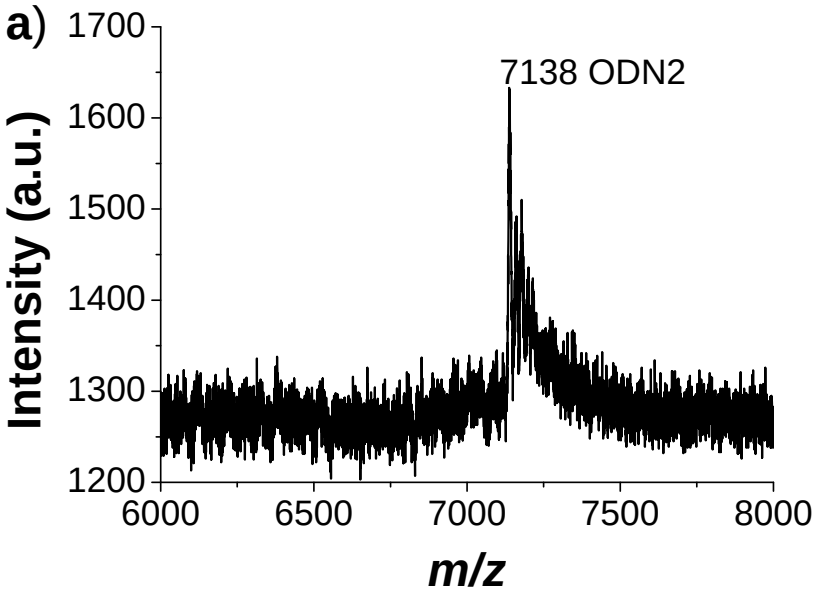


Figure S6. Emission spectra of ssDNA-Ag NCs in the presence of increasing concentrations of Cu^{2+} ions solution. (a) 1, ODN1 ssDNA-Ag NCs; 2-10, 1 + Cu^{2+} ions (μM): 0.5, 2.5, 5, 10, 20, 40, 80, 320, 640; (b) 1, ODN2 ssDNA-Ag NCs; 2-10, 1 + Cu^{2+} ions (μM): 0.5, 2.5, 5, 10, 20, 40, 80, 320, 640. The inserted figure displays the curves between the fluorescence ratio (F/F_0) and various concentrations of copper (II) ions.


a)
Intensity (a.u.)
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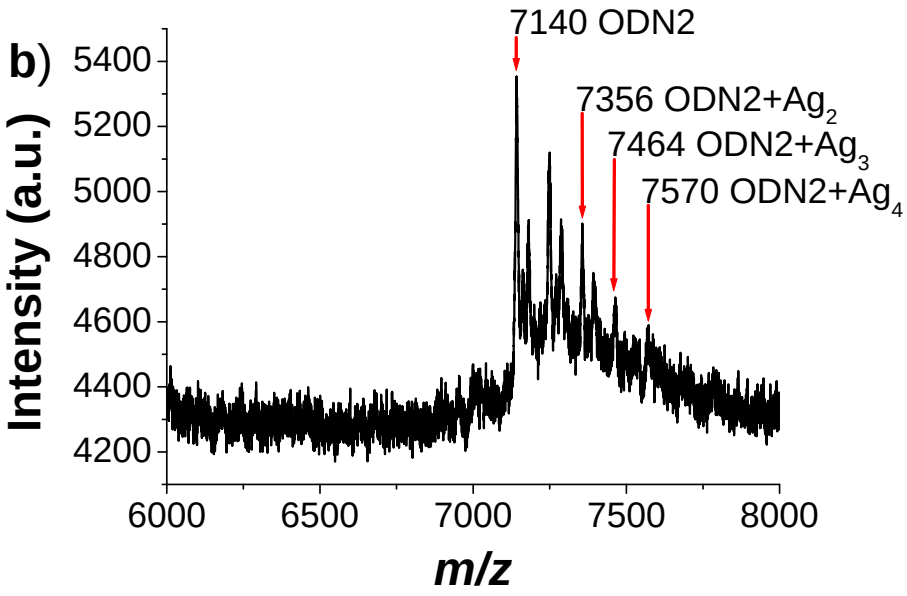
1600
1500
1400
1300
1200
7138 ODN2
6000
6500
7000
7500
8000
m/z


b)
Intensity (a.u.)
5400
5200
5000
4800
4600
4400
4200
7140 ODN2
7356 ODN2+Ag2
7464 ODN2+Ag3
7570 ODN2+Ag4
6000
6500
7000
7500
8000
m/z

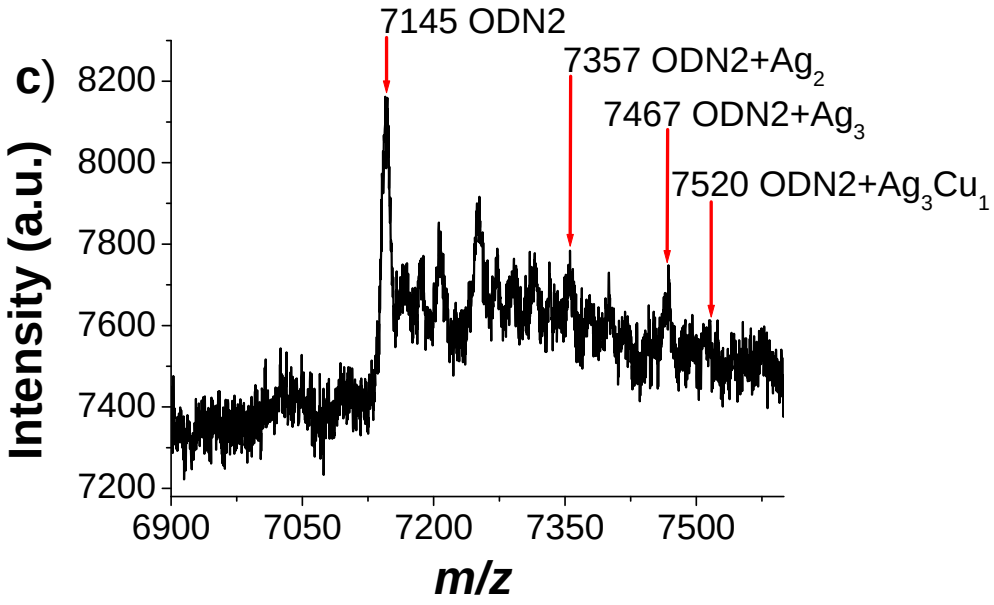


Figure S7. MALDI-TOF mass spectra of ODN2 ssDNA (a), synthesized ODN2 ssDNA-Ag NCs in the absence (b) and presence (c) of 1 mM Cu^{2+} ions.

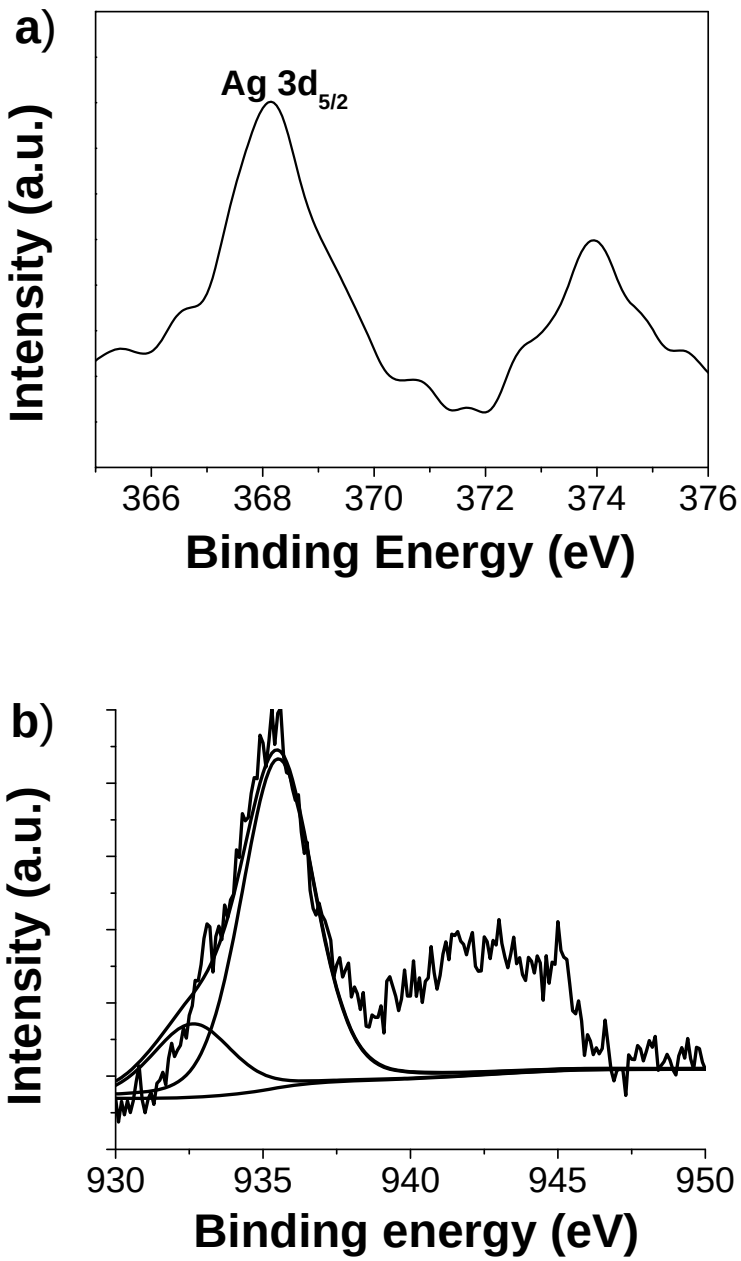


Figure S8. (a) Ag3d XPS spectrum of prepared ODN2 ssDNA-Ag NCs. (b) Cu2p XPS spectra of ODN2 ssDNA-Ag NCs in the presence of Cu^{2+} ions solution (1 mM).

Table S5. The Ag/Cu atom ratios calculated by XPS analysis.

ssDNA-Ag NCs	Ag/Cu atom ratios
ODN1 ssDNA-Ag NCs	2.18:1
ODN2 ssDNA-Ag NCs	1.29:1

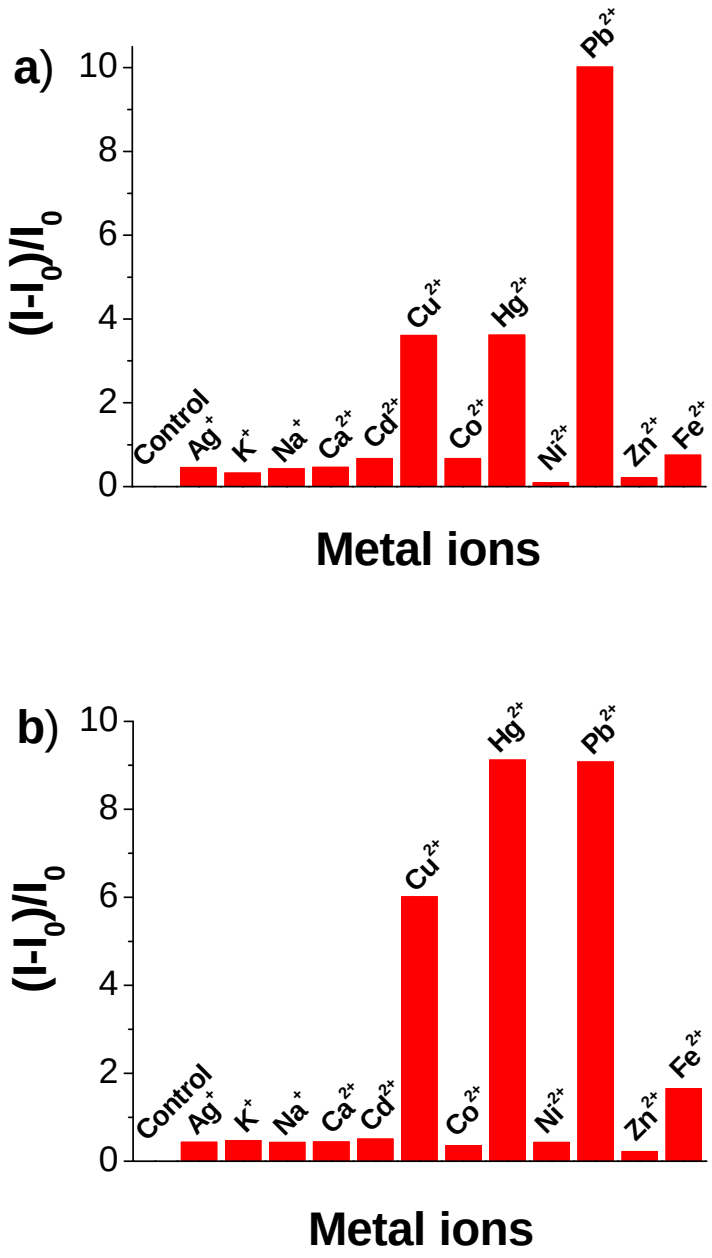


Figure S9. AGRR of DNA-Ag NCs with metal ions monitored by light-scattering technique. (a), ODN1 ssDNA-Ag NCs; (b), ODN2 ssDNA-Ag NCs. Conditions: The concentrations of metal ions used: Ag^+, 100 mM; K^+, Na^+, 10 mM; other metal ions, 1 mM.