Electronic Supplementary Information

Thiolated DNA-templated silver nanoclusters with strong fluorescence emission and long shelf-life

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Table of contents

Section S1. Materials

Silver nitrate ($AgNO_3$, 99.99%) was purchased from Sigma-Aldrich (Beijing, China). $NaBH_4$ (98%) was purchased from J & K Chemical Technology (Beijing, China). Oligonucleotides were synthesized and purified by Sangon Biotechnology (Shanghai, China). Deionized water was prepared using a Millipore Milli-Q water purification system (18.2 MΩ cm).

Section S2. Instruments

The UV–visible (UV–Vis) and fluorescence spectra of AgNCs were obtained using a Perkin Elmer Lambd-35 and a Perkin Elmer LS55 spectrometer, respectively. Circular dichroism (CD) spectra were obtained on a Chirascan CD spectrometer (Applied Photophysics, England). X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Kratos AXIS X-ray photoelectron spectrometer. Electrochemical experiments were performed with a CHI 832B electrochemical workstation (Chenhua Instruments Corp., Shanghai, China). Electrospray ionization mass spectrometry (ESI-MS) was performed with MS-QP2010Uita (Shimadzu Corporation, Japan). Time-resolved measurements were performed by using the time-correlated single-photon counting (TCSPC) option on the Fluorolog 3 spectrofluorometer (Jobin-Yvon Inc.).

Section S3. Synthesis of DNA–SH–AgNCs

DNA–SH and $AgNO_3$ solutions were added to phosphate buffer solution (PBS, 5 mM, pH 7.5). The mixed solution was then placed in an ice water bath for 15 min. Then, fresh $NaBH_4$ solution was quickly added to the mixed solution to initiate reduction. The mixed solution was shocked for 30 s, stored in the dark at room temperature for 2 h, and preserved at 4 ℃ overnight. The final concentrations of DNA–SH, $AgNO_3$, and $NaBH_4$ were 10, 60, and 60 μM, respectively (molar ratio was 1:6:6).

Section S4. Transmission electron microscopy

Transmission electron microscopy (TEM) measurements were performed on a Tecnai G2 F20 high-resolution transmission electron microscope operated at an accelerating voltage of 200 kV. The morphology of formed silver nanoclusters (AgNCs) was characterized by TEM. Unlike the plasmonic systems, TEM investigations have not been hugely successful for these clusters.[1] TEM has two main drawbacks. First, the size of the clusters is too small to be observed using standard TEM.[2] Second, electron-beam-induced growth clusters is observed during microscopic examination. Clusters in the size regime of 1 nm undergo electron-beam-induced coalescence, leading to larger particles.[3]

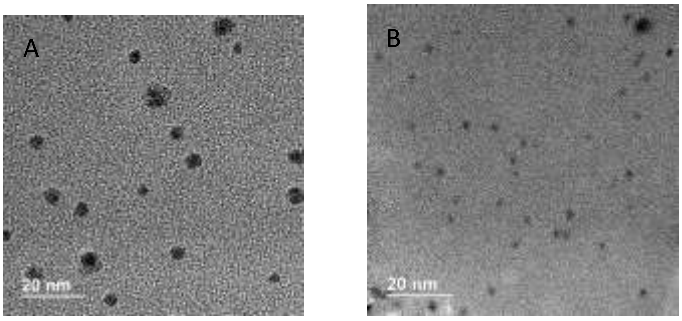

Fig. S1 TEM images of dC_{12}–Ag NCs (A) and dC_{12}–SH-Ag NCs (B).

TEM images of dC_{12}–AgNCs (A) and dC_{12}–SH–AgNCs (B) were shown in Figure S5. TEM images showed that the dC_{12}–SH–AgNCs were monodispersed. MS data showed that AgNCs formed with 2 to 6 silver atoms and bonded to the DNA strands. Changes in stoichiometric ratio were possibly because of the sample treatment (desaltation and lyophilization) that was performed before the MS measurement of DNA–Ag NCs. Given that the radius of silver atom is 0.160 nm,[4] AgNCs possibly undergo electron-beam-induced coalescence, leading to larger particles. The formation of DNA–Ag NCs was characterized by UV-Vis and fluorescence spectra.

Section S5. Lifetime measurement

Time-resolved measurements were performed by using the time-correlated single-photon counting (TCSPC) option on the Fluorolog 3 spectrofluorometer (Jobin-Yvon Inc.). A 572 nm NanoLEDs laser was used to excite the sample. Signals were collected using an IBH DataStation Hub photon counting module. Data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH). The goodness of fit was assessed by minimizing the reduced chi-squared function (x^2) and visual inspection of the weighted residuals.

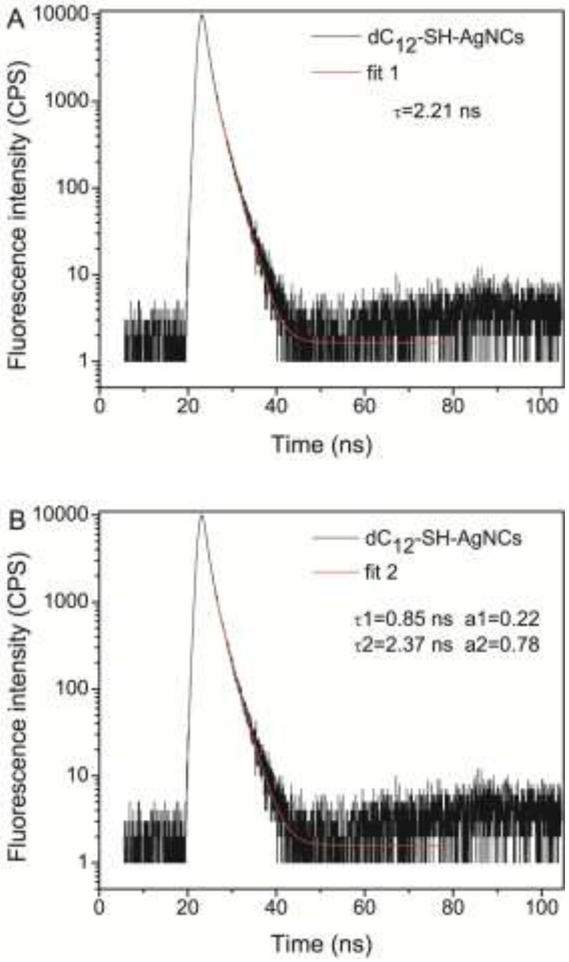

Fig. S2. Fluorescence decay curves of dC_{12}–SH–AgNCs. The time-dependent data can be fitted to a (A) monoexponential decay of 2.21 ns and (B) biexponential decay of 0.85 and 2.37 ns.

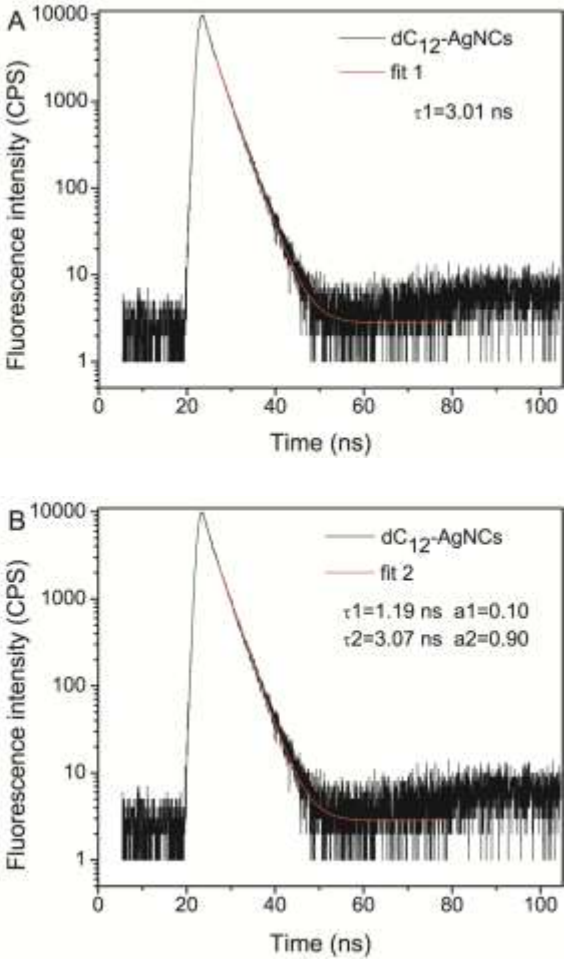

Fig. S3. Fluorescence decay curves of the dC_{12}–AgNCs. The time-dependent data can be fitted to a (A) monoexponential decay of 3.01 ns and (B) biexponential decay of 1.19 and 3.07 ns.

Section S6. Effect of pH on fluorescence emission of AgNCs

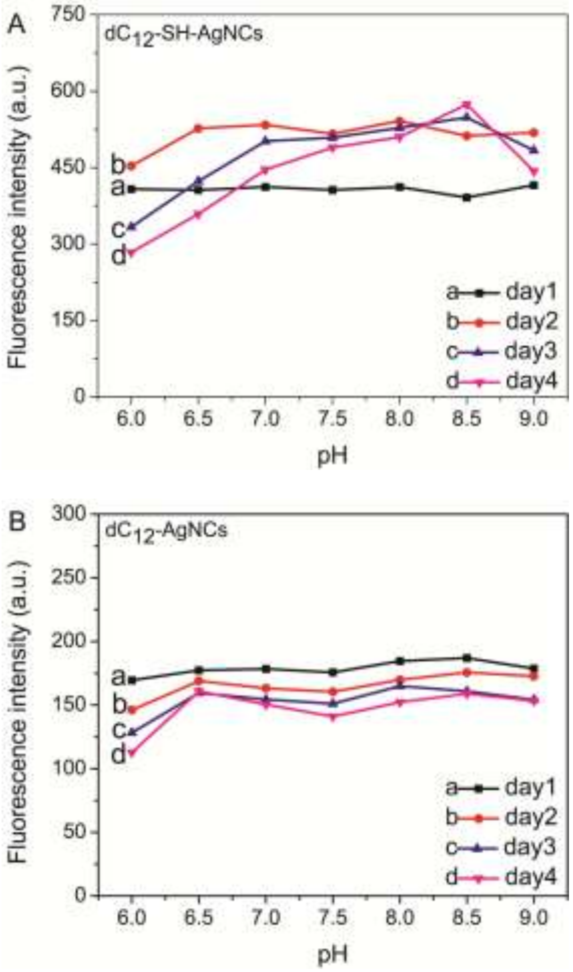

Fig. S4. Effect of pH on fluorescence emission of the dC_{12}–SH–AgNCs (A) and dC_{12}–AgNCs (B).

Section S7. UV-Vis and fluorescence spectra of the DNA–SH–AgNCs

The prepared AgNCs solution was diluted thrice with PBS (5 mM, pH 7.5) and stored at 4 ℃. Then, the UV-Vis absorption and fluorescence spectra of the solution were obtained at regular intervals. The wavelength range of the UV-Vis absorption spectrum of the synthetic AgNCs was 400–700 nm.

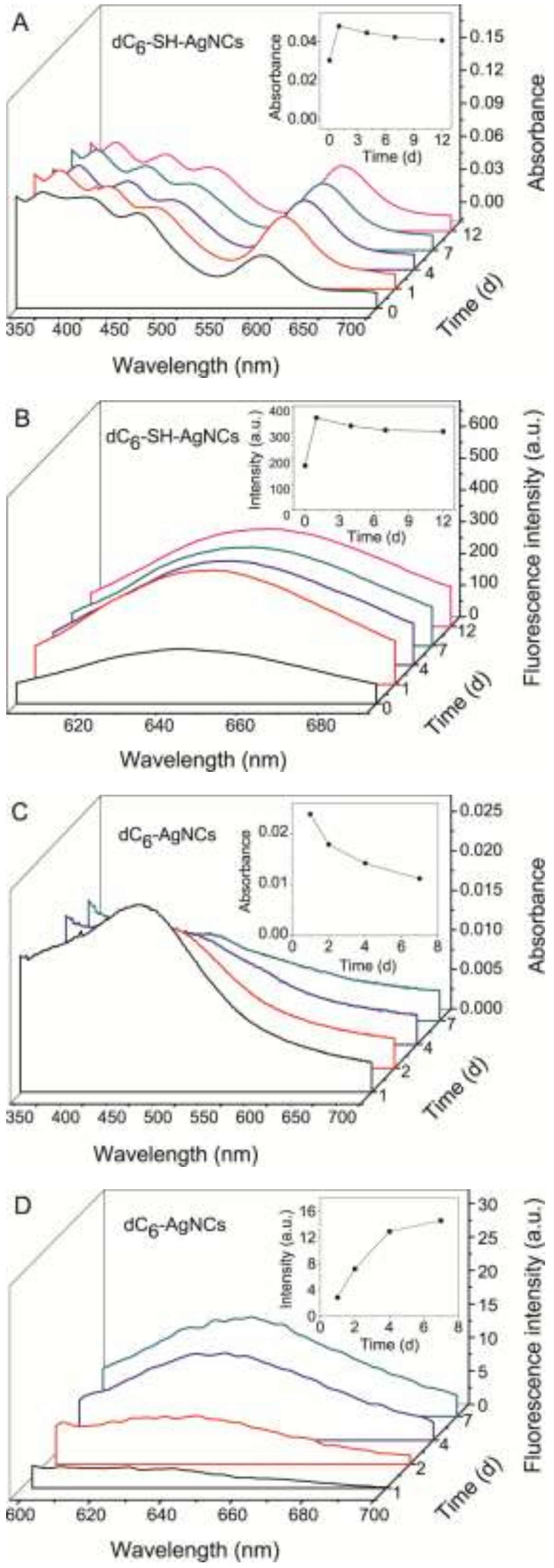

Fig. S5. UV–Vis and fluorescence spectra of the dC$_6$–SH–AgNCs (A and B, respectively) and dC$_6$–AgNCs (C and D, respectively).

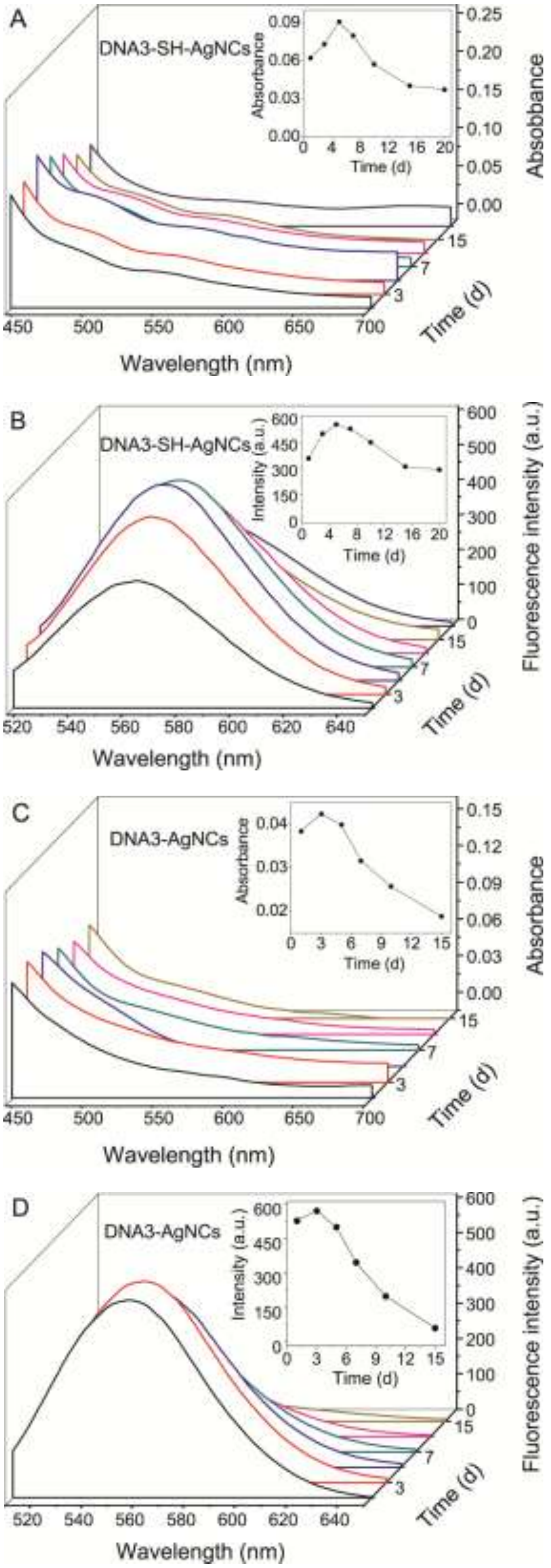

Fig. S6. UV–Vis and fluorescence spectra of the DNA3–SH–AgNCs (A and B, respectively) and DNA3–AgNCs (C and D, respectively).

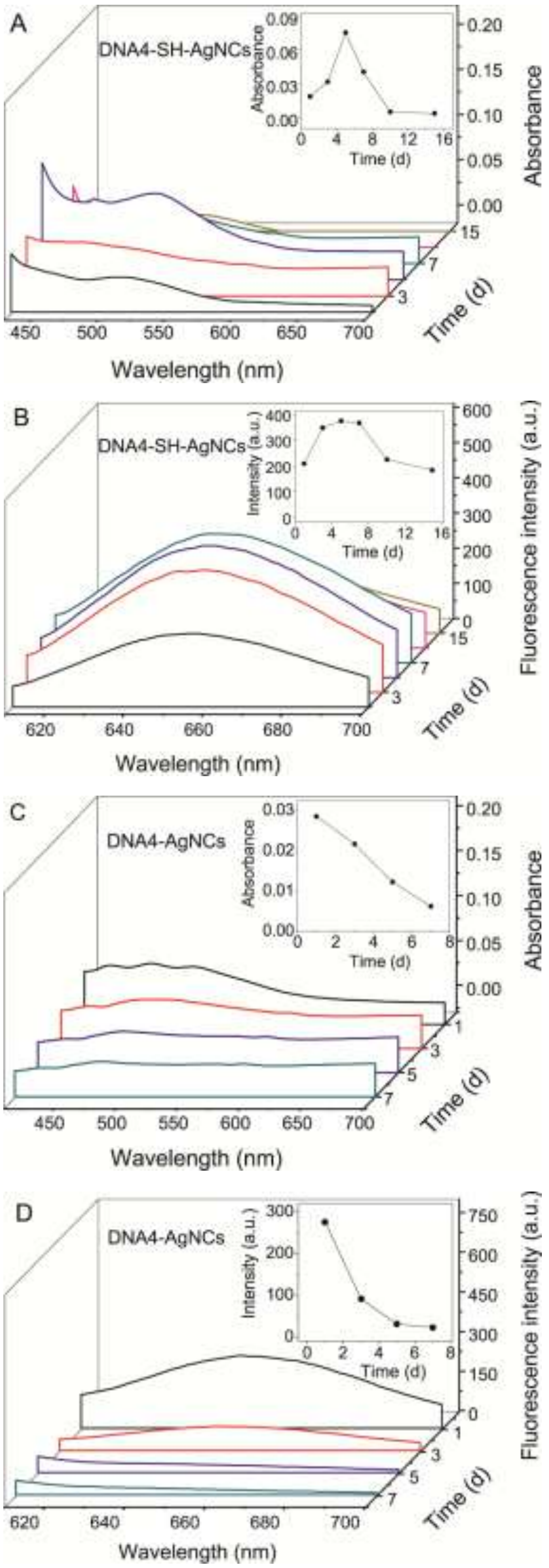

Fig. S7. UV–Vis and fluorescence spectra of the DNA4–SH–AgNCs (A and B, respectively) and DNA4–AgNCs. (C and D, respectively).

Section S8. Circular dichroism spectra

Circular dichroism (CD) studies were performed using a Chirascan CD spectrometer (Applied Photophysics, England). CD spectra were recorded in the wavelength range of 200–400 nm and at 200 nm/min.

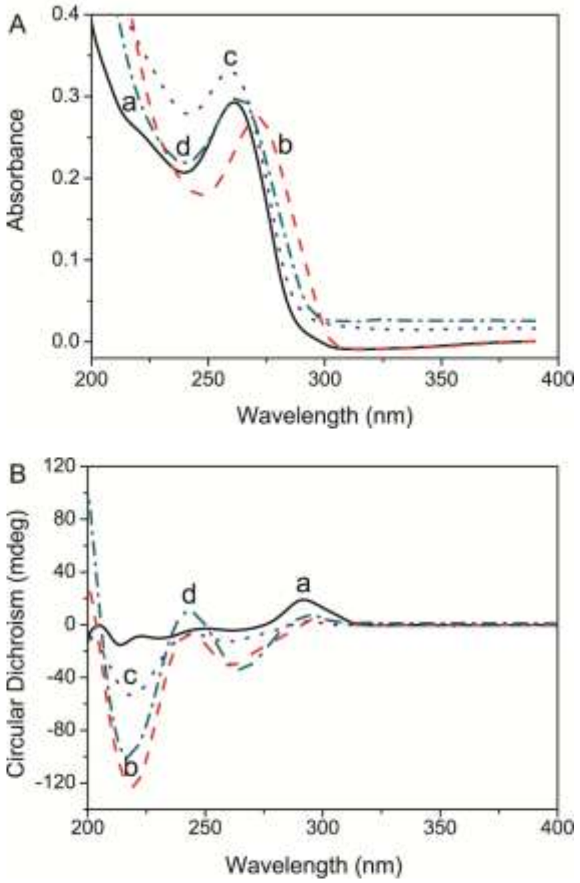

Fig. S8. (A) UV–Vis and (B) CD responses associated with the electronic transition of the oligonucleotide bases to associate with Ag and dC$_{12}$–AgNCs. The spectroscopic conditions were as follows: A (B): a. 10 μM oligonucleotide solution; b. oligonucleotide with 60 μM Ag; c. 2 min (2 h) after the addition of 1 BH$_4$:1 Ag to the oligonucleotide/Ag solution; and d. 18 h (72 h) after the addition of BH$_4$ to the oligonucleotide/Ag solution.

Section S9. X-ray photoelectron spectroscopy

The sample solution was dropped on a sample plate with a conductive ribbon, dried, and then the sample solution was repeatedly dropped depending on concentration. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos Axis Ultra X-ray photoelectron spectrometer equipped with a monochromatic aluminum X-ray source (1486.6 eV) operating at 300 W. Data were collected under a broad-spectrum scanning pass energy of 50 eV, a specific-position scanning pass energy of 20 eV, and an operating pressure of 5.0×10^{-10} mbar. To avoid the influence of C1s, calibration was performed at a bonding energy of 285 eV.

Section S10. Determination of quantum yields

Quantum Yields (QYs) were recorded on a Hamamatsu Photonics C9920-02G absolute photoluminescence QYs measurement system equipped with an integrating sphere apparatus and 150 W CW xenon light source.

Section S11. Electrospray ionization mass spectrum

Deionized water was added to DNA–$AgNO_3$ solution, and the resultant solution was placed in an ice water bath for 15 min. Fresh $NaBH_4$ solution was quickly added to the DNA–$AgNO_3$ solution to initiate reduction. The reduced DNA–$AgNO_3$ solution was shocked for 30 s, stored in the dark at room temperature for 2 h, and preserved at 4 ℃ overnight. The ultimate concentrations of DNA–SH, $AgNO_3$, and $NaBH_4$ were 15, 90, and 90 μM, respectively. Mass spectra were obtained on MS-QP2010Uita (Shimadzu Corporation, Japan) by electrospray ionization. The spectra were acquired in negative-ion mode with a 2.5 kV needle and 40 V cone voltages.

Section S12. Electrochemistry

The electrochemical properties of the AgNCs were investigated by cyclic voltammetry (CV). CV experiments were performed at room temperature with a CHI 832B electrochemical workstation with PBS (5 mM, pH 7.5) as the electrolyte. The three-electrode setup for CV consisted of a glassy carbon working electrode (disk Ø = 2.0 mm), a Pt wire auxiliary electrode, and a standard Ag/AgCl reference electrode (E^{o} = 0.205 V *vs.* NHE). The working electrode was mechanically ground and polished as previously described.[5] The treated glassy carbon working electrode was placed in $K_3[Fe(CN)_6]$ and an aqueous solution supporting the electrolyte. Voltammetry curves were plotted to check whether the electrode was completely processed. Cyclic voltammograms were then acquired at the scan rates of 200–5000 mV s^{-1} and run for at least three full cycles at the selected scanning potential range (−0.7 to +0.8 V *vs.* Ag/AgCl). All sample solutions were tested under a nitrogen atmosphere.

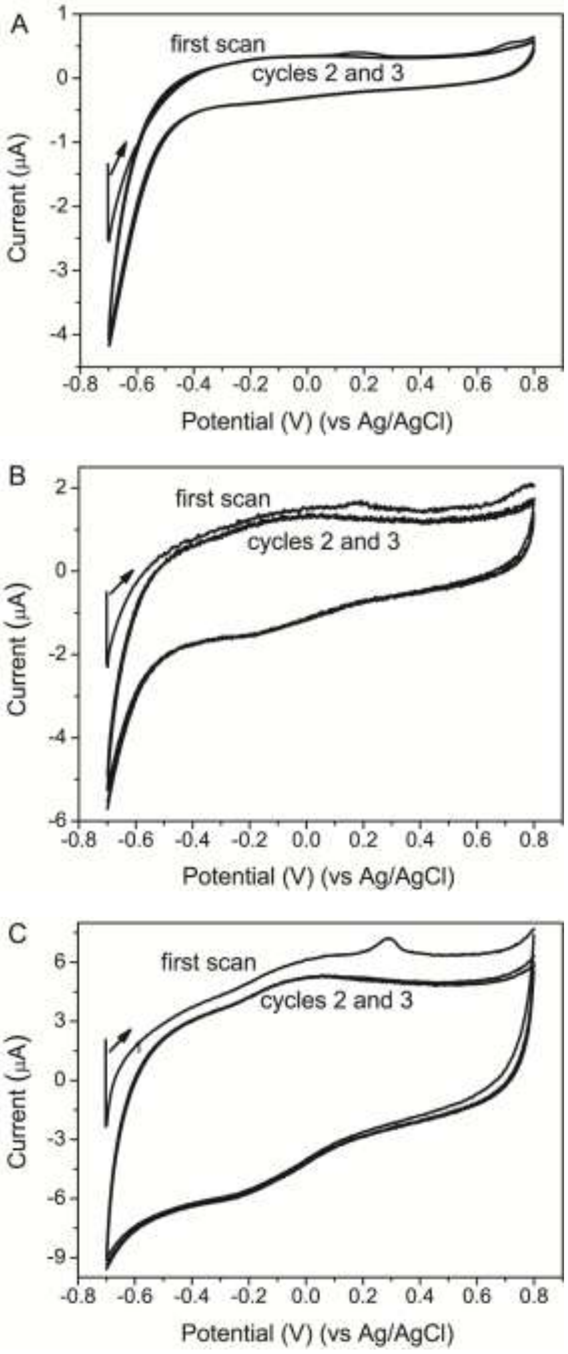

Fig. S9. Cyclic voltammograms of the dC_{12}–AgNCs at various scan rates. The scan rates of A, B, and C are 0.2, 1.0, and 5.0 V/s, respectively. .

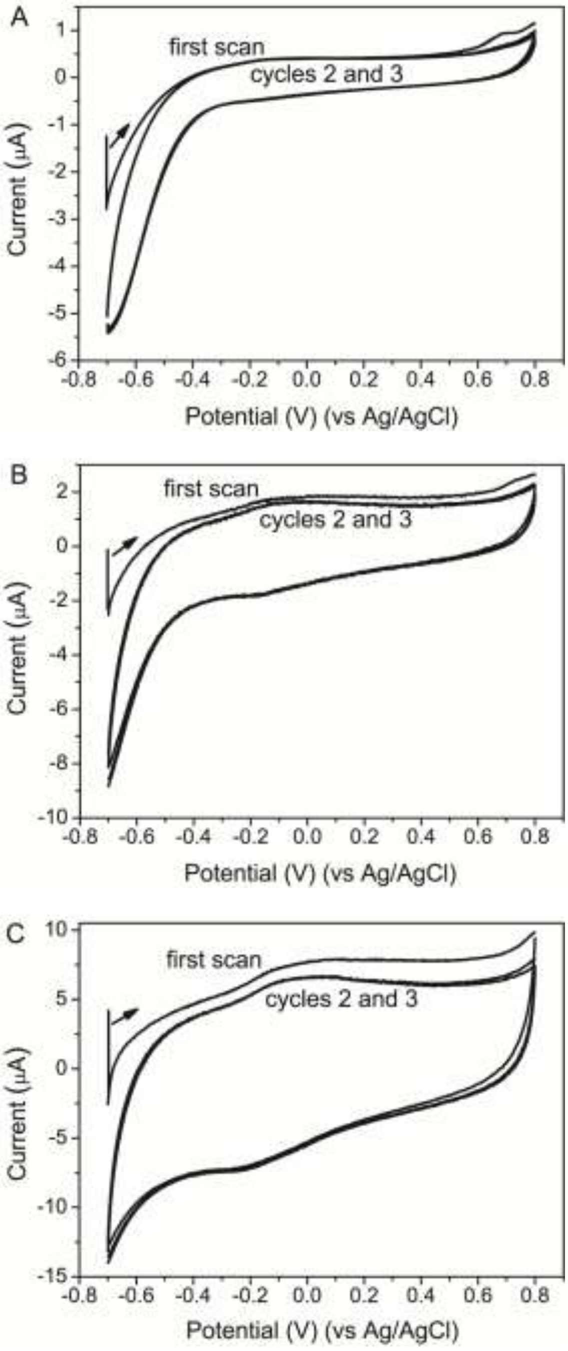

Fig. S10. Typical cyclic voltammograms of the dC_{12}–SH–AgNCs at various scan rates. The scan rates of A, B, and C are 0.2, 1.0, and 5.0 V/s, respectively.

Section S13. References

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