

Real-time monitoring of silver nanoparticles and nanowires dissolution kinetics in aquatic environment using an aggregation-induced emission fluorogen

Neng Yan^{a,b}, Sheng Xie^c, Ben Zhong Tang^{c*}, Wen-Xiong Wang^{a,b*}

^aDepartment of Ocean Science, The Hong Kong University of Science and Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong, China.

^bMarine Environmental Laboratory, HKUST Shenzhen Research Institute, Shenzhen 518057, China

^cDepartment of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, HKUST, Clear Water Bay, Kowloon, Hong Kong, China

*Corresponding author, tangbenz@ust.hk and wwang@ust.hk

1. Synthesis and characterization of AgNPs with different sizes and coatings/stabilizers

Different sizes of citrate-capped AgNPs were prepared according to the previously reported method.¹

For the synthesis of 20 nm AgNPs, 6.0 mL of a freshly prepared 5 mM NaBH₄ was added into a mixed solution containing AgNO₃ (100 mM, 250 µL) and citrate (100 mM, 250 µL) under vigorous stirring. The resulting yellow solution was stirred for another 30 min. The AgNPs of 60 nm in diameter were prepared by injecting citrate (34 mM, 2 mL) to a boiling solution of AgNO₃ (1 mM, 100 mL) under vigorous stirring. For the synthesis of 60 nm tween-20 stabilized AgNPs, 10% (v/v) tween-20 was added into the solution containing 60 nm citrate coated AgNPs (15.204 mg L⁻¹, 57.35 mL) under vigorous stirring, after stirring for 30 min. All the synthetic AgNPs were filtered through a 0.45 µm filter (Millex) and stored at 4°C until used.

The synthetic AgNPs was characterized by dynamic light scattering (DLS) on Malvern Zetasizer Nano-ZSat (UK) and transmission electron microscopy (TEM) on HT7700 (Hitachi, Japan) TEM instrument at 100 kV (Figure S1). Total Ag concentration in AgNPs stock was determined by inductively coupled plasma mass spectrometry (ICP-MS; Perkin-Elmer NexIONtm 300X) after digestion in 65% HNO₃ at 80 °C.

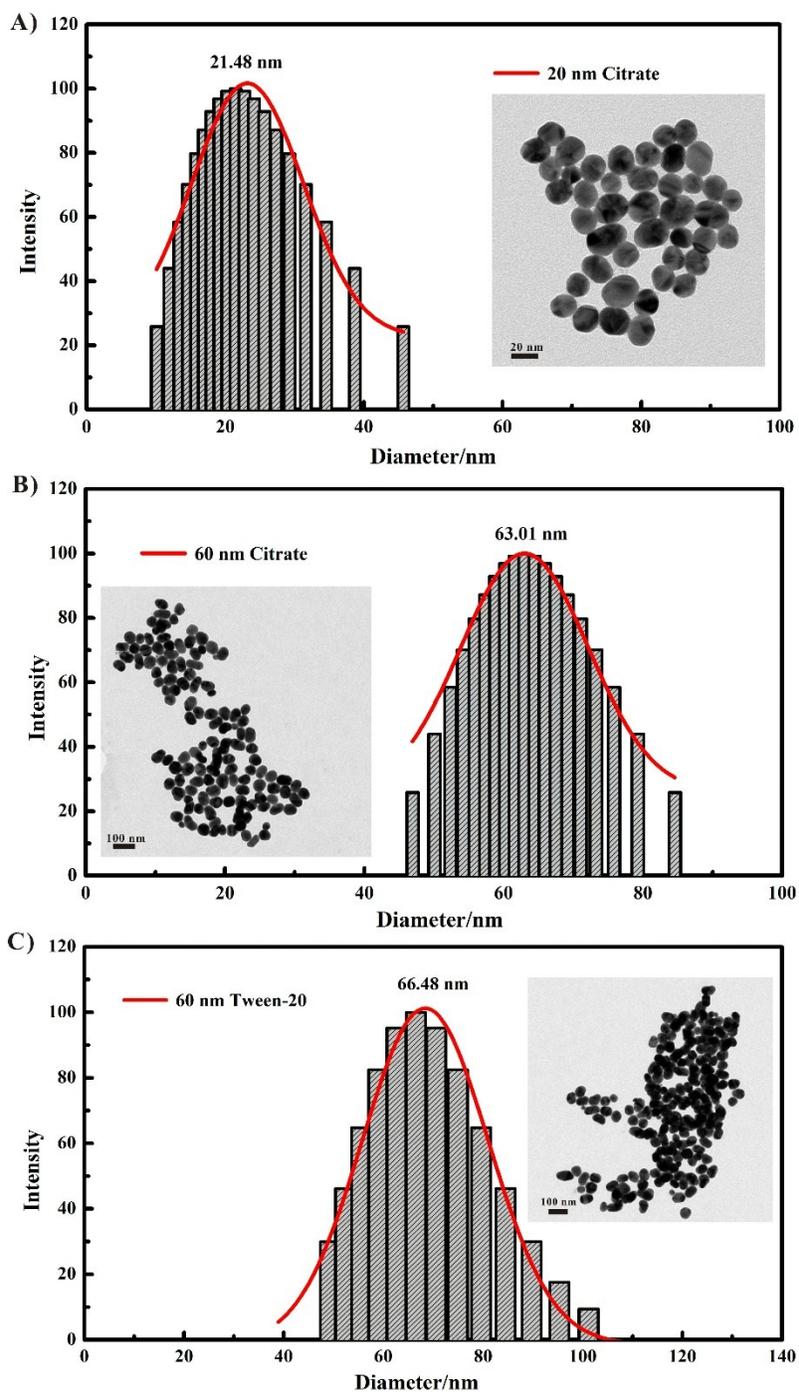


Figure S1. TEM images and DLS histogram of size distribution fitted with Gaussian function of (a) 20 nm citrate coated AgNPs, (b) 60 nm citrate coated AgNPs and (b) 60 nm tween-20 stabilized AgNPs.

2. Equilibrium speciation of silver in simplified M7 medium

All the experiments were conducted in modified simplified M7 medium (containing 0.04 mM NaHCO₃, 0.35 mM CaSO₄, 0.50 mM MgSO₄, 0.05 mM KNO₃ and pH at 7.0-8.0). Equilibrium speciation calculations in SM7 was performed using visual MINTEQ (version 3.0) (Figure S2). In SM7 solutions, free silver ion (Ag⁺) is the dominant soluble silver species, accounting for more than half of all soluble silver species (Figure S2). The SM7 medium is widely used in the culture of aquatic organisms.

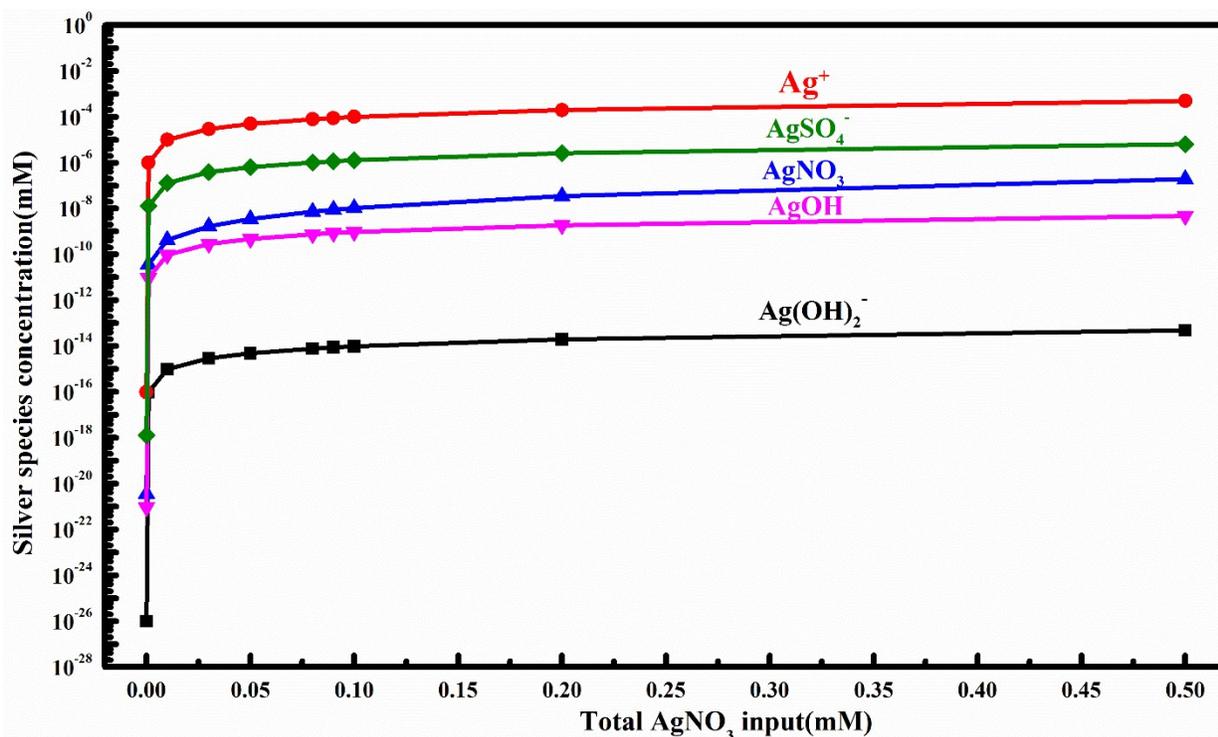


Figure S2. Equilibrium speciation and chemical pathways of silver speciation as a function of total input AgNO₃ concentration in SM7 with total input other species fixed at certain concentration (containing 0.04 mM NaHCO₃, 0.35 mM CaSO₄, 0.50 mM MgSO₄, 0.05 mM KNO₃ and pH at 7.0-8.0).

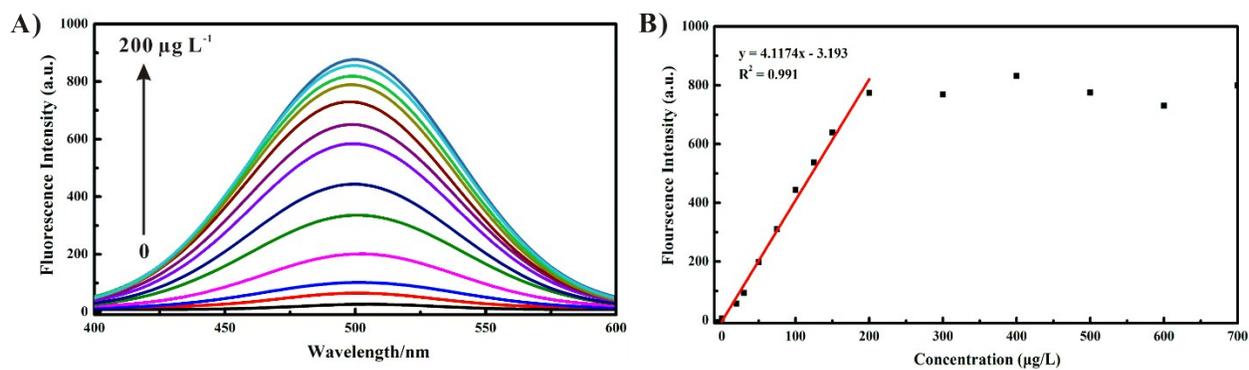


Figure S3. (A) Fluorescence spectra of fluorogenic TEZ-TPE-1 (3.0×10^{-5} M) in SM7 medium in the presence of increasing amounts of AgNO₃ (from 0 to 600 µg L⁻¹), $\lambda_{\text{ex}}=365$ nm; (B) Plot of the fluorescence intensity (I 501 nm) vs the concentration of AgNO₃ in SM7 medium.

3. ITC detection of AgNPs with NaCl, cysteine and fluorogenic TPE derivatives

Isothermal titration calorimetry was performed at 25.00 ± 0.01 °C on a MicroCal VP-ITC apparatus. AgNO₃ solutions for the ITC experiments were prepared in SM7 medium at pH 7.4. For a typical titration, a series of 5 μ L aliquots of AgNO₃ solution were injected into the fluorogenic TPE derivatives containing solution at 180 s intervals. The heat for each injection was determined by the integration of the peak area in the thermogram with respect to time. Blank titration was conducted by injecting fluorogenic TPE derivatives into the sample cell containing only SM7 medium under the same conditions. The interaction heat was corrected by subtracting the blank heat from that for the AgNO₃/ fluorogenic TPE derivatives vesicle titration. The binding constants were derived by fitting the isotherm curves with Origin 6.0 software.

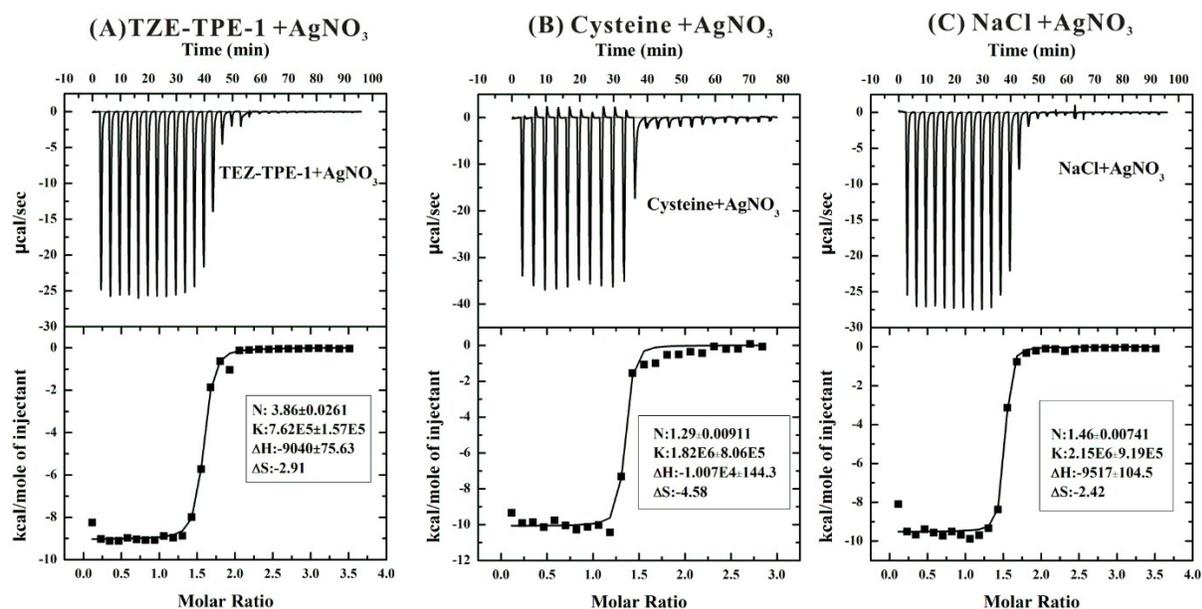


Figure S4. ITC data for 10 mM AgNO₃ binding to 0.6 mM NaCl (A), 0.6 mM Cysteine (B) and 0.6 mM fluorogenic TEZ-TPE-1 (C). Top of each ITC titration is raw data, bottom is the binding isotherm fitted to one sets of site model. Derived values for dissociation equilibrium constant (K), variation in enthalpy (ΔH) and entropy (ΔS) are inset.

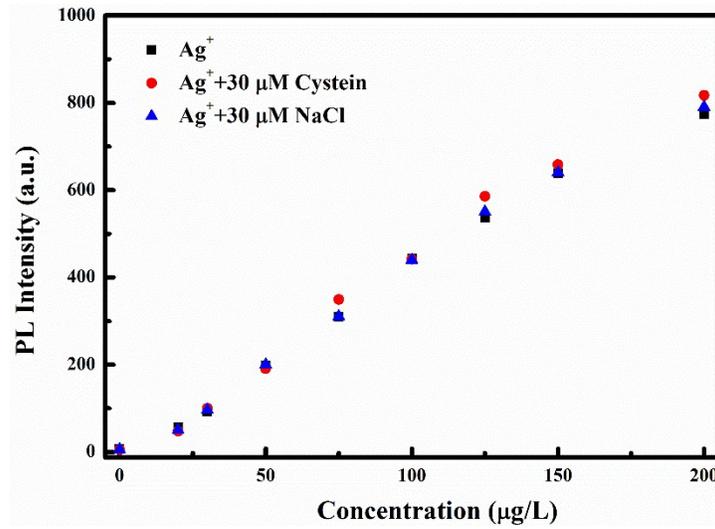


Figure S5. Influence of coexistence cysteine (30 μM) and Cl^- (30 μM) on the sensing of Ag^+ by the proposed AIE method.

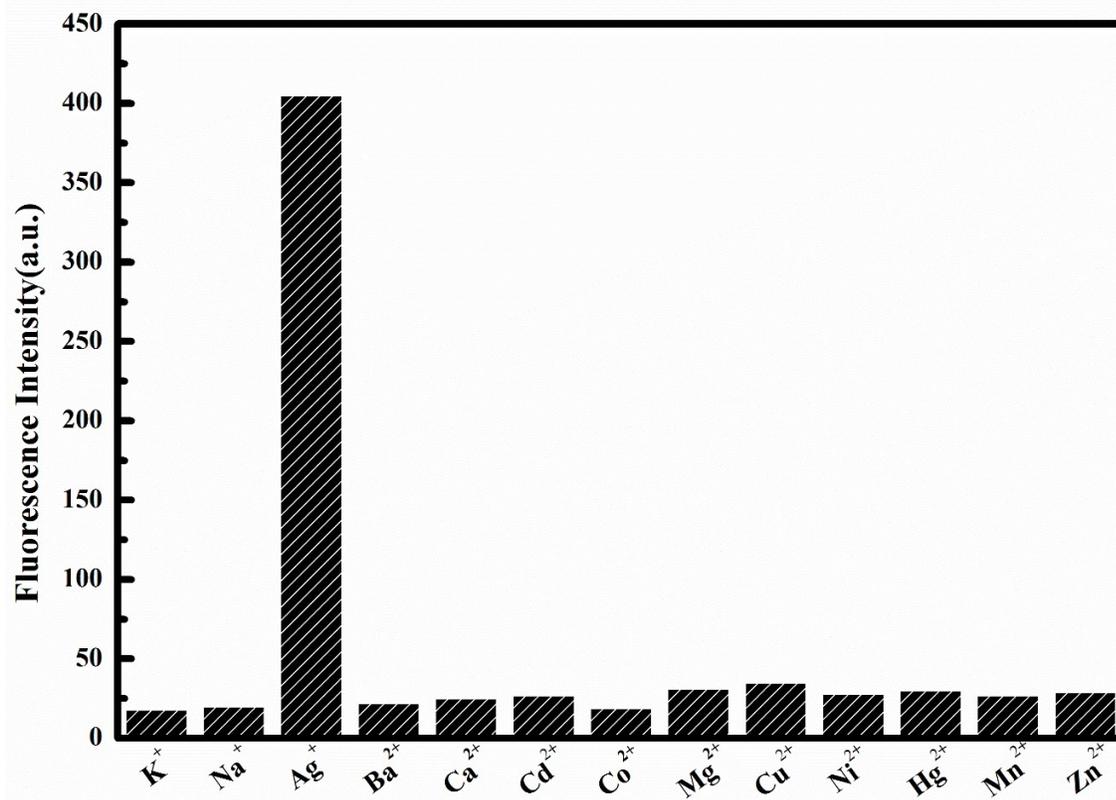


Figure S6. Fluorescence intensity (501 nm) of fluorogenic TPE derivative in the presence of 1.0 equiv of the respective metal ions, $\lambda_{ex}=365$ nm.

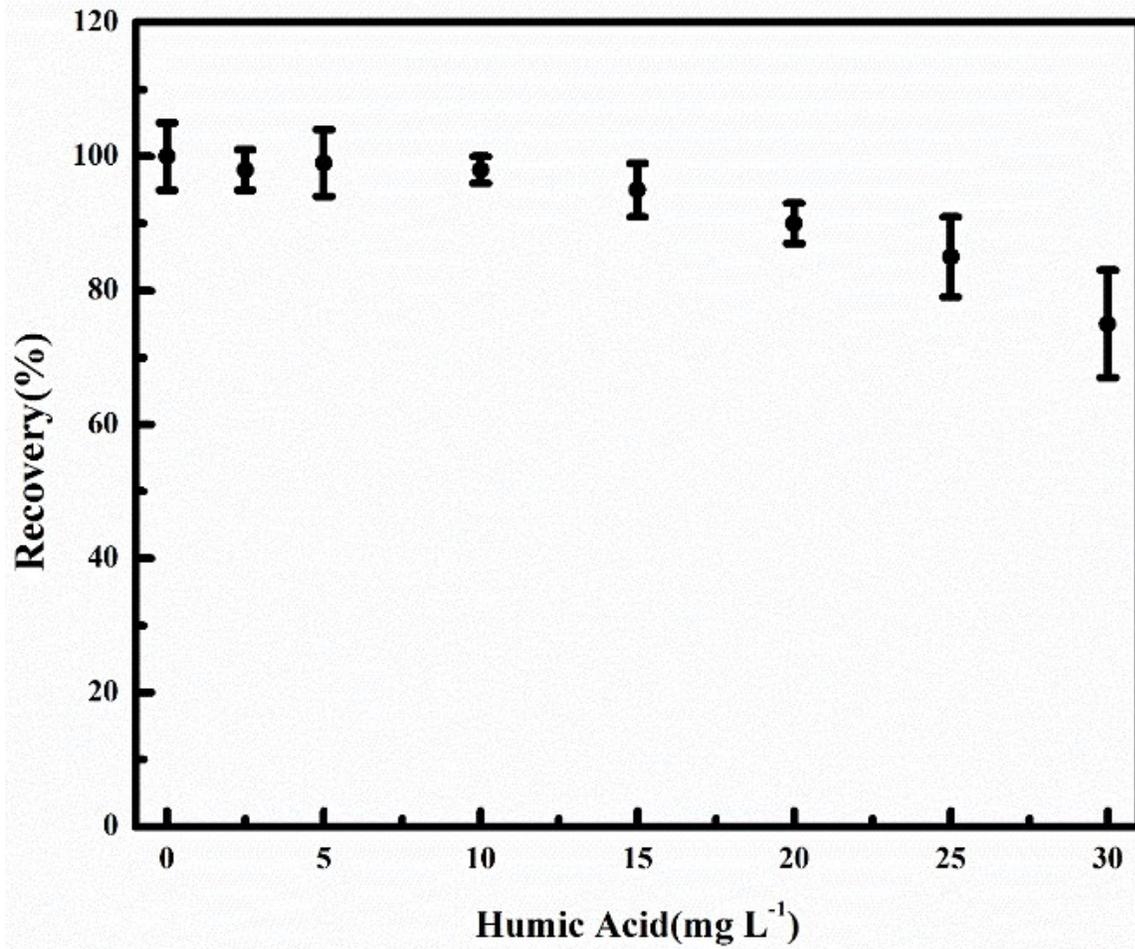


Figure S7. Influence of humic acid of on the sensing of Ag⁺ (20 $\mu\text{g L}^{-1}$) by the proposed AIE method.

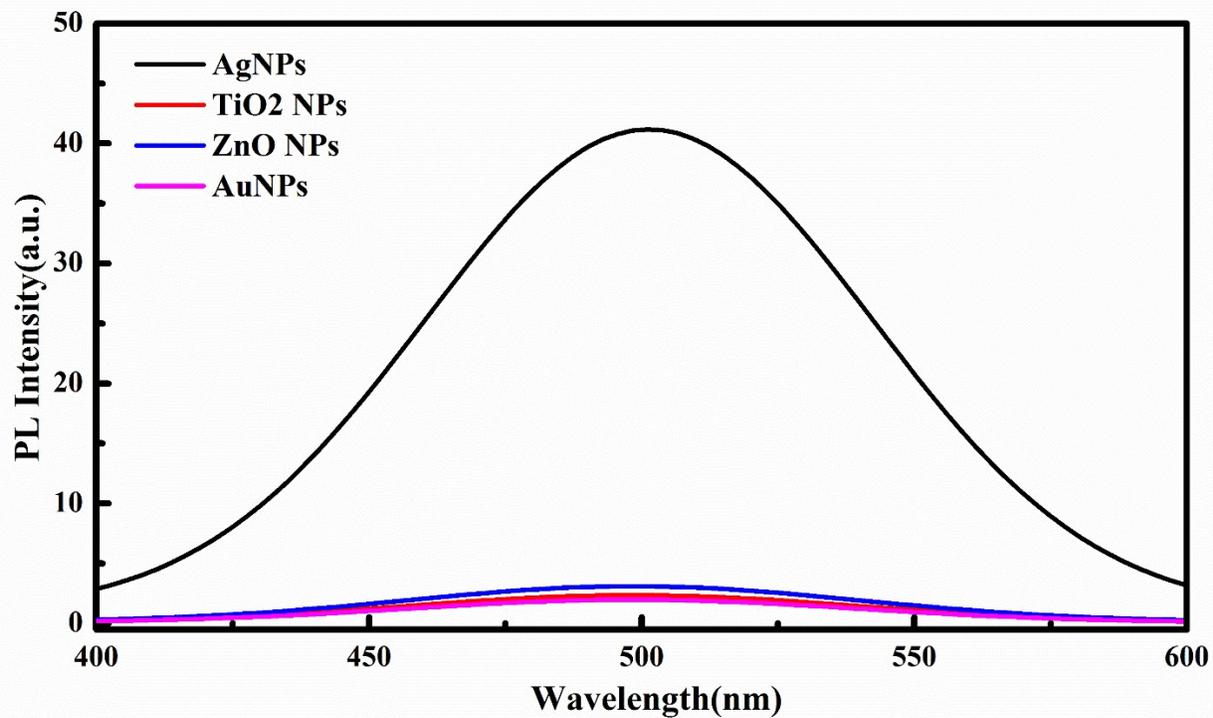


Figure S8. Fluorescence spectra of fluorogenic tetrazole-functionalized tetraphenylethylene derivative 1 (3.0×10^{-5} M) in H₂O in the presence of AgNPs, TiO₂ NPs, ZnO NPs and AuNPs. $\lambda_{\text{ex}}=365$ nm.

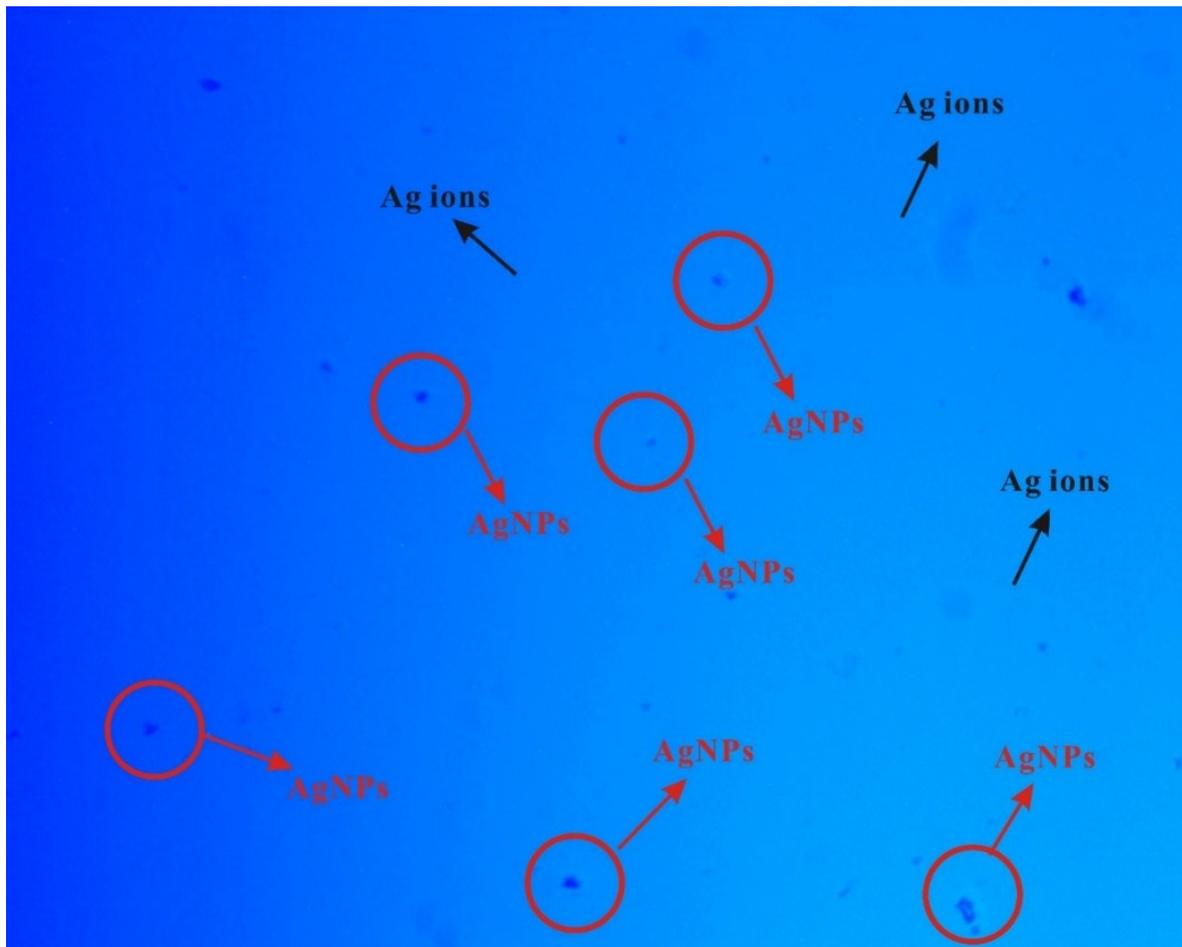


Figure S9: Fluorescence microscopy image of AIEgens added into the solution containing both AgNPs and Ag⁺. The 20-nm sized AgNPs were added into the SM7, after 12h, TEZ-TPE-1 was added and the corresponding fluorescence image was recorded. Black dot stands for AgNPs and the blue/green light stands for Ag⁺ in the solution.

Table S1. Measurement of dissolution kinetics of different NPs using the ICP-MS method and the new method.

Batch	Surface-coating	NP size	Half-life of release		Equilibrium time	
			This method	ICP-MS	This method	ICP-MS
1	Citrate	20 nm	5.7 h	4.7 h	35.5 h	31.3 h
2	Citrate	60 nm	13.2 h	6.8 h	55.9 h	44.6 h
3	Tween-20	60 nm	13.8 h	12.3 h	55.8 h	48.1 h

4. Detection of AgNPs dissolution kinetics by AIE technique

The release kinetics of soluble Ag from different sizes (20, 60 nm) and different coatings/stabilizers (citrate, tween-20) AgNPs were determined by novel AIE technique and ultracentrifugation followed with ICP-MS detection respectively. Specifically, the AgNPs suspensions ($500 \mu\text{g L}^{-1}$) were added into the SM7 medium containing 3 mM fluorogenic TPE derivatives, the mixture solution was detected by fluorescence spectrophotometer (Perkin-Elmer LS 55 spectrofluorometer) at different time points (0, 2, 4, 8, 12, 24, 30, 36, 48, 60, 72 and 96 h). For the comparison, the release kinetics of soluble Ag^+ from AgNPs were determined by conventional ultracentrifugation followed with ICP-MS detection. AgNPs concentrations in SM7 medium were determined by ultracentrifugation through 3 kD membrane (pore size around 1 nm, Millipore, USA). Specifically, the AgNPs suspensions were centrifuged at 4000 rpm for 20 min. After that, the filtrate containing the soluble Ag (nanoparticles were trapped on the membrane), was sampled at different time points (0, 2, 4, 8, 12, 24, 30, 36, 48 and 72 h). The Ag concentrations in the filtrate were measured by ICP-MS.

The aggregation kinetic of in the SM7 medium were measured by dynamic light scattering. AgNPs with different sizes (20, 60 nm) and different coatings/stabilizers (citrate, tween-20) at $500 \mu\text{g L}^{-1}$ were irradiated by the 35 mW red solid-state laser (660 nm wavelength), and the effective diameters (based on the intensity of light) were obtained in 48 h.

5. Synthesis and characterization of AgNWs

AgNWs were prepared according to the previously reported method.² The synthetic AgNWs were diluted with deionized water and then deposited on silicon substrates, and characterized by Bruker scanning electron microscopy (SEM) equipped with an EDAX attachment.

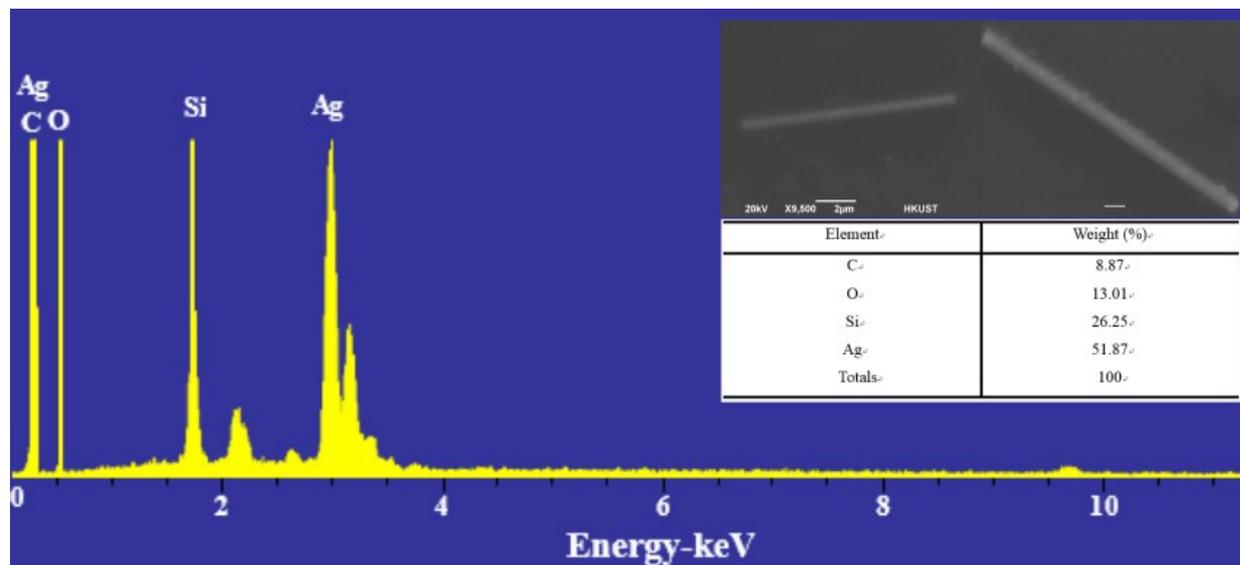


Figure S10. EDX results self-prepared AgNWs. Insets: SEM images of AgNWs and calculated percent elemental analyses. Scare bar: 2 μm .

References

1. J. Liu and R. H. Hurt, *Environ. Sci. Technol.*, 2010, **44**, 2169-2175.
2. Y. Sun and Y. Xia, *Adv. Mater.*, 2002, **14**, 833-837.