Supplementary Material (ESI) for Chemical Communications

Supporting Information

Silver Nanoclusters as Fluorescent Probes for Selective and Sensitive Detection of Copper Ions

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EXPERIMENTAL SECTION

Chemicals. All the metal salts, and sodium borohydride (powder, 98%) were purchased from Aldrich (Milwaukee, WI, USA). Sodium phosphate dibasic anhydrous and sodium phosphate monobasic monohydrate, which were used to prepare the phosphate buffer (50 mM, pH 3.0–10.0), were obtained from J. T. Baker (Phillipsburg, NJ, USA). Silver(I) nitrate (99+%, A.C.S. reagent) was obtained from Acros (Morris Plains, New Jersey, USA). The DNA sample (5′-CCCTTAATCCCC-3′) was purchased from Integrated DNA Technology, Inc. (Coralville, IA, USA). Montana soil (SRM 2710) was obtained from the National Institute of Standards and Technology (Gaithersburg, MD, USA). Milli-Q ultrapure water was used in all experiments.

Synthesis of DNA-Ag NCs. For the preparation of the DNA-Ag NCs, $AgNO_3$ solution (1 mM) was added to aliquots (85 μL) of 50 μM DNA solution (sequence: 5′-CCCTTAATCCCC-3′) in 20 mM phosphate (pH 7.0) buffer to provide a Ag^+-to-DNA molar ratio of 6:1;[1] after 15 min, this mixture was reduced by quickly adding 15 μL $NaBH_4$ (2 mM) under vigorously shaking (the $NaBH_4$ solution must be freshly prepared prior to use). For simplicity, we denote the concentration of the solution of these as-prepared DNA-Ag NCs as "1X". The fluorescence spectra of the as-prepared DNA-Ag were recorded using a Varian spectrofluorometer (Walnut Creek, CA, USA). When excited at 480 nm, the DNA-Ag NCs exhibited fluorescence peaks centered at 564 nm.

DNA-Ag NC-Based Sensor for Cu^{2+} Ions. Aliquots of Cu^{2+} solutions (0-750 nM) were diluted from the stock solution (1 mM) with 20 mM phosphate (pH 6.0). After the preparation of 30 min (reduced by $NaBH_4$), the as-prepared DNA-Ag NCs (50 μL, 0.04 X) were added to the aliquots of Cu^{2+} solutions to give final volumes of

500 μL. The mixture was reacted for another 30 min at 40 ^{o}C and then left at room temperature for 10 min prior to fluorescence measurement. When excited at 480 nm, the solutions of DNA-Ag NCs in the presence of Cu^{2+} ions emitted fluorescence at the maximum wavelength of 562 nm. Circular dichroism (CD) spectra of the DNA solution and the DNA-Ag and DNA-Cu/Ag NCs were recorded using a JASCO 720 instrument (Jasco, Inc., Easton, Maryland).

Analysis of Soil and Pond Water Samples. Acidic digestion of soil samples (1 g) was preformed according to the EPA Method 305B.[2] Aliquots of the soil sample were diluted (dilution factor: 10,000) with 20 mM phosphate solution (pH 6.0). The diluted samples (450 μL) were then spiked with standard Cu^{2+} solutions over the concentration range 25–250 nM. A water sample collected from a pond on the campus of National Taiwan University was filtered through a 0.2-μm membrane. Aliquots of this pond water (250 μL) were spiked with standard Cu^{2+} solutions (15–100 nM) that had been prepared in 20 mM phosphate solution (pH 6.0). The spiked samples were then analyzed separately using both ICP-MS and the present sensing technique.

Reference:

1. C. I. Richard, S. Choi, J.-C. Hsiang, Y. Antoku, T. Vosch, A. Bongiorno, Y.-L. Tzeng, R. M. Dickson, *J. Am. Chem. Soc.* **2008**, *130*, 5038–5039.
2. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, USEPA SW-846, 3rd edn., 1996, December.

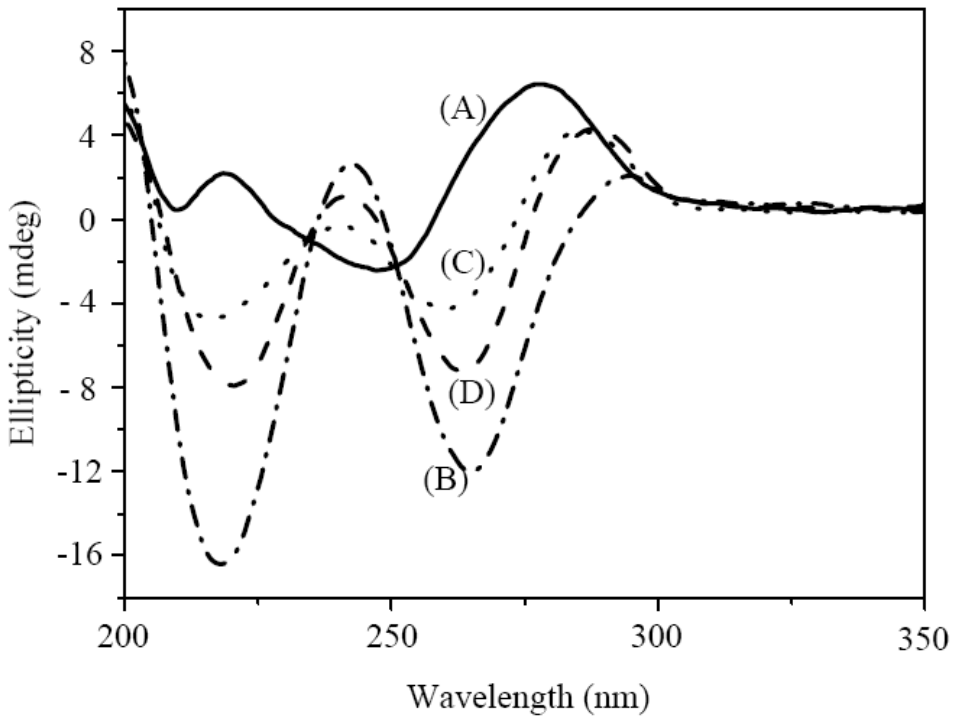

Figure S1. CD spectra of solutions of (A) DNA (3 μM), (B) DNA (3 μM) and $AgNO_3$ (18 μM), (C) DNA-Ag NCs (0.06 X), and (D) DNA-Cu/Ag NCs (0.06 X). (C): A mixture containing 20 mM phosphate (pH 7.0), $AgNO_3$ (300 μM), DNA (50 μM), and $NaBH_4$ (300 μM) that had reacted for 120 h**.** (D): A mixture identical to that in (C), except that $AgNO_3$ (225 μM) had reacted with $NaBH_4$ for 0.5 h prior to the addition of $Cu(NO_3)_2$ (75 μM); the mixture was then reacted for another 1.5 h.

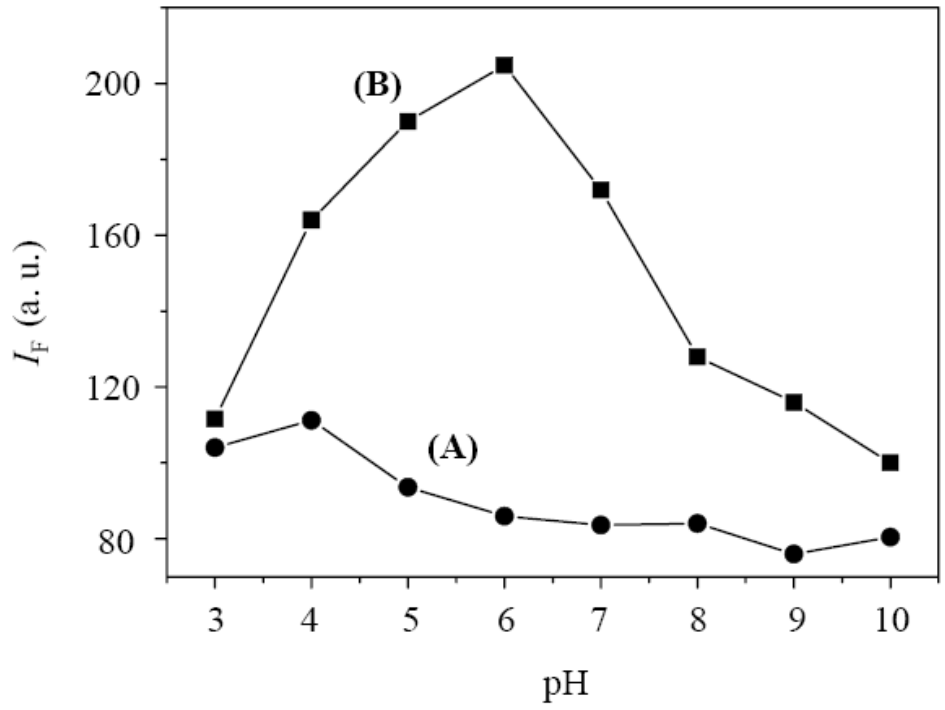

Figure S2. The effect of pH on the fluorescence intensity of DNA-Ag NCs in the (A) absence and (B) presence of Cu^{2+} ions (200 nM). DNA-Ag NCs were diluted with 20 mM phosphate solution to a final concentration of 0.004 X.

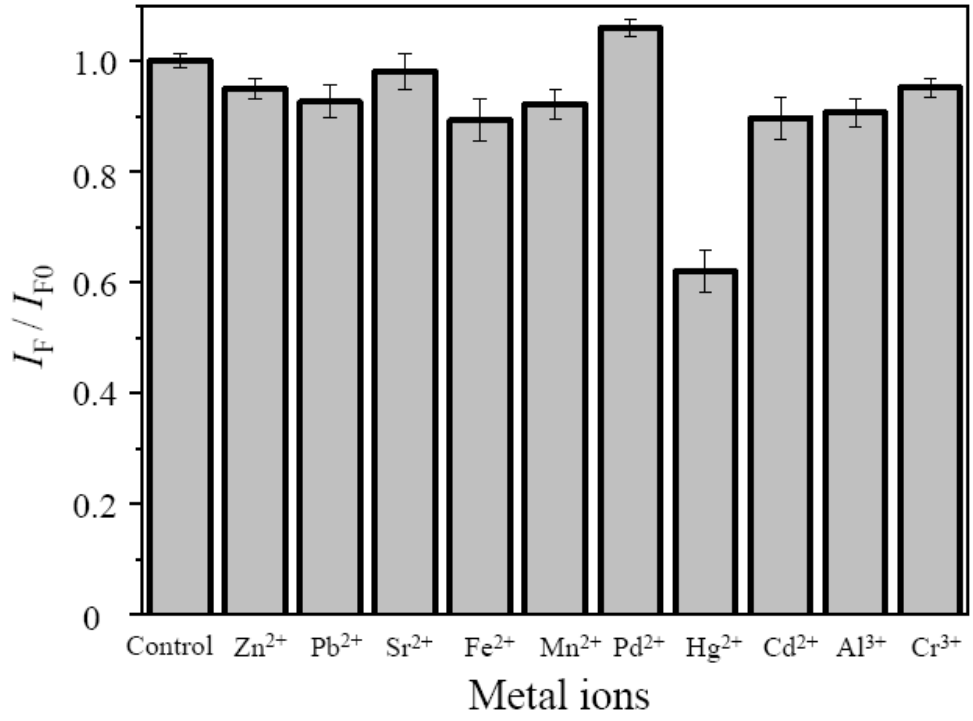

Figure S3. Values of I_F/I_{F0} of the DNA-Ag NC probe in the presence of Cu^{2+} ions (0.2 μM) and one of the metal ions (each was 2 μM). Other conditions were the same as those described in Figure 3. I_{F0} and I_F are the fluorescence intensities of the mixtures of the DNA-Ag NCs and Cu^{2+} ions in the absence and presence of other metal ions, respectively. Error bars represent standard deviations from three repeated experiments.

Table 1. Comparison of the present approach with other reported methods for the detection of Cu^{2+} in aqueous solution

Method	LOD	Linearity	Ref.
ICP-AES	4 nM	—	17
ICP-MS	Several nM	—	18
Fluorescent fiber optical probe	1.2 μM	0.78 – 6.3 μM	19
DNA-Ag NC probe	8 nM	10 - 200 nM	This Work

—: The value was not provided in the literature.