Electronic Supplementary Information for

Characterization and Application to the Detection of Single-Stranded DNA Binding Protein of Fluorescent DNA-Templated Copper/Silver Nanoclusters

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DNA-Ag and DNA-Cu/Ag NCs. When excited at 480 nm, the DNA-Ag and DNA-Cu/Ag NCs exhibited fluorescence peaks centered at 572 and 570 nm, respectively. The close emission wavelengths of DNA-Cu/Ag NCs (570 nm) and DNA-Ag NCs (572 nm) suggest that their electron transitions follow the same free-electron model of metallic behaviour.[1,2] We further conducted ICP-MS measurement to determine the amounts of Ag in the as-prepared DNA-Ag and DNA-Cu/Ag NCs. The ICP-MS results revealed that there was no Ag destruction in the preparation of the DNA-Cu/Ag NCs from the DNA-Ag NCs. We used 5 mW solid-state lasers with outputs at 375 and 475 nm from Uniphase (Mantence, CA, USA) to irradiate DNA-Ag and Cu/Ag NCs solutions under homogeneously stirring to check whether the absorbance bands centered at 425 and 480 nm (Figure S2) were from same absorbing species. To study the roles of remaining Ag and Cu ions played in solution, we added $NaBH_4$ (0, 1, 10, 30, 50, 100 and 200 μM) to the as-prepared DNA-Ag and Cu/Ag NC solutions. The fluorescence spectra (Figure S3) were recorded after reactions for 1 h.

The binding energies (BE) of Ag were 368.5/368.2 eV before/after Cu^{2+} addition (Figure S4), revealing only slight changes in its oxidation state (Ag^0).[3] A double-beam UV–Vis spectrophotometer (Cintra 10e, GBC, Victoria, Australia) was used to measure the absorptions of solutions of $Cu(NO_3)_2$ and the DNA-Ag and DNA-Cu/Ag NCs.

ESI-MS Measurements. The m/z~548.5, 560, and 563.5 of DNA-Ag NCs corresponded to $[DNA - 13H + 6Na + 2Ag]^{7-}$, $[DNA - 17H + 10Na + 2Ag]^{7-}$, and $[DNA - 18H + 11Na + 2Ag]^{7-}$, respectively. The most abundant peak of the DNA-Cu/Ag NCs was at 573.7309 amu (–7 charge state), revealing that there were 2 Ag and 1 Cu atoms in the DNA-Cu/Ag NCs. The calculated isotopic masses are 573.2889, 573.4320, 573.5752, 573.7179, 573.8610, 574.0038, and 574.1469, with a maximum value at 573.7179 that is quite close to our experimental value. We obtained similar results for the DNA clusters composition having charge states of –6: the bare DNA strand at *m*/*z* 582.5557 amu, the DNA-Ag NCs at *m*/*z* 635.8788 amu, and the DNA-Cu/Ag NCs at *m*/*z* 675.1584 amu.

References:

1. Patel S A, Richards C I, Hsiang J-C, Dickson R M 2008 *J Am. Chem. Soc.* **130** 11602

2. Zheng J, Nicovich P R, Dickson R M 2007 *Annu. Rev. Phys. Chem.* **58** 409

3. Muñoz-Rojas D, Subías G, Fraxedas J, Gómez-Romero P, Casañ-Pastor N, 2005 *J Phys. Chem. B* **109** 6193

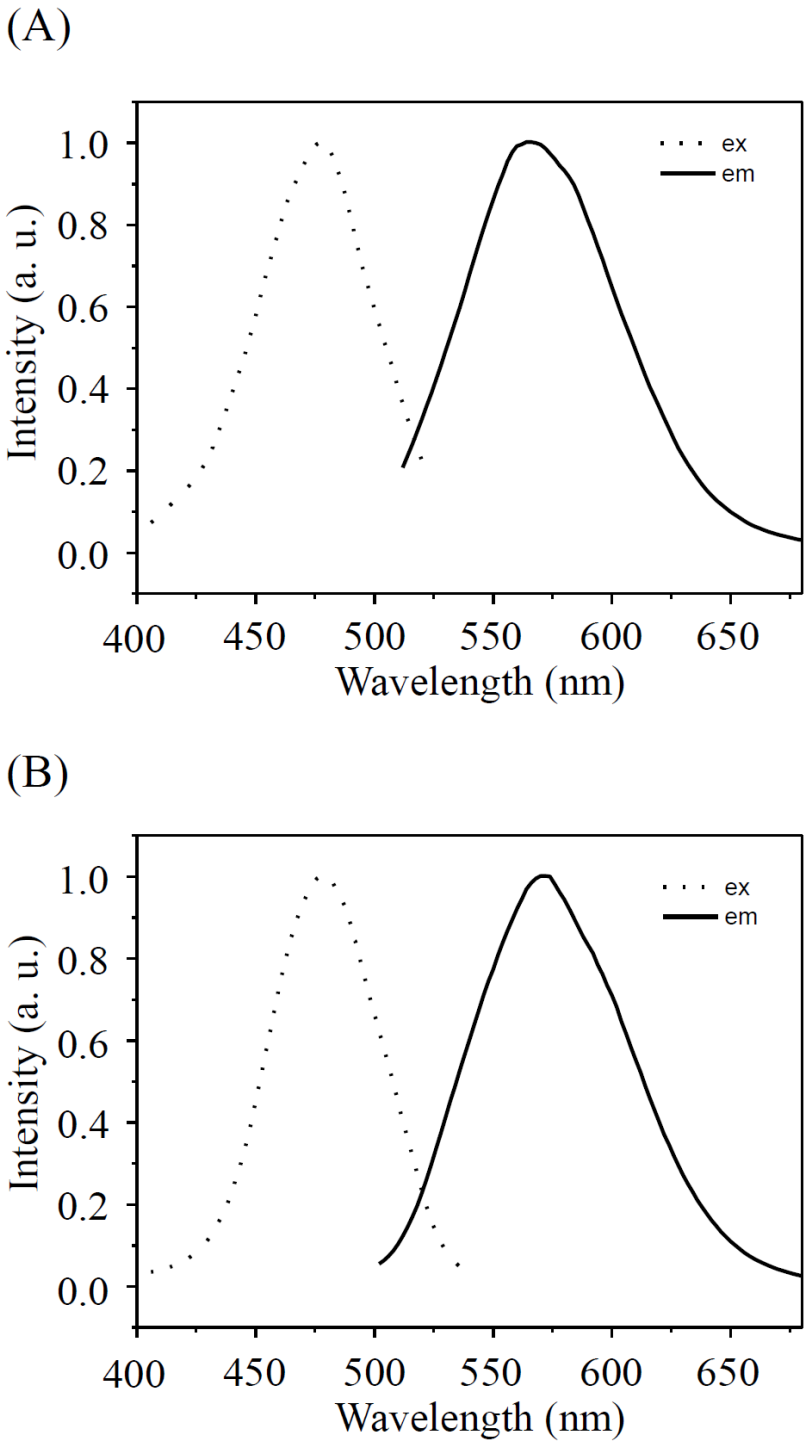

Fig. S1. Excitation and emission spectra of the (A) DNA-Ag NCs and (B) DNA-Cu/Ag NCs. The excitation wavelengths of DNA-Ag and Cu/Ag NCs were collected at emission of 572 and 570 nm, respectively.

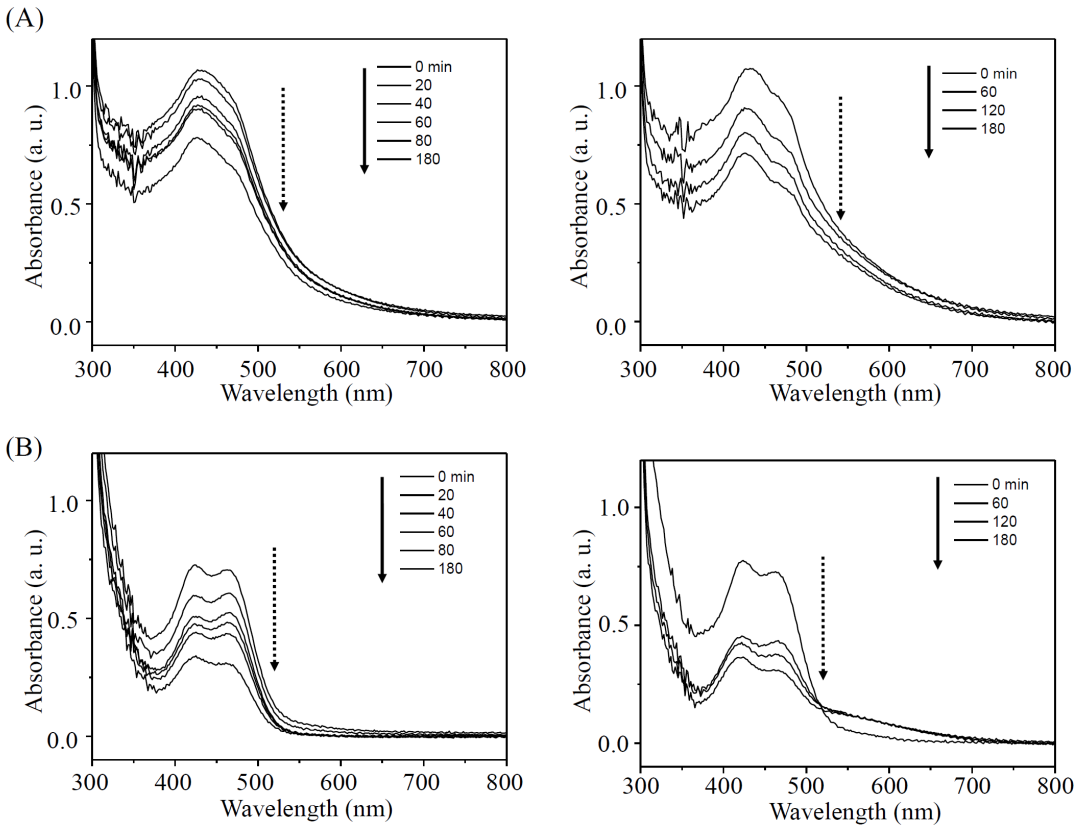

Fig. S2. Absorption spectra of (A) DNA-Ag NCs and (B) DNA-Cu/Ag NCs after laser irradiation for different periods. Laser output: (Left) 475 nm and (Right) 375 nm.

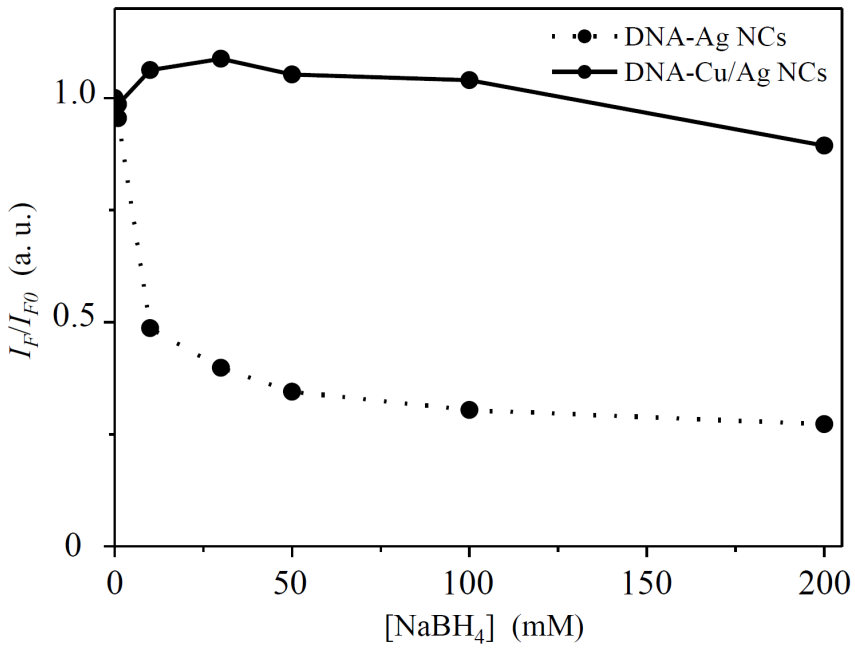

Fig. S3. Representative normalized fluorescence intensity of the as-prepared DNA-Ag and Cu/Ag NCs against $NaBH_4$ concentration (0–200 μM). I_{F0} and I_F are the fluorescence intensities of the DNA-Ag or Cu/Ag NCs in the absence and presence of $NaBH_4$, respectively.

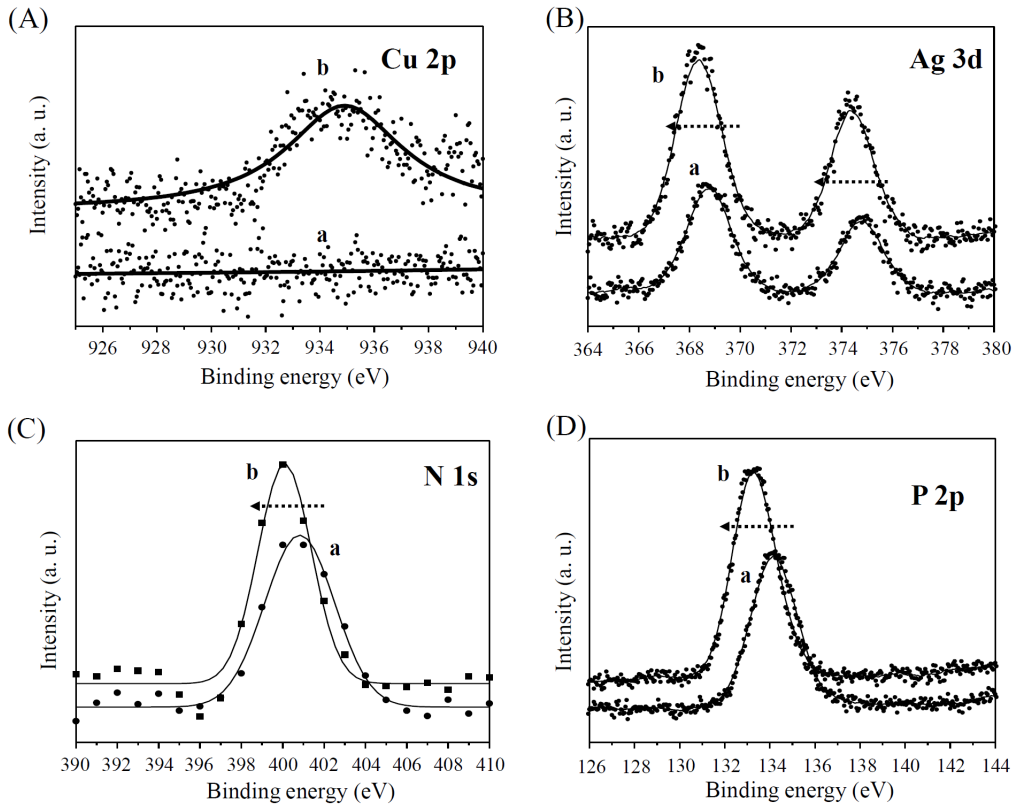

Fig. S4. XPS spectra of the (a) Cu 2p, (b) Ag 3d, (c) N 1s, and (d) P 2p energy levels of the (A) DNA-Ag and (B) DNA-Cu/Ag NCs. The Ag 3d, N 1s, and P 2p binding energies in curve (A) shifted to lower energy in curve (B). Fitting parameters were chosen for a consistent fit for all samples in the series (filled circles for raw data, thick lines for total fits). Other conditions were the same as those used to obtain Figure 1.

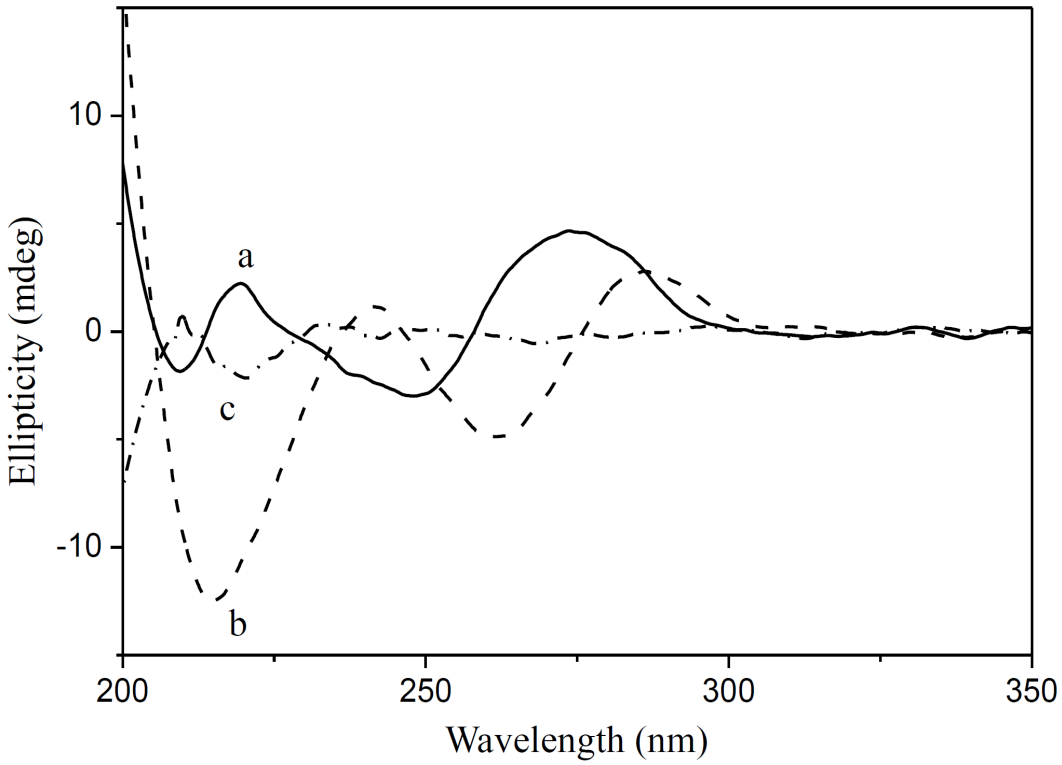

Fig. S5. CD spectra of solutions of (a) free single-stranded DNA (3 μM), (b) and (c) DNA-Cu/Ag NCs (3 μM) in the absence and presence of SSB (300 nM), respectively.

Table S1. Limits of detection for SSB provided by different DNA based approaches

Detection	DNA recognition elements	LOD (nM)	Refs.
Electrochemistry	NH_2-CAAGAC CACCACTTCGAAACC	132	Kerman et al. (2005)
Electrochemistry	HS-$(CH_2)_6$-CGGGCTAT AT*(MB)AAGGGGCGTTTTCTTATATAG (MB = methylene Blue)	10	Ricci et al. (2009)
Fluorescence	$(T)_n$ (n = 8, 16, 30-40)	10	Krauss et al. (1981)
Fluorescence	CCCTTAATCCCC	2	This work