Electronic Supplementary Information

Divalent Metal Ion-Mediated Assembly of Spherical Nucleic Acids: The Case Study of Cu^{2+}

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M^{2+}	Slope (^{o}C/mM)	R^2
Cu^{2+}	-46.4	0.9854
Mg^{2+}	2.48	0.9758
Cd^{2+}	-1.27	0.9020
Co^{2+}	1.49	0.9807
Na^{+}	0.495	0.9833
Ni^{2+}	0.811	0.9496
Zn^{2+}	1.14	0.9316
Mn^{2+}	3.00	0.9948

Table S1. The slopes of the curves of T_m of duplex-interconnected SNA assemblies (**S1** and **S2**, $[Na^+]$ = 0.15 M) against $[M^{2+}]$, and their R^2 values (goodness-of-fit of linear regression). The slopes and R^2 values were obtained by OriginPro 8 (OriginLab Corporation).

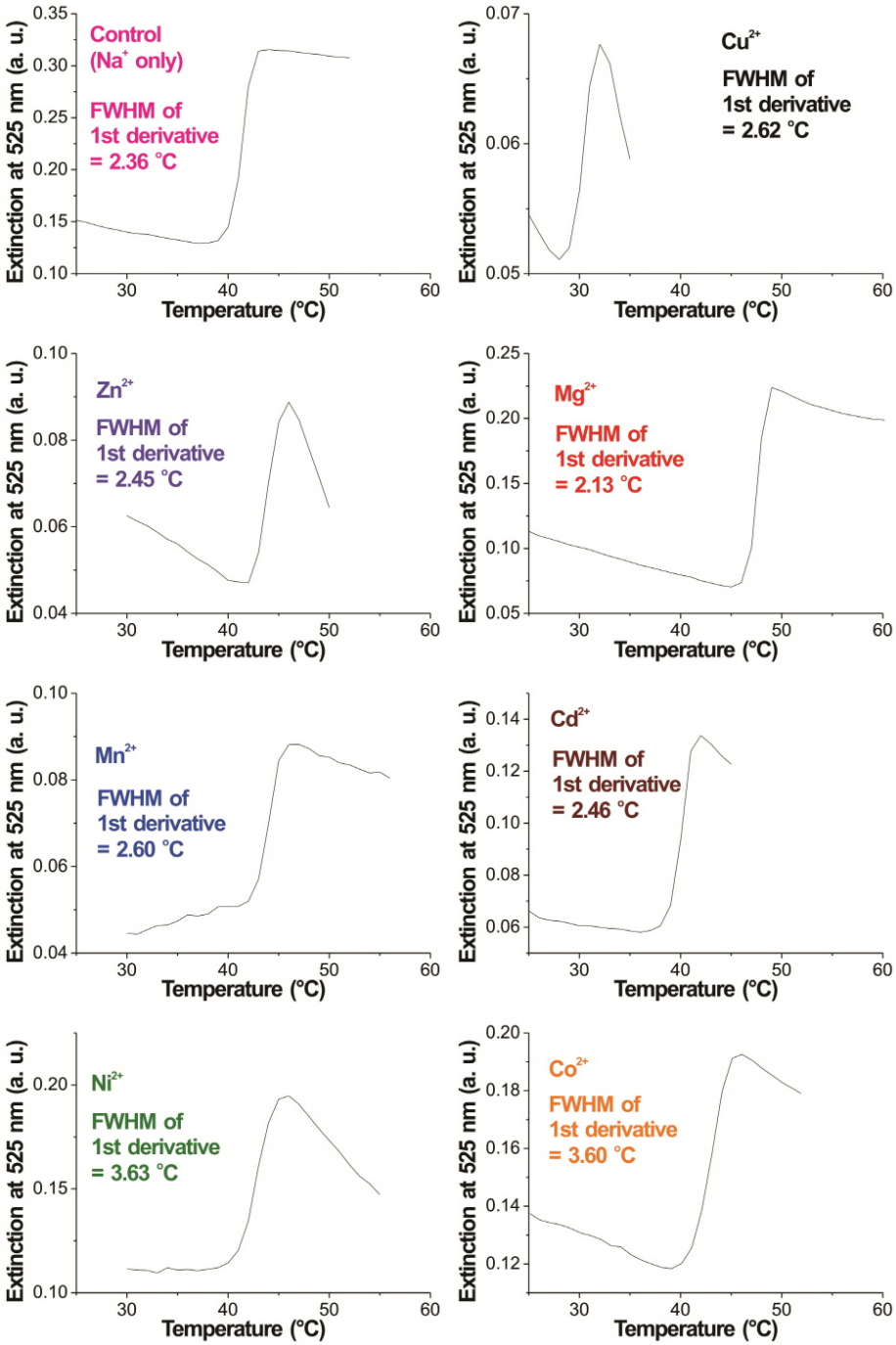

Figure S1. Melting transitions of duplex-interconnected SNA (**S1** and **S2**, $[Na^+]$ = 0.15 M)) assemblies and their full-width at half-maximum (FWHM) of the first derivatives in the presence of M^{2+} at 2 mM (2.5 mM in case of Zn^{2+} and Ni^{2+}, 1 mM in case of Mn^{2+}, and 0.25 mM in case of Cu^{2+}). Note that the cooperativity of the melting transitions is generally reduced by M^{2+} (except Mg^{2+}) compared to Control.

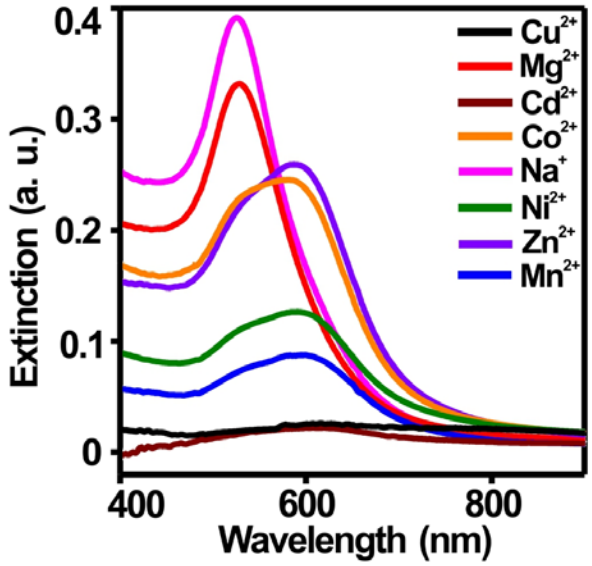

Figure S2. UV-vis spectra of SNAs (**S1** at 1 nM) with various divalent metal ions (Cu^{2+}, Mg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}. Zn^{2+}, and Mn^{2+}) and a monovalent metal ion (Na^{+}). The final concentration of metal ions is 1 mM. Note that even single-type SNAs assemble into clusters and large aggregates in the presence of divalent metal ions, without any complementary SNAs or organic/polymeric materials.

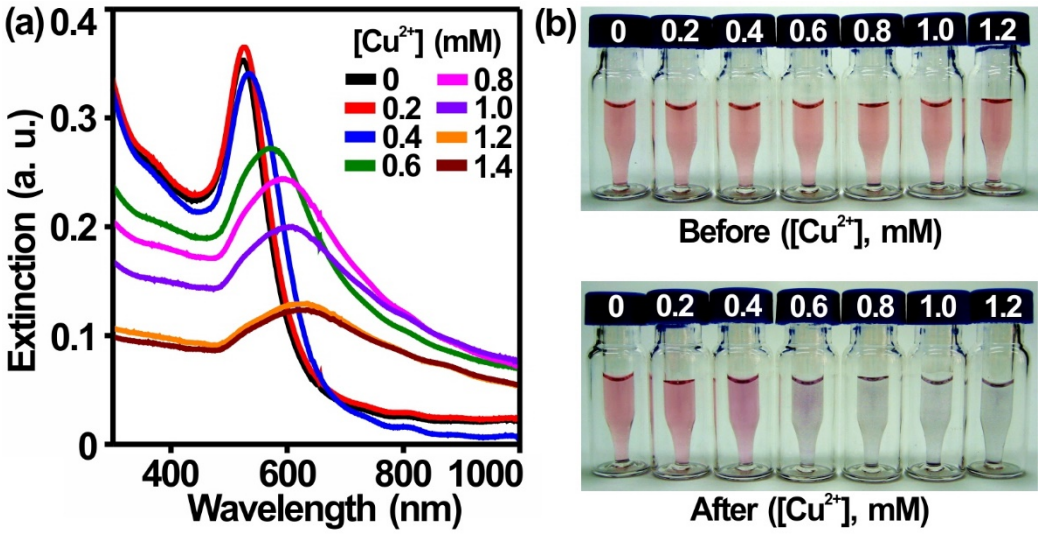

Figure S3. (a) UV-vis spectra of SNAs (**S1**) at various concentrations of Cu^{2+} from 0 to 1.4 mM after 12 hours of incubation. As the $[Cu^{2+}]$ increases, the maximum extinction decreases while the wavelength where the maximum extinction takes place red-shifts (b) The SNA solutions before and after the addition of Cu^{2+} at various concentrations from 0 to 1.2 mM. The SNAs and Cu^{2+} were allowed to react for 12 hours, exhibiting clear color changes from red to blue, depending on the $[Cu^{2+}]$.

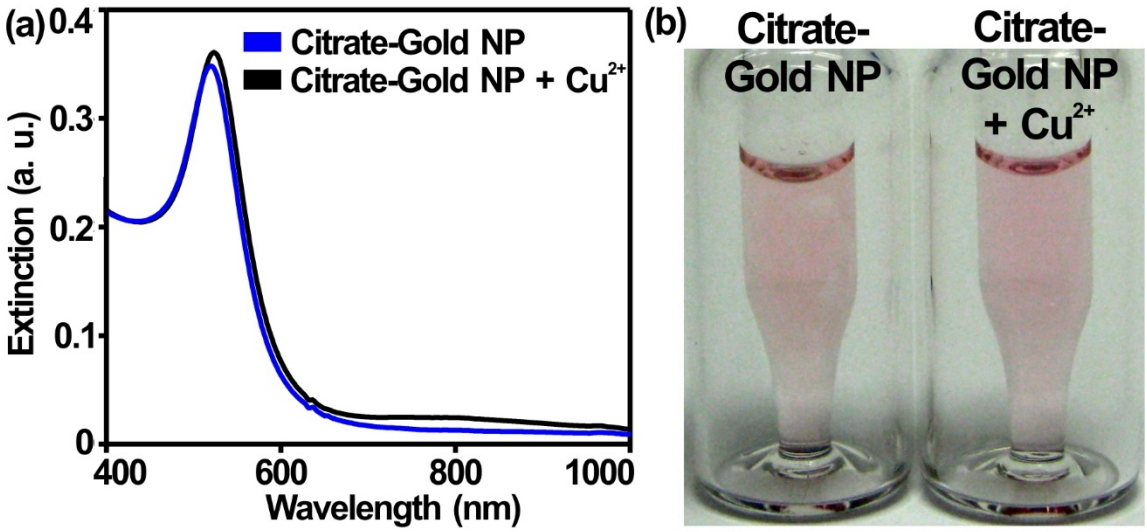

Figure S4. (a) UV-vis spectra of citrate-gold nanoparticles without Cu^{2+} (blue) and with Cu^{2+} at 1 mM (black). (b) The solutions of citrate-gold nanoparticles without Cu^{2+} (left) and with Cu^{2+} at 1 mM (right). Note that both the spectroscopic and visual data of both batches are in good agreement.

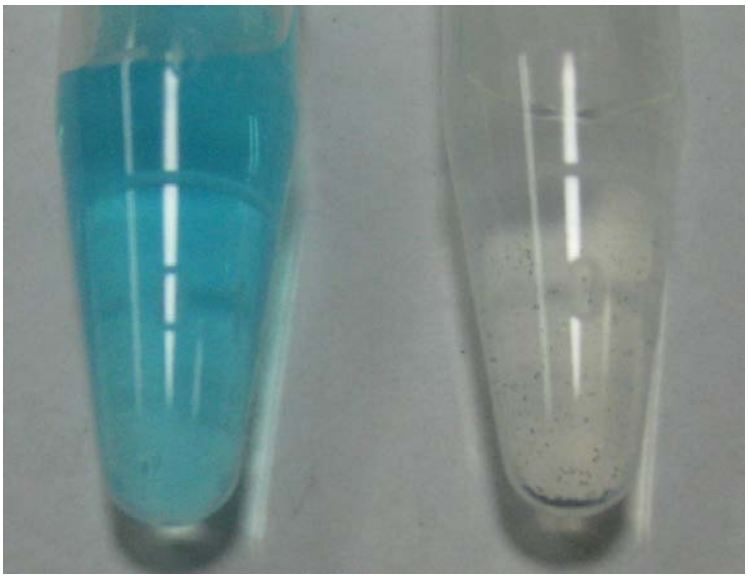

Figure S5. (Left) A solution containing dispersed SNAs (**S1**, 1 nM) and Cu^{2+} (500 mM). The blue color comes from the complex formation of Cu^{2+} with H_2O. The photo was taken as soon as the SNAs and Cu^{2+} were combined. (Right) A solution containing SNAs which were assembled by Cu^{2+} (500 mM) for 12 h, and transferred to pure water. Note that the SNAs are shown as precipitates on the bottom of the microtube.

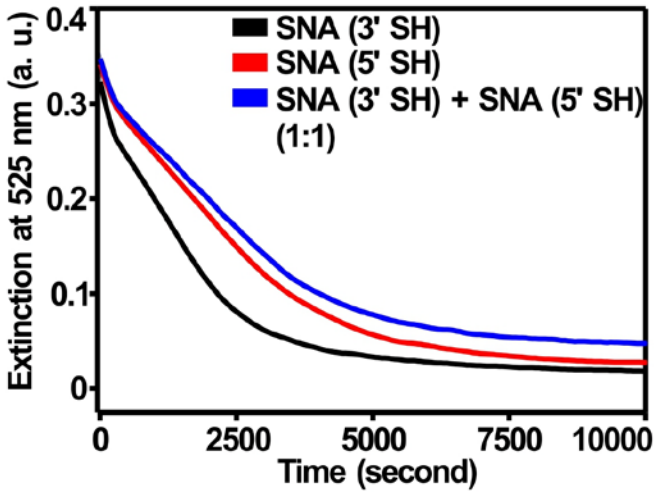

Figure S6. Assembly rates of SNAs composed of **3′ thiol-S1** (black), **S1** (5′ thiol, red), and their 1:1 mixture (blue) in the presence of Cu^{2+} (1 mM).

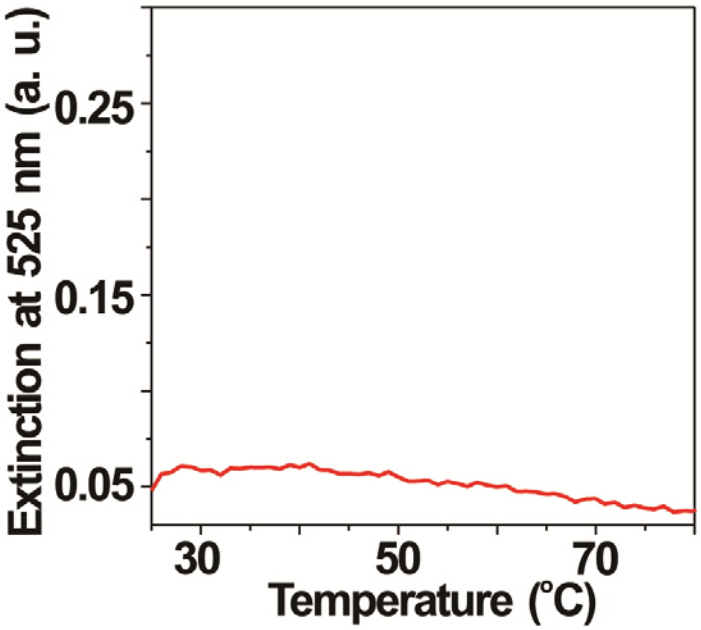

Figure S7. A graph showing the extinction of Cu^{2+}-induced SNA assemblies (**S1**) at 525 nm as a function of temperature ([SNA] = 1 nM and [Cu^{2+}] = 1 mM). Note that practically no thermal dissociation of the SNA assemblies took place in the absence of EDTA.

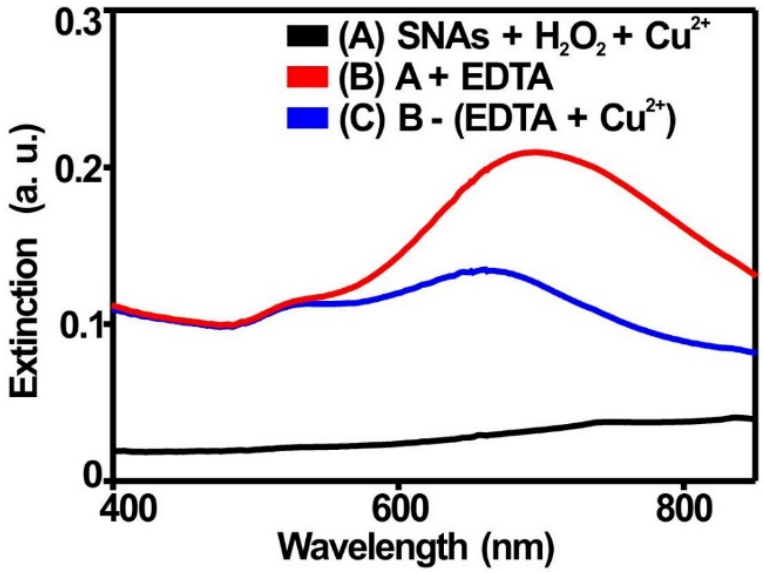

Figure S8. The UV-vis spectra of (A) SNAs (**S1**, 1 nM) combined with H_2O_2 (28 mM) and Cu^{2+} (0.5 mM) at 70 ^oC, (B) and subsequently combined with EDTA (1 mM). (C) To eliminate the contribution of Cu^{2+}-EDTA complex to the UV-vis spectrum in (B), the UV-vis spectrum of a separately prepared mixture of EDTA and Cu^{2+} at the same concentrations was obtained, and was reduced from the spectrum in (B). Note that the extinction at 525 nm is not recovered even after the addition of EDTA, indicating that the SNAs are irreversibly assembled.