Supporting Information

DNA-based sensitization of Tb^{3+} luminescence regulated by Ag^{+} and cysteine: use as a logic gate and a H_2O_2 sensor

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Experimental Section

Reagents and materials. The following metal salts: $Mg(NO_3)_2$, $Cu(NO_3)_2$, $Mn(Ac)_2$, $Zn(Ac)_2$, $Cr(NO_3)_3$, $Pb(NO_3)_2$, $Ni(NO_3)_2$, $Co(Ac)_2$, $Cd(NO_3)_2$, $Fe(NO_3)_3$, $Hg(Ac)_2$, $Ca(Ac)_2$, $CrCl_3$, $Ba(NO_3)_2$, $Al(NO_3)_3$, $NaNO_3$ and KNO_3 were reagent-grade and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The oligonucleotides used in this study were synthesized by Sangon Biotech Co. Ltd. (Shanghai, China): $[G_3T]_5$: 5'-GGGTGGGTGGGTGGGTGGGT-3'; $c[G_3T]_5$: 5'-ACCCACCCACCCACCCACCC-3'. Cysteine and other 19 amino acids were purchased from Sigma-Aldrich (St. Louis, MO). Terbium (III) nitrate hexahydrate was purchased from Diyang Chemical Co. Ltd. (Shanghai, China). Hydrogen peroxide solution (30%) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 10×Tris–HAc buffer (100 mM, pH 7.9) was prepared using metal-free reagents in distilled water purified by a Milli-Q water purification system (Millipore Corp., Bedford, MA) with an electrical resistance of 18.2 MΩ. All chemicals used in this work were of analytical reagent and obtained from commercial sources and directly used without additional purification.

Instrumentation. Fluorescence spectra were measured in a fluorescence microplate reader (infinite M200 pro, TECAN, Switzerland) using a black 384 well microplate (Fluotrac 200, Greiner, Germany). Photographs were taken with a digital camera. The excitation wavelength used was 290 nm for the emission spectra. For the time-resolved luminescence spectra, a delay time of 50 μs and a gate time of 2 ms were used.

Assays for Ag^{+} using the $Tb^{3+}/[G_3T]_5/c[G_3T]_5$ probe. The $Tb^{3+}/[G_3T]_5/c[G_3T]_5$ probe (Tb^{3+}, $[G_3T]_5$ and $c[G_3T]_5$ were used) was prepared in 10 mM Tris–HAc buffer (pH 7.9), and the mixture was incubated for 10 min at room temperature. For the luminescent "on" detection of Ag^{+}, an aliquot of the tested Ag^{+} or control samples or Mill-Q water (as blank sample) was added to the $Tb^{3+}/[G_3T]_5/c[G_3T]_5$ probe. The final concentration of Tb^{3+}, $[G_3T]_5$ and $c[G_3T]_5$ was 5 μM, 4 μM and 4 μM, respectively. The mixture was vortexed to mix all the reagents and then incubated for 10 min at room temperature and after that an aliquot of 0.1 mL mixture was placed in the black 384 well microplate to measure the luminescence intensity (excited at 290 nm, a delay time of 50 μs and a gate time of 2 ms).

Assays for Cys using the $Tb^{3+}+[G_3T]_5/c[G_3T]_5+Ag^{+}$ sensing system. The

Tb^{3+}+$[G_3T]_5$/c$[G_3T]_5$+Ag^+ sensing system (Tb^{3+}, $[G_3T]_5$, c$[G_3T]_5$ and Ag^+ were used) was prepared in 10 mM Tris–HAc buffer (pH 7.9), and the mixture was incubated for 10 min at room temperature. For the luminescent "off" detection of Cys, an aliquot of the tested Cys or control samples or Mill-Q water (as blank sample) was added to the Tb^{3+}+$[G_3T]_5$/c$[G_3T]_5$+Ag^+ sensing system. The final concentration of Tb^{3+}, $[G_3T]_5$, c$[G_3T]_5$ and Ag^+ was 5 μM, 4 μM, 4 μM and 40 μM, respectively. The mixture was vortexed to mix all the reagents and then incubated for 10 min at room temperature and after that an aliquot of 0.1 mL mixture was placed in the black 384 well microplate to measure the luminescence intensity (excited at 290 nm, a delay time of 50 μs and a gate time of 2 ms).

Assays for H_2O_2 via reversing the Cys-mediated luminescence changes in the Tb^{3+}+$[G_3T]_5$/c$[G_3T]_5$+Ag^+ sensing system. 40 μM Cys was firstly treated with various H_2O_2 concentrations for 20 min in 10 mM Tris–HAc buffer (pH 7.9), and the resulting solution was then transferred to the Tb^{3+}+$[G_3T]_5$/c$[G_3T]_5$+Ag^+ sensing system. The final concentration of Tb^{3+}, $[G_3T]_5$, c$[G_3T]_5$ and Ag^+ was 5 μM, 4 μM, 4 μM and 40 μM, respectively. The mixture was vortexed to mix all the reagents and then incubated for 10 min at room temperature and after that an aliquot of 0.1 mL mixture was placed in the black 384 well microplate to measure the luminescence intensity (excited at 290 nm, a delay time of 50 μs and a gate time of 2 ms).

Data analysis. The GraphPad Prism 5.0 software (GraphPad Software, San Diego, CA) was employed to perform the data processing. Each sample was repeated in duplicate, and data were averaged.