Electronic Supplementary Information

Catalytic formation of luminescent lanthanide complexes using entropy-driven DNA circuit

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Oligonucleotides. ODNs were synthesized by a conventional phosphoramidite method on a universal CPG (controlled pore glass) column (Glen Research). Cleavage from the CPG support and deprotection was carried out by incubation in aqueous ammonia (28 %) for 8 h at 80 °C. The aqueous ammonia was evaporated under reduced pressure. From these crude mixtures, the resulting ODNs were purified with a conventional two-step procedure using RP-HPLC (linear gradient: 0.1 M triethylammonium acetate (TEAA), pH 7.0/acetonitrile) and identified with MALDI-TOF/MS. For the synthesis of **Phen-DNA** and **EDTA-DNA**, 5'- and 3'-aminohexsyl-linked DNAs were purified.

Synthesis of EDTA-DNA. The purified 3'-aminohexsyl-linked DNA (20 nmol) was dissolved in 20 μL of 0.5 M carbonate-Na buffer (pH 9.37). To this solution, was added phen active ester (2 μmol) dissolved in 40 μL DMSO. The resulting solution was stirred at ambient temperature for 24 h. After dilution to 300 μL with 0.5 M EDTA solution (pH 8.0), the mixture was purified by RP-HPLC under the following conditions: column: InertSustain C18, GL Sciences; room temperature; flow rate: 1.0 mL min^{-1}; eluent A: 0.1 M TEAA (pH 7.0); eluent B: acetonitrile; linear gradient, 0–20 % B in 30 min. MALDI-TOF/MS: calcd for [**EDTA-DNA** − H]$^-$: m/z = 16182.59, found: 161680.80.

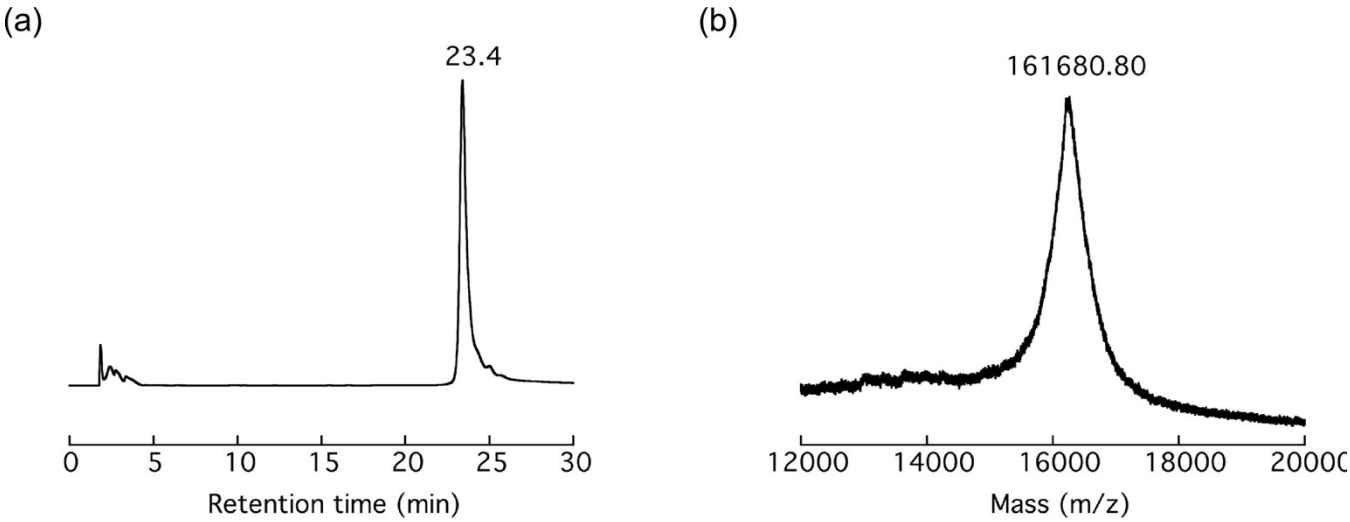

Fig. S1. (a) RP-HPLC chromatogram of the reaction mixture containing **EDTA-DNA**. Column: InertSustain C18 (4.6 mm (*Φ*) x 150 mm (w), GL Sciences); eluent A: 0.1 mM TEAA buffer (pH = 7.0); eluent B: acetonitrile; linear gradient: 0-20 % B in 30 min; flow rate: 1.0 mL/min. (b) MALDI-TOF MS spectrum of the fraction at 23.4 min in Fig. S1a.

Synthesis of Phen-DNA. The purified 5'-aminohexsyl-linked DNA (20 nmol) was dissolved in 30 μL of 0.5 M carbonate-Na buffer (pH 9.37). To this solution, was added phen active ester (2 μmol) dissolved in 60 μL DMSO. The resulting solution was stirred at 60 °C for 24 h. The mixture was subjected to GPC (NAP10 Column, Sephadex G-25, GE Healthcare Life Sciences) to remove excess hydrolyzed ester. After lyophilization, the residue was redissolved in 300 μL of 0.5 M EDTA solution (pH 8.0), and then purified by RP-HPLC under the following conditions: column: InertSustain C18, GL Sciences; room temperature; flow rate: 1.0 mL min^{-1}; eluent A: 0.1 M TEAA (pH 7.0); eluent B: acetonitrile; linear gradient, 0–20 % B in 30 min. MALDI-TOF/MS: calcd for [**Phen-DNA** − H]$^-$: m/z = 13635.98, found: 13636.26.

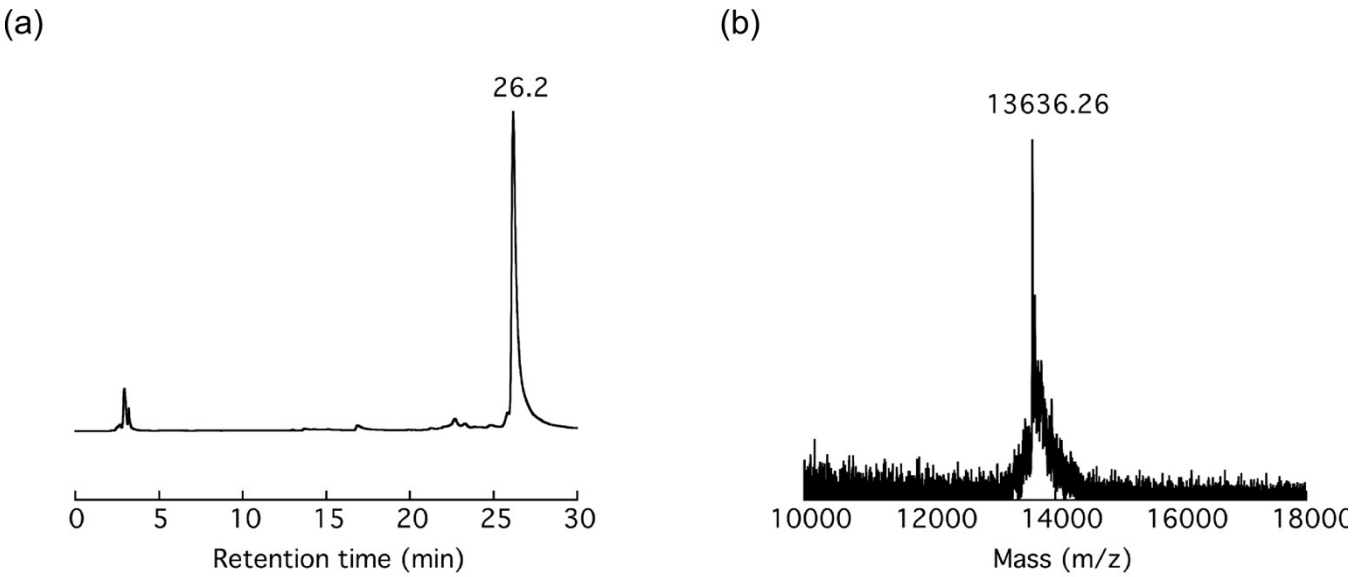

***Fig. S2*.** (a) RP-HPLC chromatogram of the reaction mixture containing **EDTA-DNA**. Column: InertSustain C18 (4.6 mm (*Φ*) x 150 mm (w), GL Sciences); eluent A: 0.1 mM TEAA buffer (pH = 7.0); eluent B: acetonitrile; linear gradient: 0-20 % B in 30 min; flow rate: 1.0 mL/min. (b) MALDI-TOF MS spectrum of the fraction at 26.2 min in Fig. S2a.

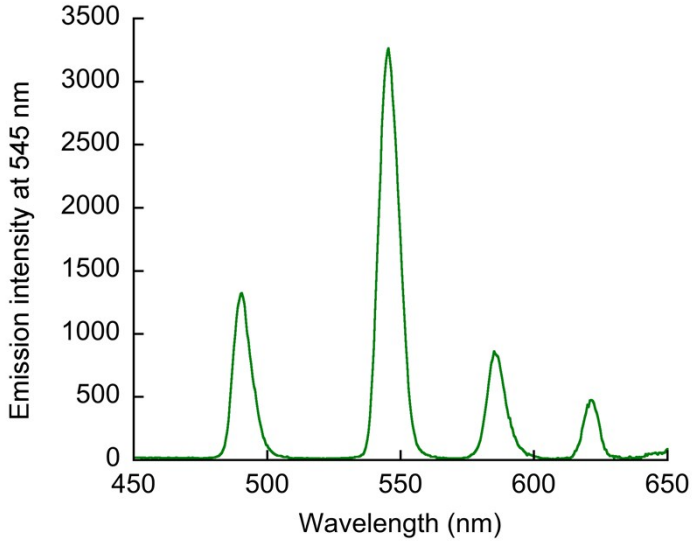

***Fig. S3*.** Time-resolved emission spectra of the solutions containing **EDTA-DNA**/**Phen-DNA** in the presence of Tb(III) at 10 °C. Concentrations of **EDTA-DNA**, **Phen-DNA**, and Tb(III) were 1.0 μM, 1.0 μM, and 1.2 μM, respectively. Excitation wavelength was 280 nm. Measurement was carried out in 10 mM HEPES buffer (pH 7.2) containing 200 mM NaCl after equilibration at 10 °C for 30 min. Delay time: 50 μs. Gate time: 2 ms.

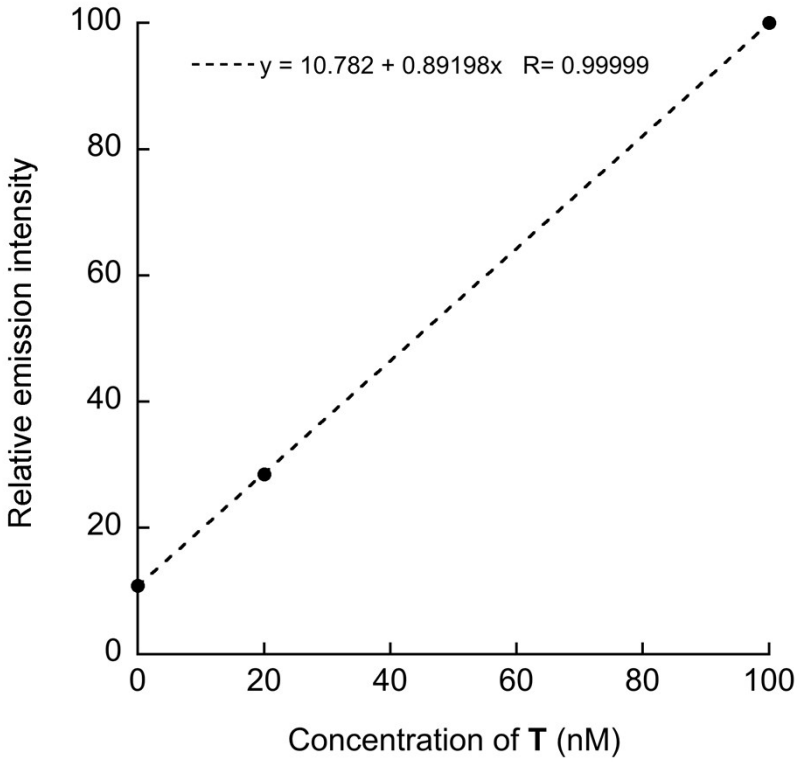

Fig. S4. Calibration curve for the emission intensities at 1 h as a function of the concentration of **T**. Detection limits was calculated to be 12 nM by defining as the concentration of **T** which gave two times larger emission intensity than that without **T**.