## **Supporting Information**

## Versatile allosteric molecular devices based on the reversible formation of luminous lanthanide complex

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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 the 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 conventional two-step procedure using RP-HPLC (linear gradient: 0.1 M triethylammonium acetate (TEAA), pH7.0/acetonitrile) and identified with MALDI-TOF/MS. For the synthesis of LCMB1 and LCMB2, 5'- and 3'-aminohexsyl-linked ODN (5'-MMT-amino-C6-MB1-C6-3'-amino and 5'-MMT-amino-C6-MB2-C6-3'-amino) was purified without deprotection of 5'-MMT (monomethoxytrityl) group.

Synthesis of LCMB. The syntheses of LCMB1 and LCMB2 were carried out according to Fig. S1. The purified 5'-MMT-amino-C6-MB1-C6-3'-amino (100 nmol) was dissolved in 30 µL of 0.5 M carbonate-Na buffer (pH 9.35). To this solution, was added phen active ester (10 µmol) dissolved in 60 µL DMSO. The resulting suspension was stirred at ambient temperature overnight. After centrifugation and filtration, the solution was diluted to 300 µL with 0.5 M EDTA solution (pH 8.0). The mixture was purified by RP-HPLC under the following conditions: column: Wakosil-II 5C18 RS; room temperature; flow rate: 1.0 mL min<sup>-1</sup>; eluent A: 0.1 M TEAA (pH 7.0); eluent B: acetonitrile; linear gradient, 5-40 % B in 30 min. After evaporation under reduced pressure, detrithylation of 5'-MMT was carried out by treating with 80 % acetic acid for 30 min. After evaporation under reduced pressure, the residue was dissolved in a 200 µL of 0.5 M EDTA solution (pH 8.0). After filtration, the mixture was purified by RP-HPLC under the same conditions as described above. After evaporation under reduced pressure, the purified 5'-detrithylate and 3'-phen modified ODN, 5'-amino-C6-MB1-C6-3'-phen (100 nmol) was dissolved in a 30 µL of 0.5 M carbonate-Na buffer (pH 9.35). To this solution, was added anhydride of EDTA (10 µmol) dissolved in 60 µL DMSO. The resulting solution was stirred at ambient temperature overnight. The solution was diluted to 400 µL with 0.5 M EDTA solution (pH 8.0). After additional stirring for 24 h, the mixture was purified by RP-HPLC under the same conditions as described above. The synthesis and purification of the LCMB2 was also carried out according to the same procedure as LCMB1. MALDI-TOF/MS: calcd for [5'-amino-C6-MB1-C6-3'-phen - H]: m/z = 8172.40, found: 8174.01; calcd for [LCMB1 - H]: m/z = 8446.63, found: 8446.28; calcd for [5'-amino-C6-MB2-C6-3'-phen - H]: m/z = 8252.51, found: 8253.35; calcd for [LCMB2 - H]<sup>-</sup>: m/z = 8530.70, found: 8529.01.

**Optimization of the linker length.** The effect of the linker lengths on the emission intensities were assessed by using several sets of a EDTA and phen modified 10 mer ODNs with a trimethylene (C3) or hexamethylene (C6) linker. Assuming the stem region of **LCMB**, the sequences of them were designed to be complementary to each other forming a luminescent lanthanide complex at a terminus. Syntheses of phen or EDTA modified ODNs were carried out following previously reported procedure. The emission spectra for all possible combinations between phen and EDTA modified ODNs were measured the in presence of Ln(III) using the time-gating technique. As shown in Fig. S2, the emission intensities depend on the combinations of linker lengths, however, did not so changed by the direction of the modification in the presence of equimolar amount of Ln(III). By the addition of excess amount of Ln(III), the emission intensities were gradually increased to be plateau except for the combination of 5' EDTA-modified ODN with C6 linker and 3' phen-modified ODN with C6 linker (Fig. S3). These results indicated that the luminous complex was formed at a 1 : 1 molar ratio only for this pair of the probes. For these reasons, the following experiments were carried out using 5' EDTA-modified and 3' phen-modified stem loop structured ODN with C6 linkers.

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*Fig. S2.* Time-resolved emission spectra ( $\lambda_{ex} = 280$  nm) of the solutions containing a pair of phen and EDTAmodified 10 mer conjugates in the presence of (a) Tb(III) or (b) Eu(III). Measurements were carried out in the buffered solution (10 mM HEPES containing 1.0 M NaCl, pH 7.0) at 0 °C. Concentrations of conjugates and Ln(III) were all 1.0  $\mu$ M. Delay time: 50  $\mu$ s, Gate time: 2.0 ms.

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*Fig. S3.* Luminescence titration curves for the duplexes consisting of phen and EDTA conjugates with Ln(III). All measurements were carried out in the same buffer solution and under same condition as described in Fig. S2. Concentrations of each conjugate were all  $1.0 \mu$ M.



*Fig. S4.* Calibration curve for the emission intensities as a function of the concentration of ATP. All measurements were carried out in a 10 mM HEPES buffer containing 100 mM NaCl and 5 mM MgCl<sub>2</sub> (pH 7.0)

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and under same condition as described in Fig. S2. Concentrations of LCMB2/iATP and Eu(III) were 1.0 and 5.0  $\mu$ M, respectively.