Supplementary Material for:

PARACEST Properties of a Dinuclear Neodymium (III) Complex Bound to DNA or Carbonate

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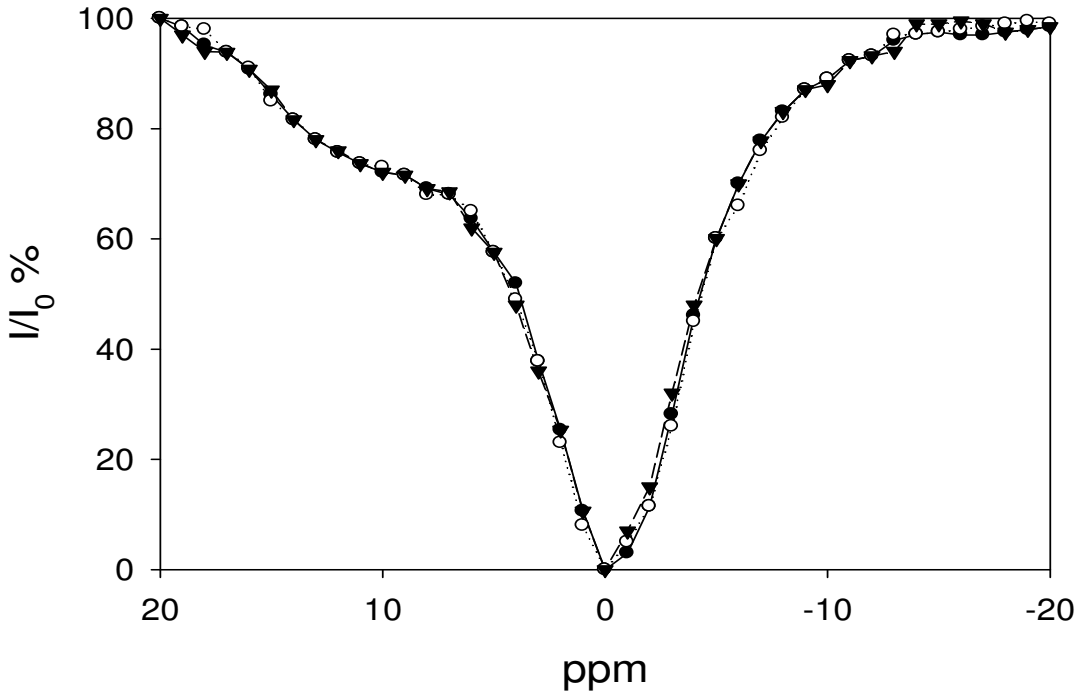


Figure S1. CEST spectra of Nd_2(**1**) (5.0 mM complex, 10 mM HEPES, 50 mM $NaNO_3$) as a function of irradiation time (●) 3s (○), (Δ) 5s and (▼) 7s. B_1 = 1,000 Hz, T = 25°C

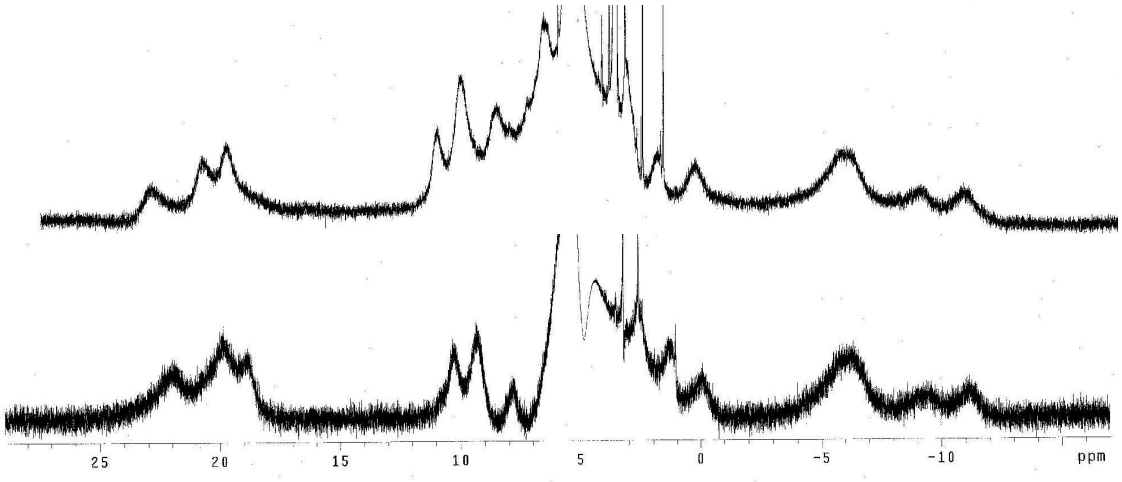


Figure S2. ^{1}H NMR spectra of 5 mM Nd_2(**1**) in H_2O (top) and D_2O (bottom) pH 7.4 (pD 7.0), 10 mM HEPES and 25ºC. Note the lack of a proton resonance corresponding to the CEST peak for the amide protons at 16-17 ppm.

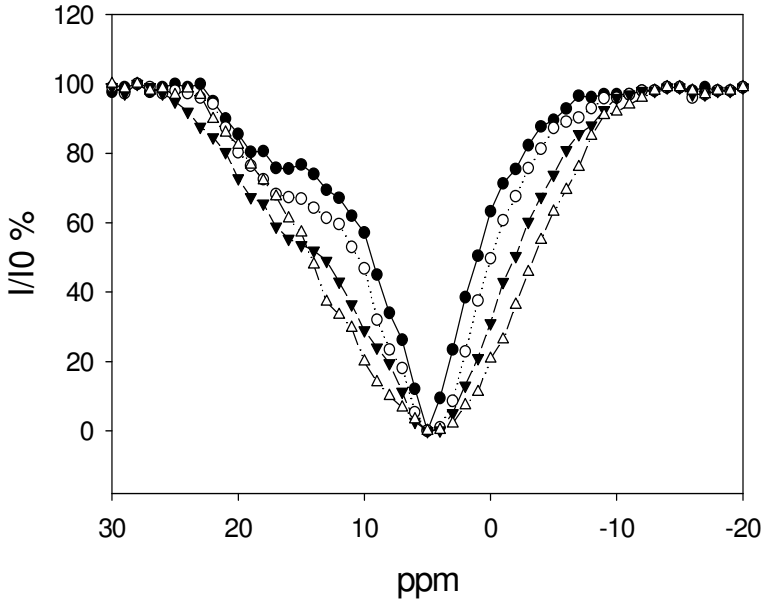


Figure S3. Top: CEST spectra of Nd_2(**11**) (5.0 mM complex, 10 mM hepes, 50 mM $NaNO_3$) at pH 6.5 (●), 7.0 (○), 7.5 (▼) and 8.0 (△). B_1 = 1,500 Hz, T = 25°C. shift water to zero

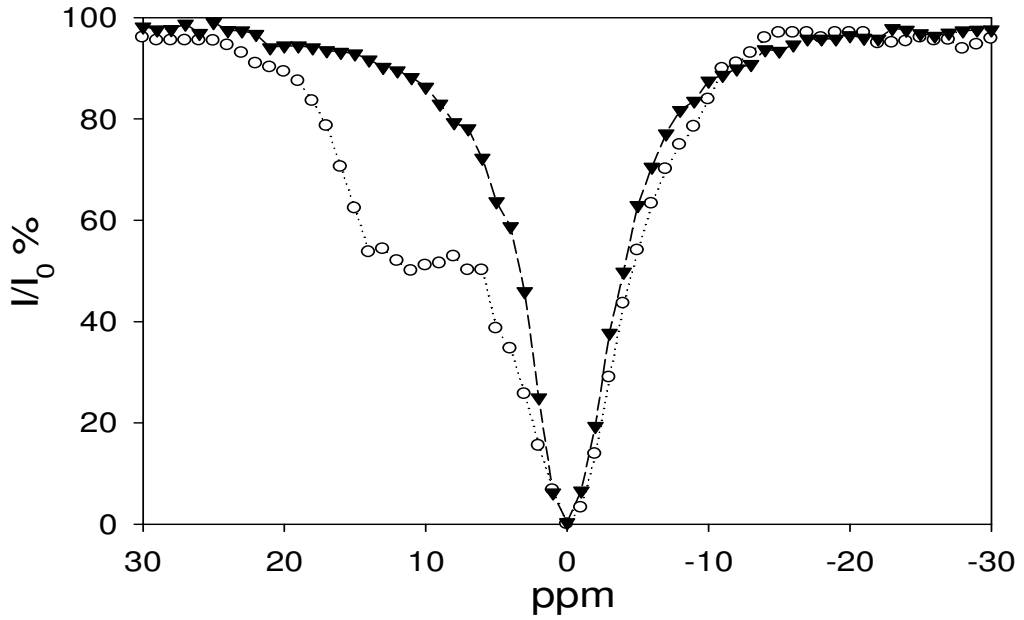


Figure S4. CEST spectra of 10 mM Nd_2(**1**) (○), and 10 mM of Eu_2(**1**)(◄) at pH 7.0, 10 mM Hepes buffer, 50 mM $NaNO_3$, 25 °C, B_1 = 1,500 Hz.

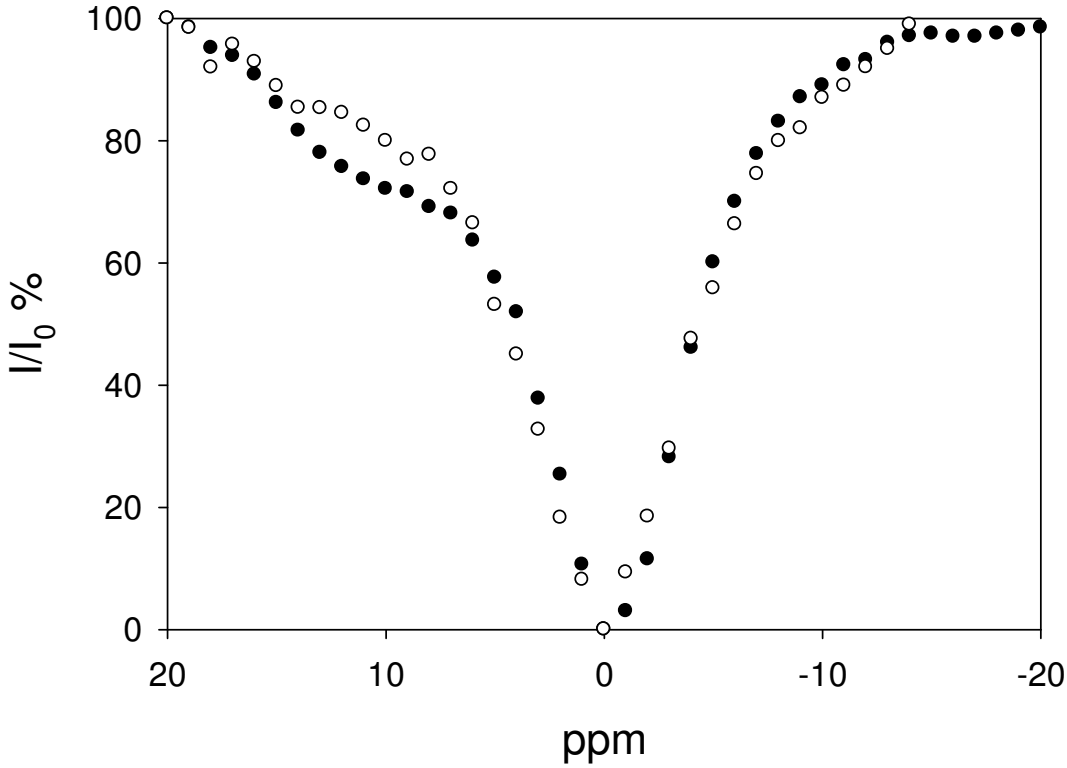


Figure S5. CEST spectra of Nd_2(**1**) 5.0 mM (●) titrated with 0 mM **DEP** (●), 5.0 mM DEP (○) at pH 7.0, 10 mM HEPES, 50 mM $NaNO_3$, 25 °C.

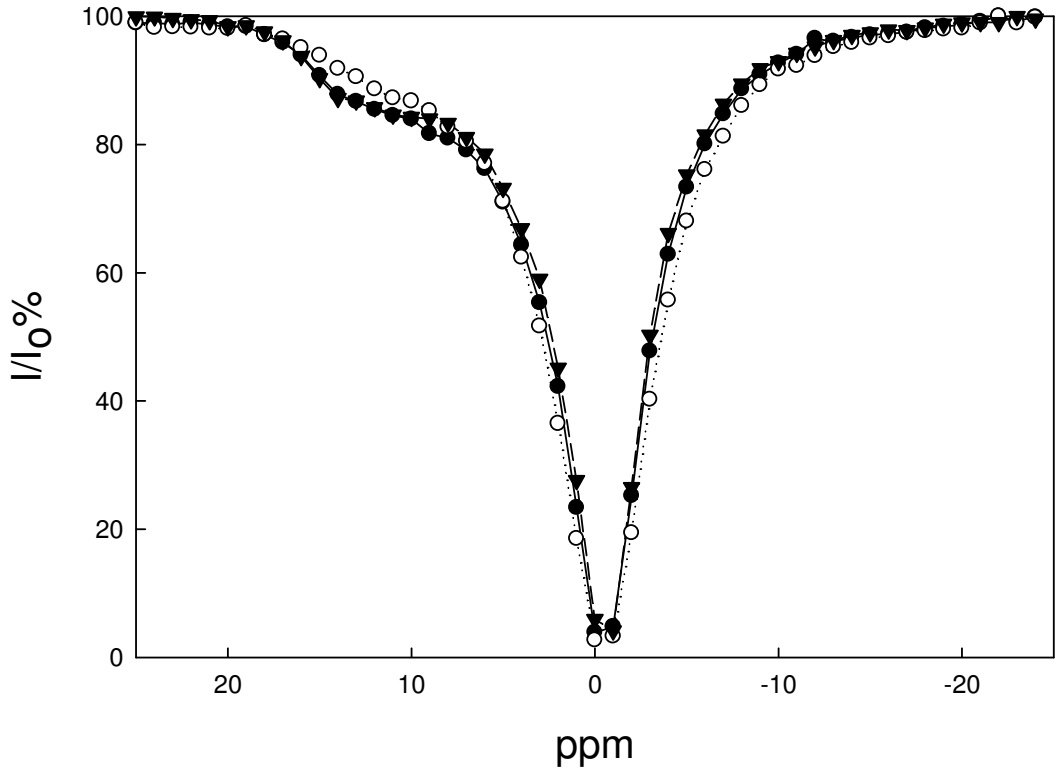


Figure S6. The CEST effect of Nd_2(1) is decreased upon addition of carbonate. CEST spectra of Nd_2(**1**) (5.0 mM complex, 10 mM HEPES, 50 mM $NaNO_3$) (●), addition of 5mM $NaHCO_3$ (○), carbonate removed by treatment with $Pb(NO_3)_2$ (▼), T = 25°C.

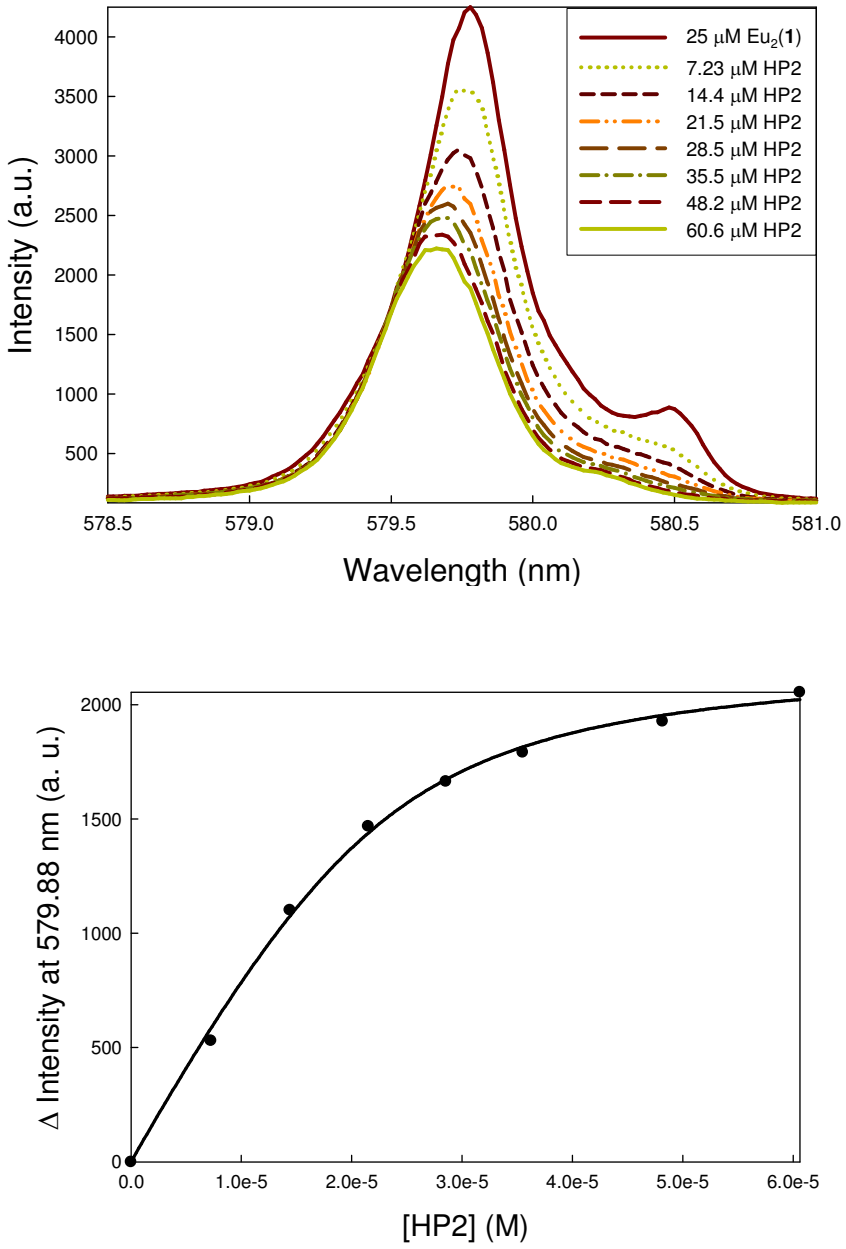
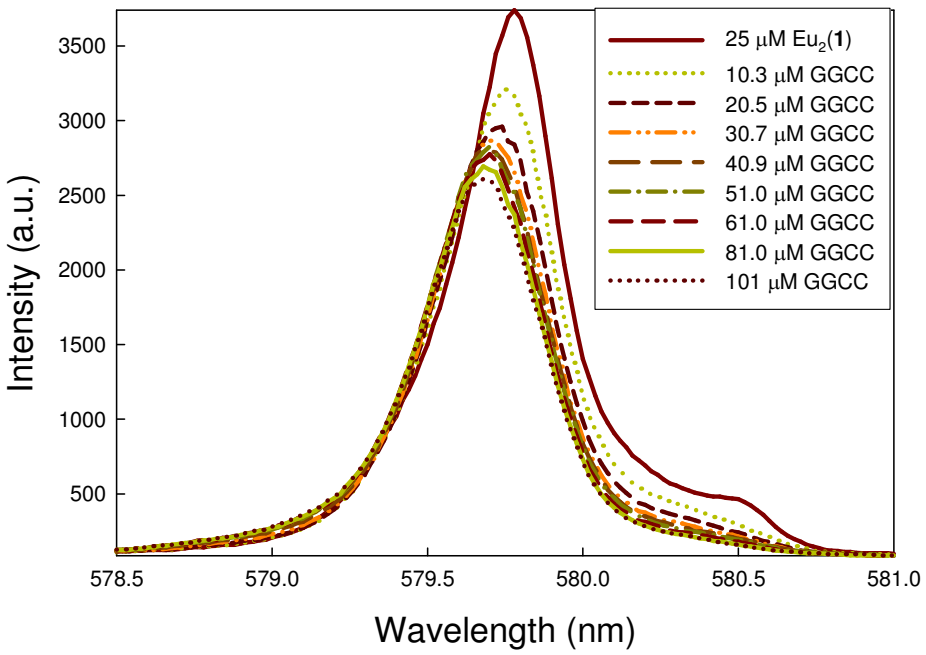


Figure S7. $^7F_0 \rightarrow {}^5D_0$ excitation spectra ($^5D_0 \rightarrow {}^7F_2$ emission) of solutions of 25 μM Eu_2(**1**) (●) titrated with **HP2** DNA at pH = 7.0, 20 mM HEPES, 50 mM $NaNO_3$. Binding isotherm is fit to eq. 3 with a K_d of 4.2 μM (n=12).



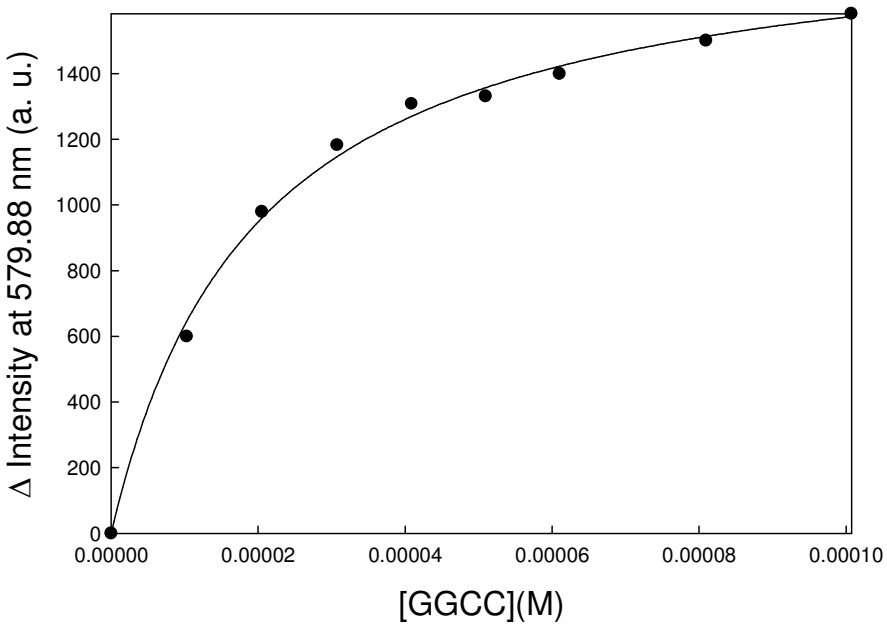


Figure S8. $^7F_0 \rightarrow {}^5D_0$ excitation spectra ($^5D_0 \rightarrow {}^7F_2$ emission) of solutions of 25 μM Eu_2(**1**) (●) titrated with double stranded **GGCCGGCC** DNA at pH = 7.0, 20 mM HEPES, 50 mM $NaNO_3$. Binding isotherm is fit to eq. 3 with K_d of 28 μM (n=6.9).

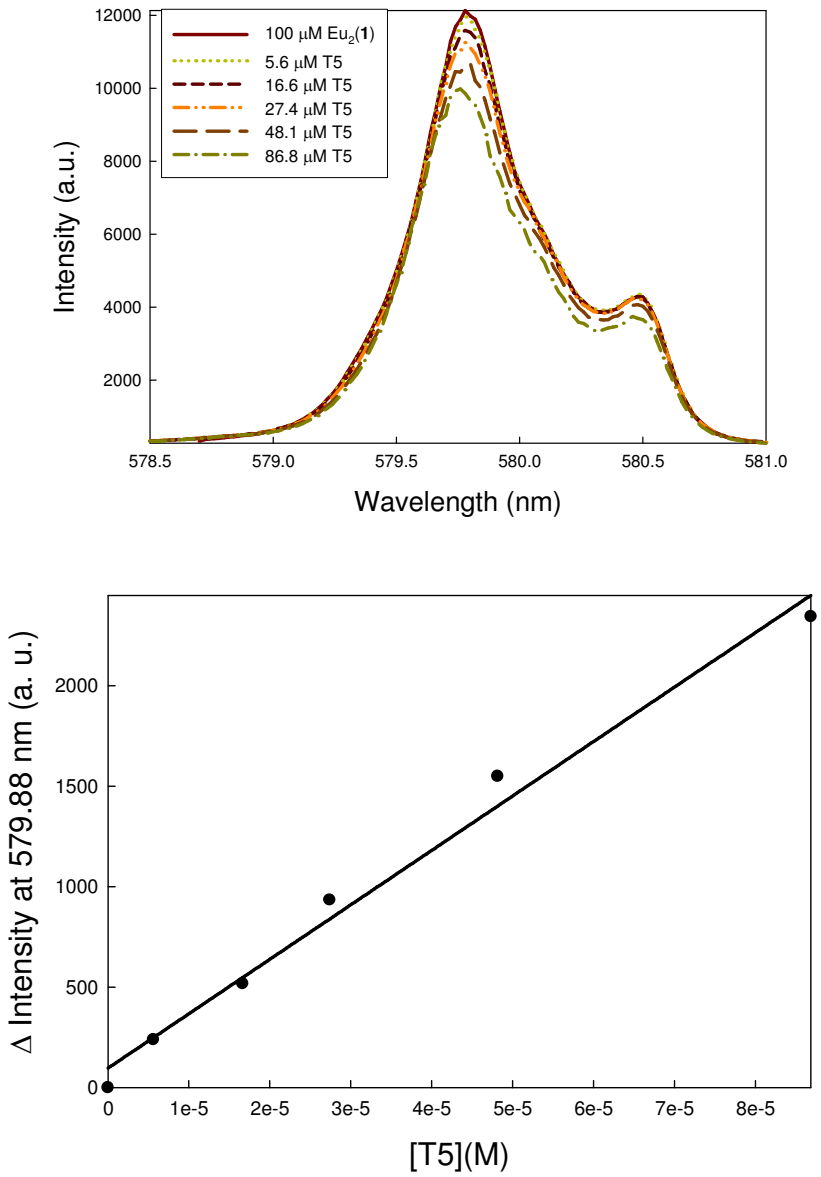


Figure S9. $^7F_0 \rightarrow {}^5D_0$ excitation spectra ($^5D_0 \rightarrow {}^7F_2$ emission) of solutions of 100 μM Eu_2(**1**) titrated with **HP1** DNA at pH = 7.0, 20 mM HEPES, 50 mM $NaNO_3$. Binding isotherm is fit a linear equation.

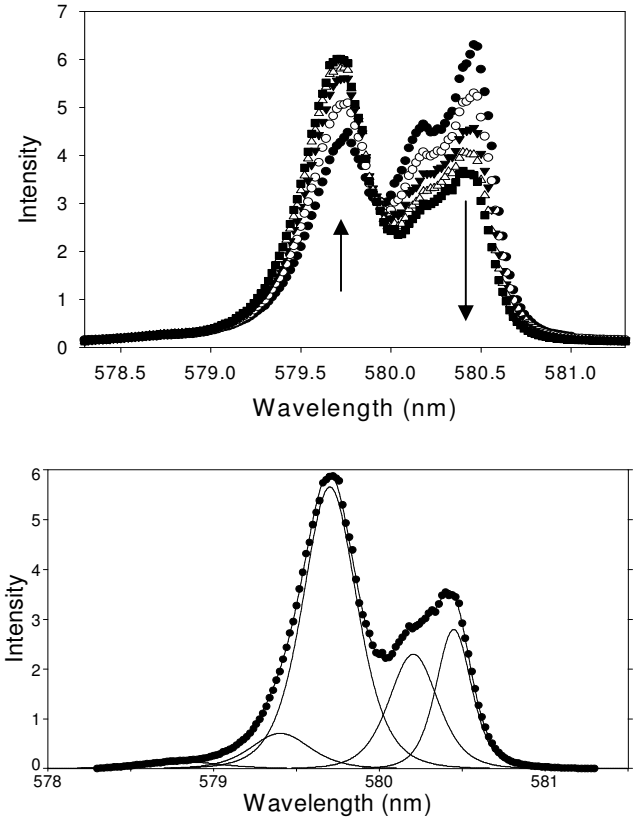


Figure S10. $^7F_0 \rightarrow {}^5D_0$ excitation spectra ($^5D_0 \rightarrow {}^7F_2$ emission) of solutions of 20 μM Eu_2(**1**) carbonate complex (●) titrated with 2 μM (○), 4 μM (▼), 6 μM (Δ) and 8 μM (■) **HP1** DNA at pH = 7.0, 20 mM HEPES, 50 mM $NaNO_3$. b) Deconvoluted $^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu_2(**1**) (20 μM) in the presence of 8 μM of **HP1** DNA. Peaks centered at 580.20 and 580.45 nm are attributed to carbonate complex. The peak that grows in at 578.82 nm is the Eu_2(**1**) complex with **HP1**.