

Supplementary data for:

Direct excitation luminescence spectroscopy of Eu(III) complexes of 1,4,7-tris(carbamoylmethyl)-1,4,7-10 tetraazacyclododecane and kinetic studies of their catalytic cleavage of an RNA analog.

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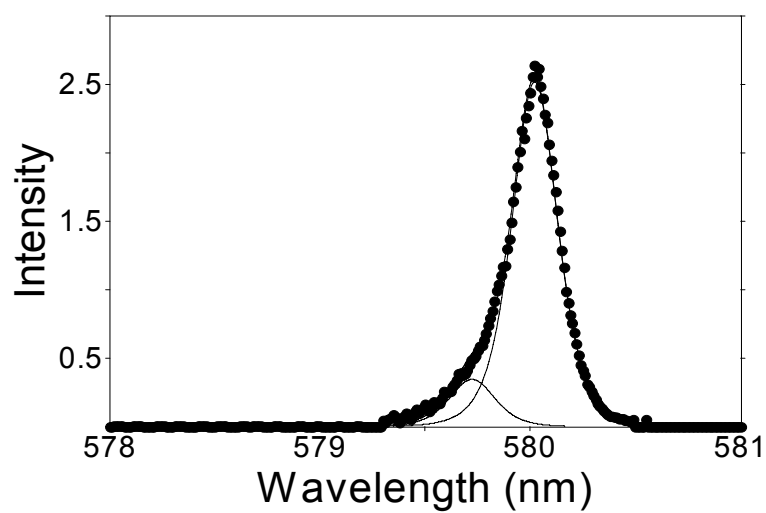


Figure S1. ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ excitation spectra (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission) of 1.00 mM $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ incubated with 1.00 mM macrocycle **1** in Hepes buffer (20mM), pH 6.5, and $I = 0.100$ M (NaNO_3) at 65 °C for 5 hours.

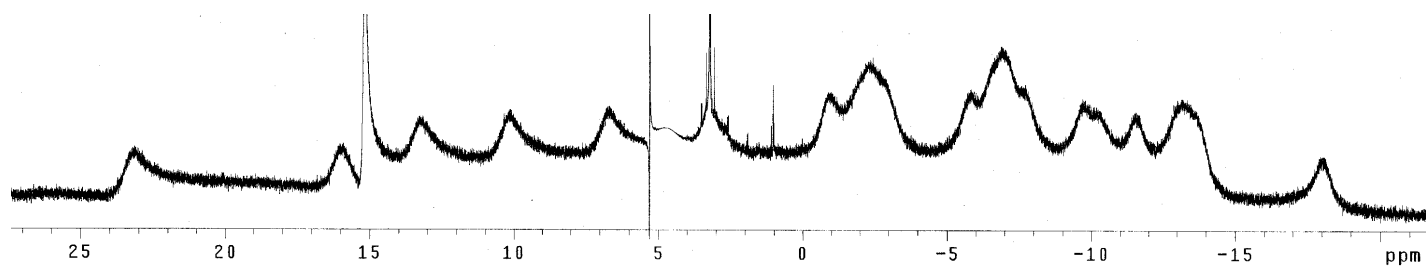


Figure S2. ^1H NMR spectrum of 5 mM Eu(**1**) at pD 7.0 with suppression of the DHO/H₂O resonance at approximately 5.5 ppm.

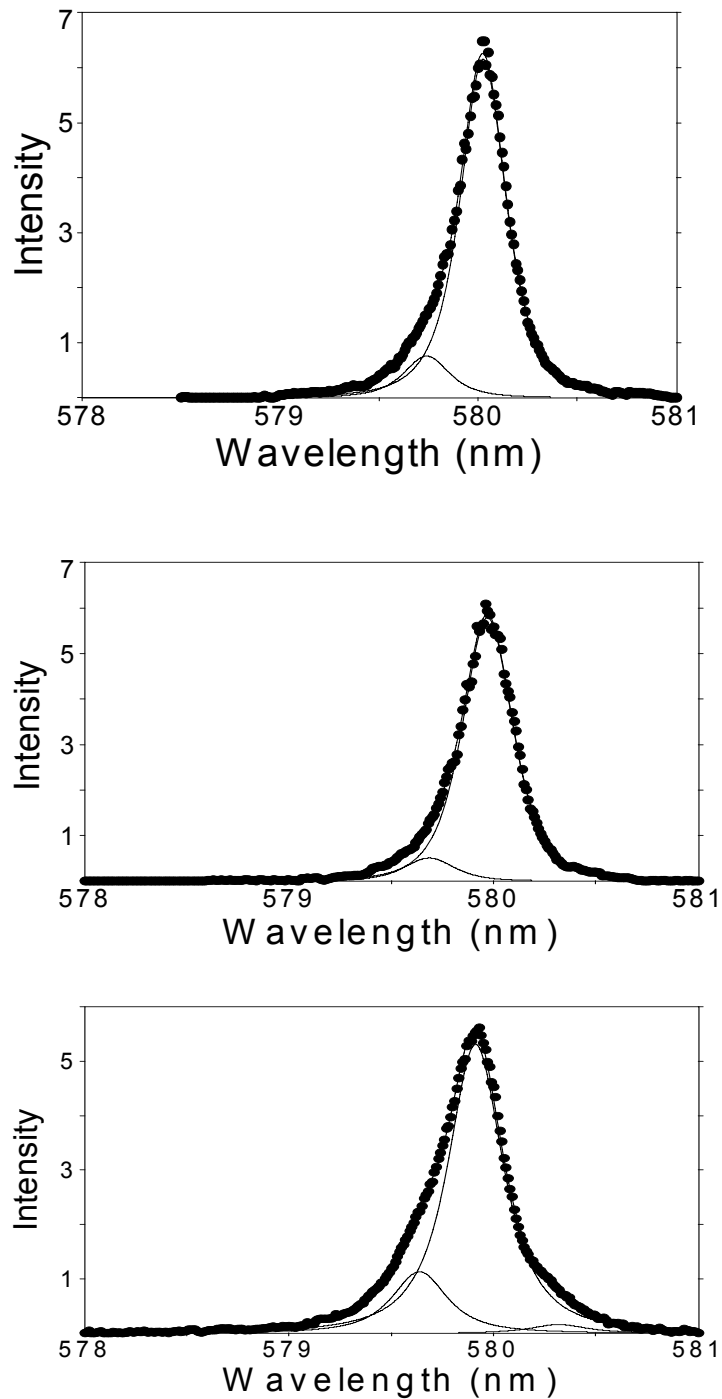


Figure S3. ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra (${}^5D_0 \rightarrow {}^7F_2$ emission) of Eu(**1**) (top) at pH 9.0 and Eu(**2**) at 8.0 (middle) and Eu(**3**) at pH 8.0 (bottom) with 20 mM buffer and $I = 0.100$ M NaNO_3 and 1.00 mM Eu(III) complex.

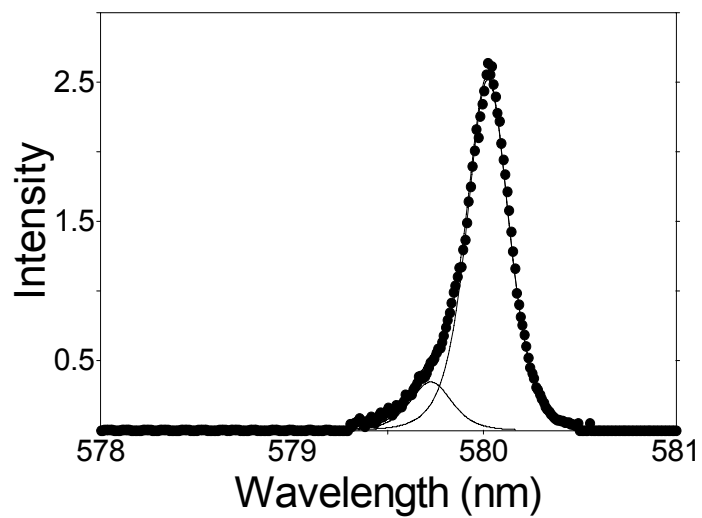


Figure S4. ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra (${}^5D_0 \rightarrow {}^7F_2$ emission) of Eu(**1**) incubated at pH 7.0, 20 mM Hepes, 1.00 mM complex for 2 weeks.

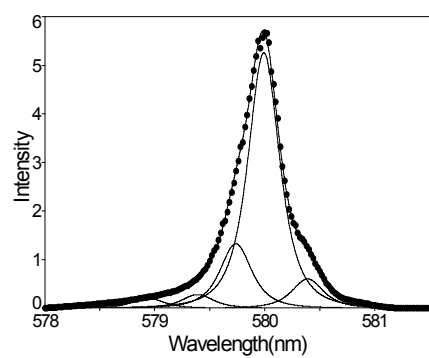
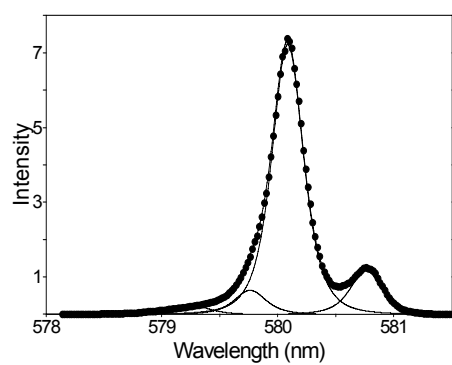
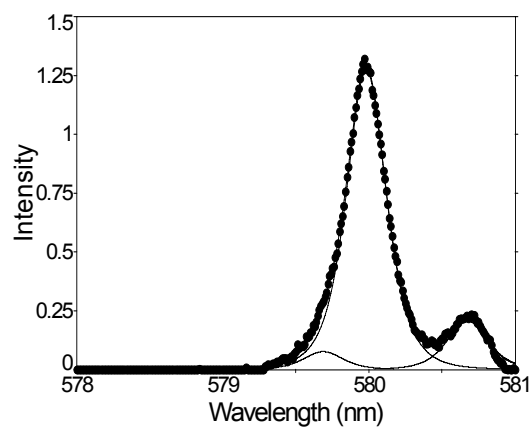


Figure S5 ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra (${}^5D_0 \rightarrow {}^7F_2$ emission) of Eu(II) complexes at pH 9.5 for Eu(1) (top), Eu(2) at pH 9.0 (middle) and Eu(3) at pH 9.0 (bottom) with 20 mM buffer and $I = 0.100$ M NaNO_3 and 1.00 mM Eu(III) complex.

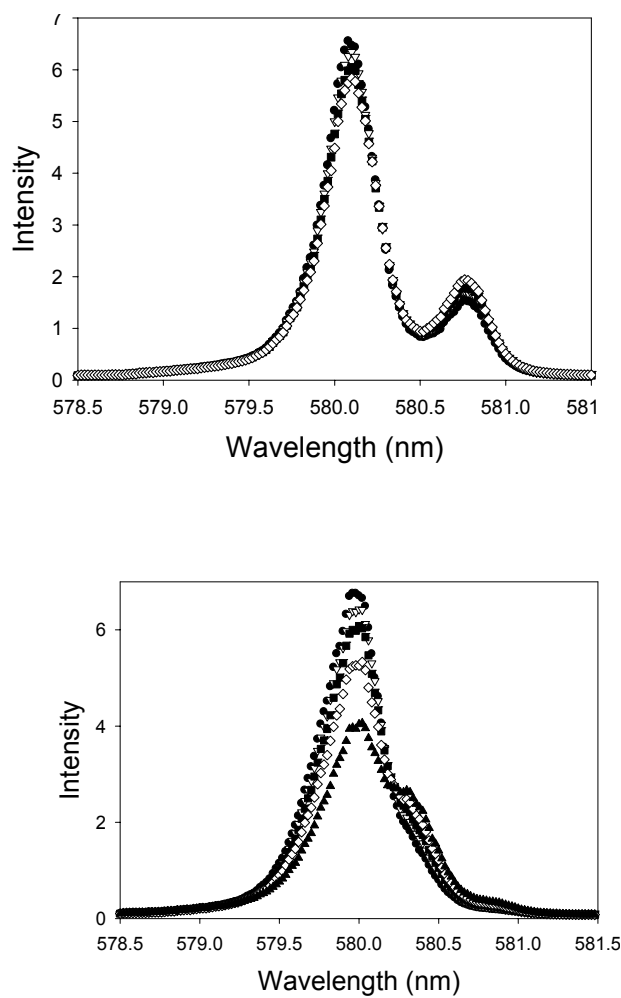


Figure S6 ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra (${}^5D_0 \rightarrow {}^7F_2$ emission) of 1.00 mM Eu(**1**) (●) at pH 9.5 titrated with ligand (**1**), 0.500 mM (▽), 1.00 mM (■), 2.00 mM (◇) (top); 1.00 mM Eu(**3**) (●) at pH 8.5 titrated with ligand (**3**), 0.500 mM, 1.00 mM (■), 2.00 mM (◇), 4.00 mM (▲) (bottom).

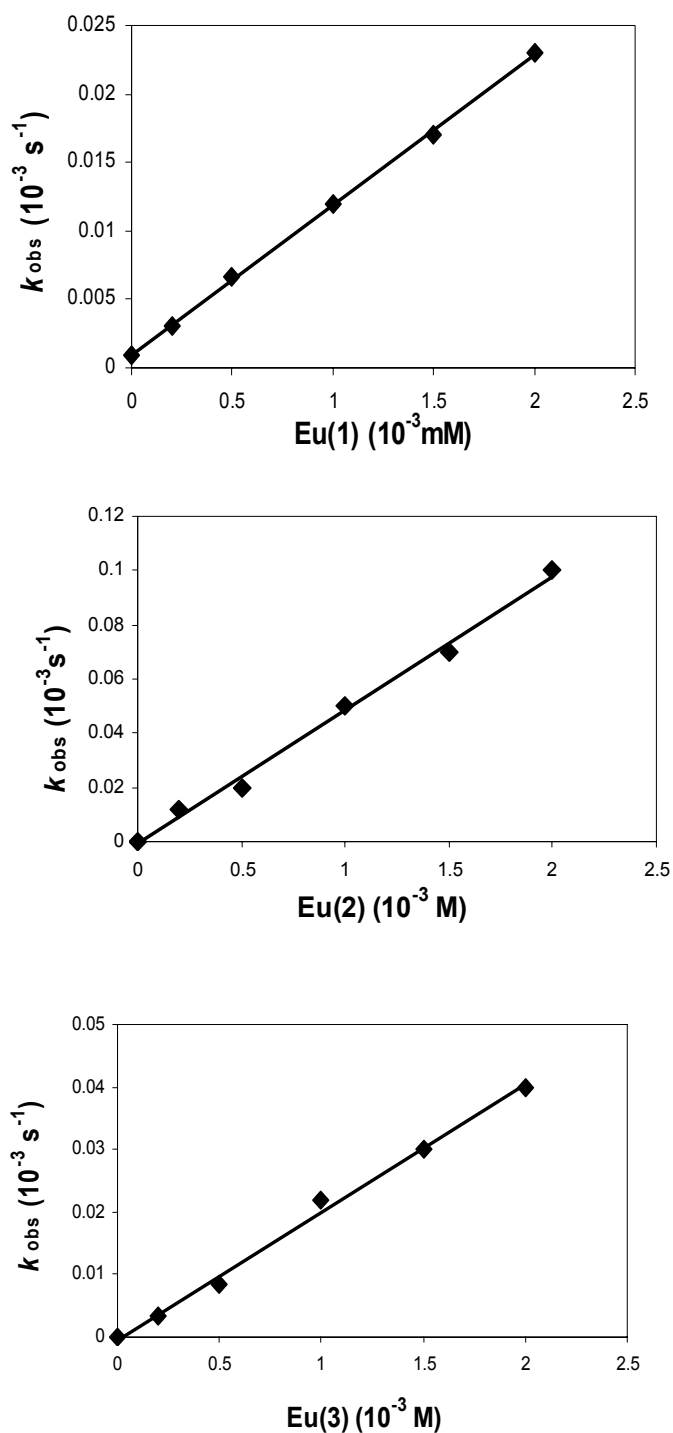


Fig. S7 Plot of first-order rate constant for the cleavage of **HpPNP** as a function of Eu(III) complex concentration for Eu(**1**) (top), Eu(**2**) (middle) and Eu(**3**) (bottom) at pH 7.0, $T = 25^\circ\text{C}$, buffer = 0.020 M, $I = 0.10 \text{ M NaNO}_3$

Table S1. Second-order rate constants (k_{Eu}) for the cleavage of **HpPNP** as a function of pH for the three Eu(III) complexes and a Eu(III) salt.

pH	Eu(1)	Eu(2)	Eu(3)	Eu(NO₃)₃
6	----	----	----	0.018
6.5	----	----	----	0.048
6.75	----	----	----	0.075
7.0	0.011	0.049	0.020	0.14
7.3	0.016	0.036	0.038	----
7.6	0.042	0.12	0.054	----
8.0	0.081	0.30	0.13	----
8.25	0.18	0.29	----	----
8.5	0.26	0.80	----	----
8.75	0.64	----	----	----
9.0	1.2	----	----	----

Second order rate constants ($k_2 \text{ M}^{-1}\text{s}^{-1}$). T = 25°C, buffer = 0.020 M, I = 0.10 M NaNO₃.