

The Basis for the Molecular Recognition and the Selective Time-Gated Luminescence Detection of ATP and GTP by a Lanthanide Complex

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SUPPORTING INFORMATION

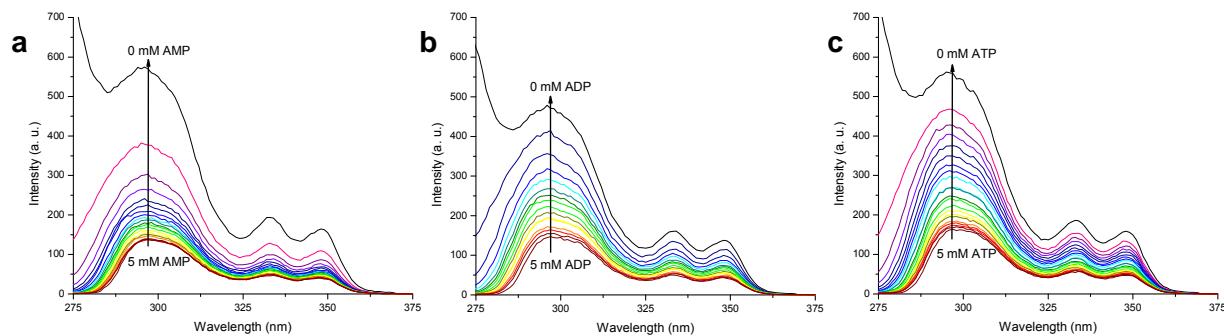


Figure S1. Time-delayed excitation spectra of a) Tb-DOTAm-Phen•AMP, b) Tb-DOTAm-Phen•ADP and c) Tb-DOTAm-Phen•ATP titrations. Experimental conditions: emission at 545 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

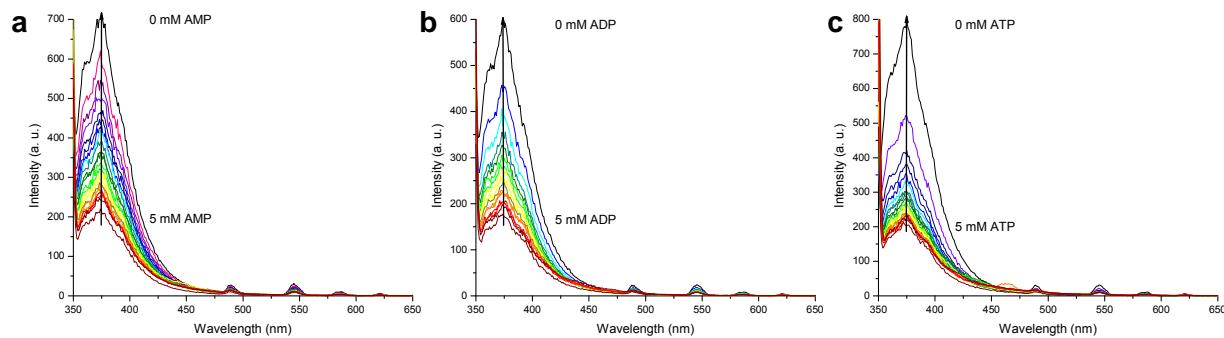


Figure S2. Fluorescence spectra of a) Tb-DOTAm-Phen•AMP, b) Tb-DOTAm-Phen•ADP and c) Tb-DOTAm-Phen•ATP titrations. Experimental conditions: excitation at 346 nm, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

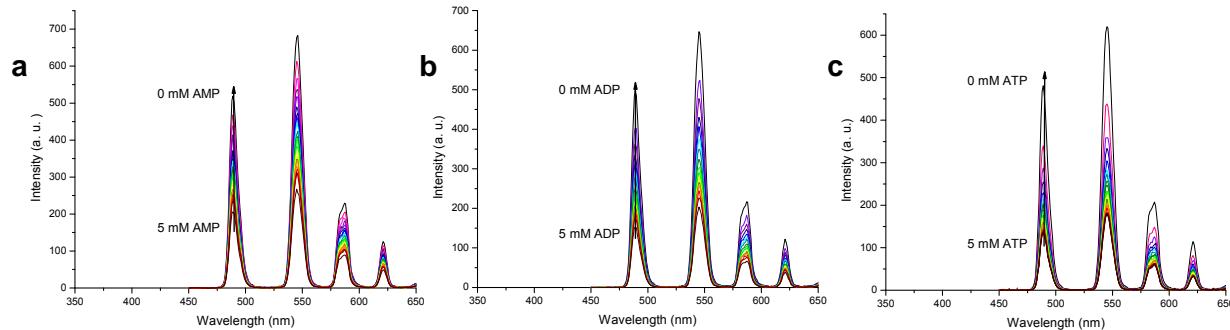


Figure S3. Time-delayed luminescence spectra of a) Tb-DOTAm-Phen•AMP, b) Tb-DOTAm-Phen•ADP and c) Tb-DOTAm-Phen•ATP titrations. Experimental conditions: excitation at 346 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

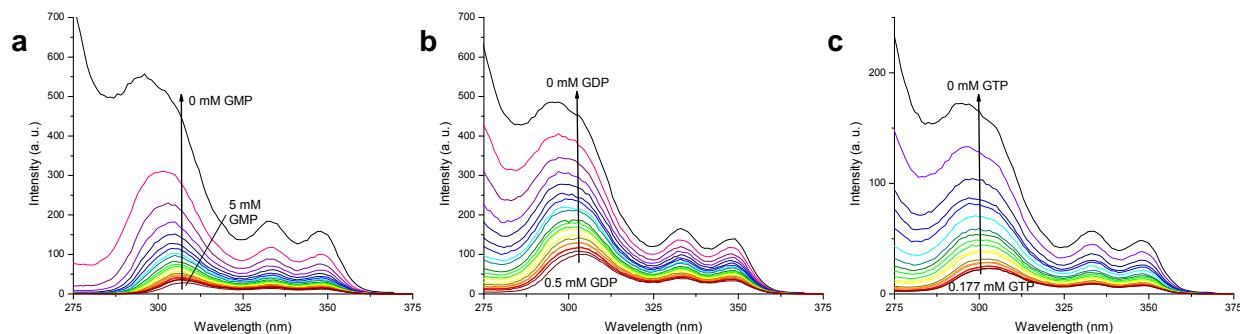


Figure S4. Time-delayed excitation spectra of a) Tb-DOTAm-Phen•GMP, b) Tb-DOTAm-Phen•GDP and c) Tb-DOTAm-Phen•GTP titrations. Experimental conditions: emission at 545 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

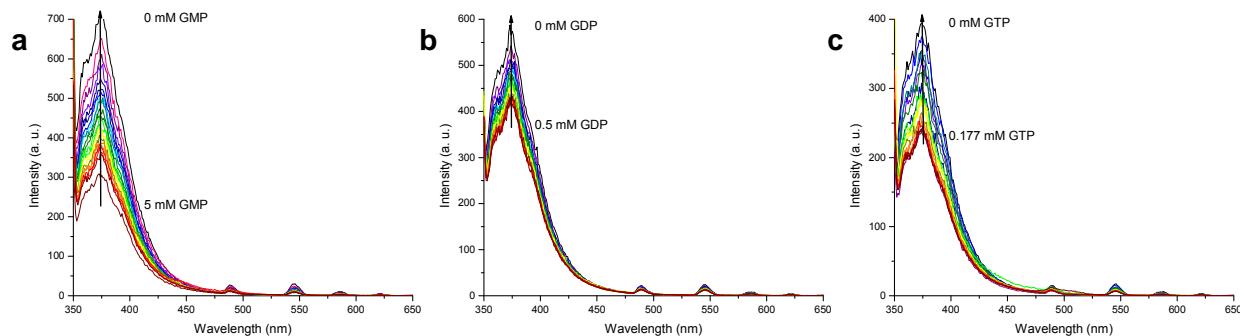


Figure S5. Fluorescence spectra of a) Tb-DOTAm-Phen•GMP, b) Tb-DOTAm-Phen•GDP and c) Tb-DOTAm-Phen•GTP titrations. Experimental conditions: excitation at 346 nm, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

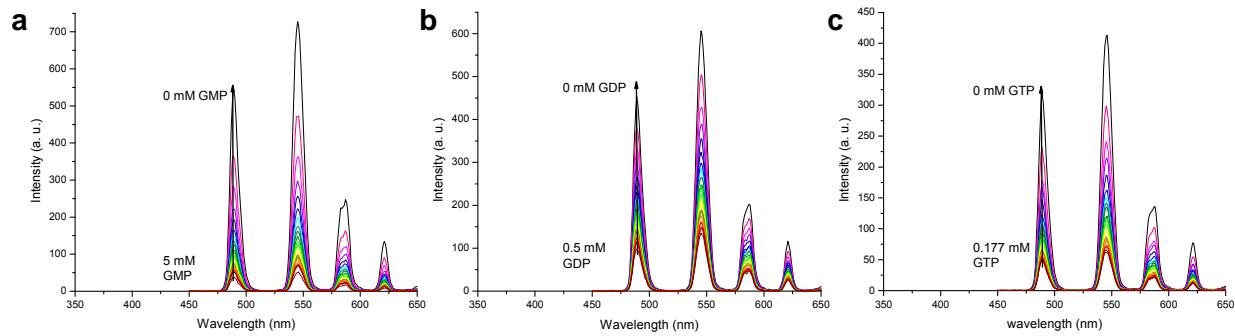


Figure S6. Time-delayed luminescence spectra of a) Tb-DOTAm-Phen•GMP, b) Tb-DOTAm-Phen•GDP and c) Tb-DOTAm-Phen•GTP titrations. Experimental conditions: excitation at 346 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

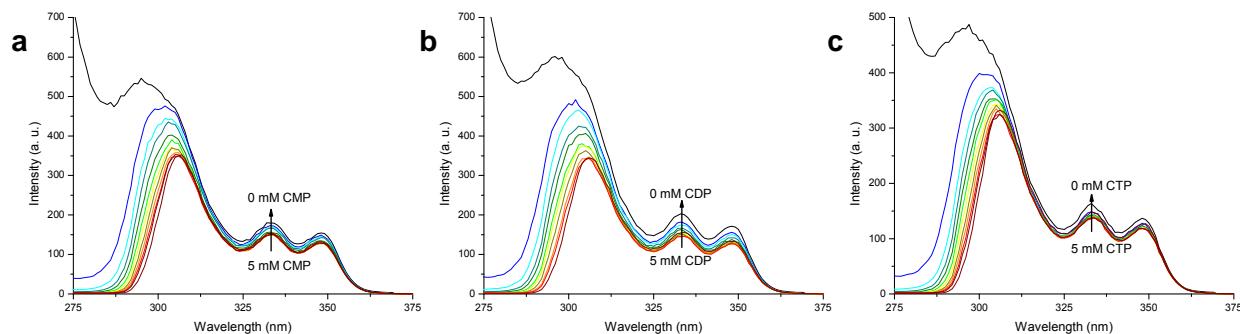


Figure S7. Time-delayed excitation spectra of a) Tb-DOTAm-Phen•CMP, b) Tb-DOTAm-Phen•CDP and c) Tb-DOTAm-Phen•CTP titrations. Experimental conditions: emission at 545 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

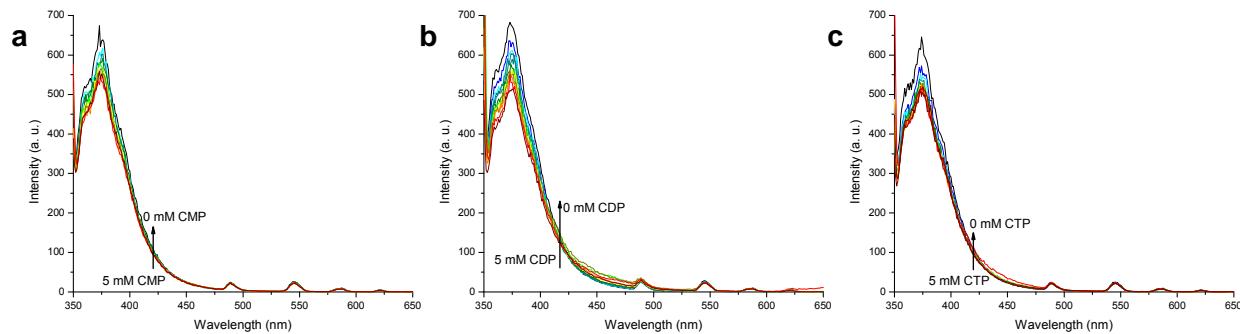


Figure S8. Fluorescence spectra of a) Tb-DOTAm-Phen•CMP, b) Tb-DOTAm-Phen•CDP and c) Tb-DOTAm-Phen•CTP titrations. Experimental conditions: excitation at 346 nm, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

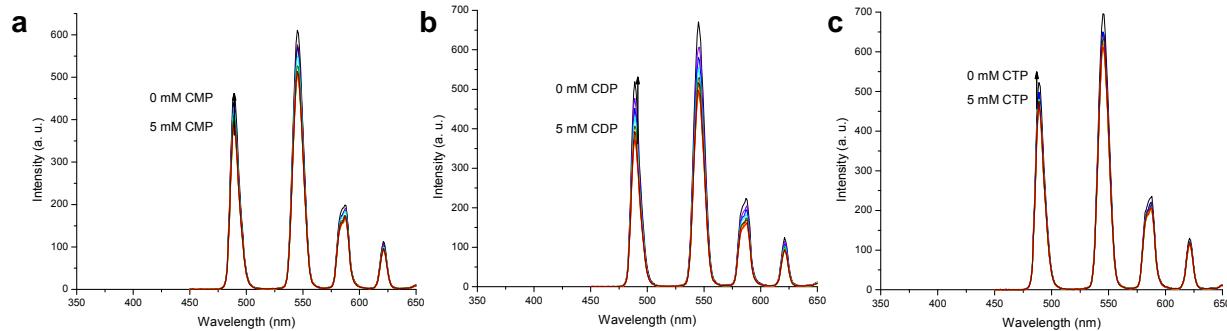


Figure S9. Time-delayed luminescence spectra of a) Tb-DOTAm-Phen•CMP, b) Tb-DOTAm-Phen•CDP and c) Tb-DOTAm-Phen•CTP titrations. Experimental conditions: excitation at 346 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

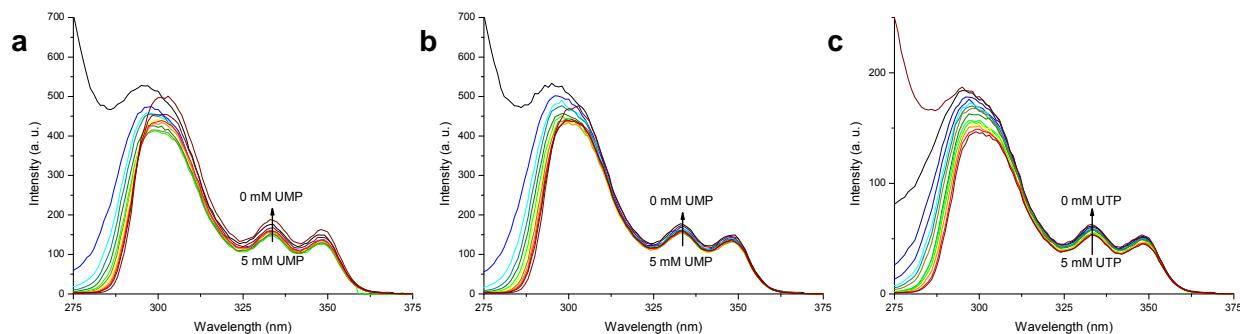


Figure S10. Time-delayed excitation spectra of a) Tb-DOTAm-Phen•UMP, b) Tb-DOTAm-Phen•UDP and c) Tb-DOTAm-Phen•UTP titrations. Experimental conditions: emission at 545 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

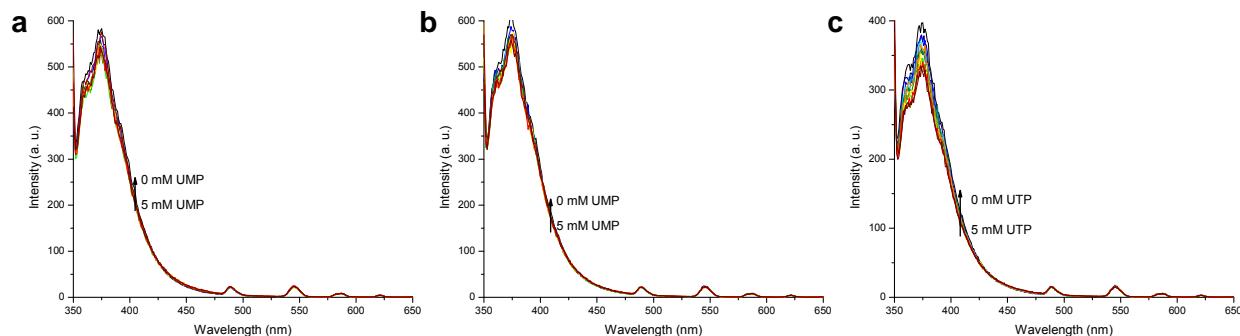


Figure S11. Fluorescence spectra of a) Tb-DOTAm-Phen•UMP, b) Tb-DOTAm-Phen•UDP and c) Tb-DOTAm-Phen•UTP titrations. Experimental conditions: excitation at 346 nm, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

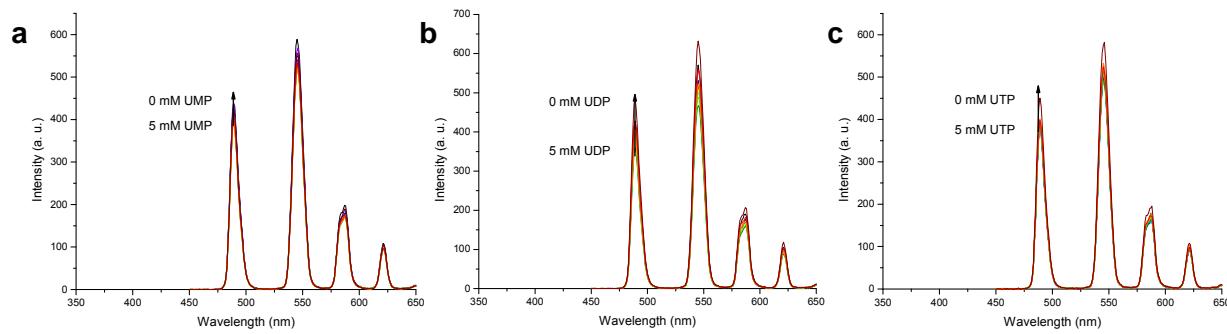


Figure S12. Time-delayed luminescence spectra of a) Tb-DOTAm-Phen•UMP, b) Tb-DOTAm-Phen•UDP and c) Tb-DOTAm-Phen•UTP titrations. Experimental conditions: excitation at 346 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Tb-DOTAm-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

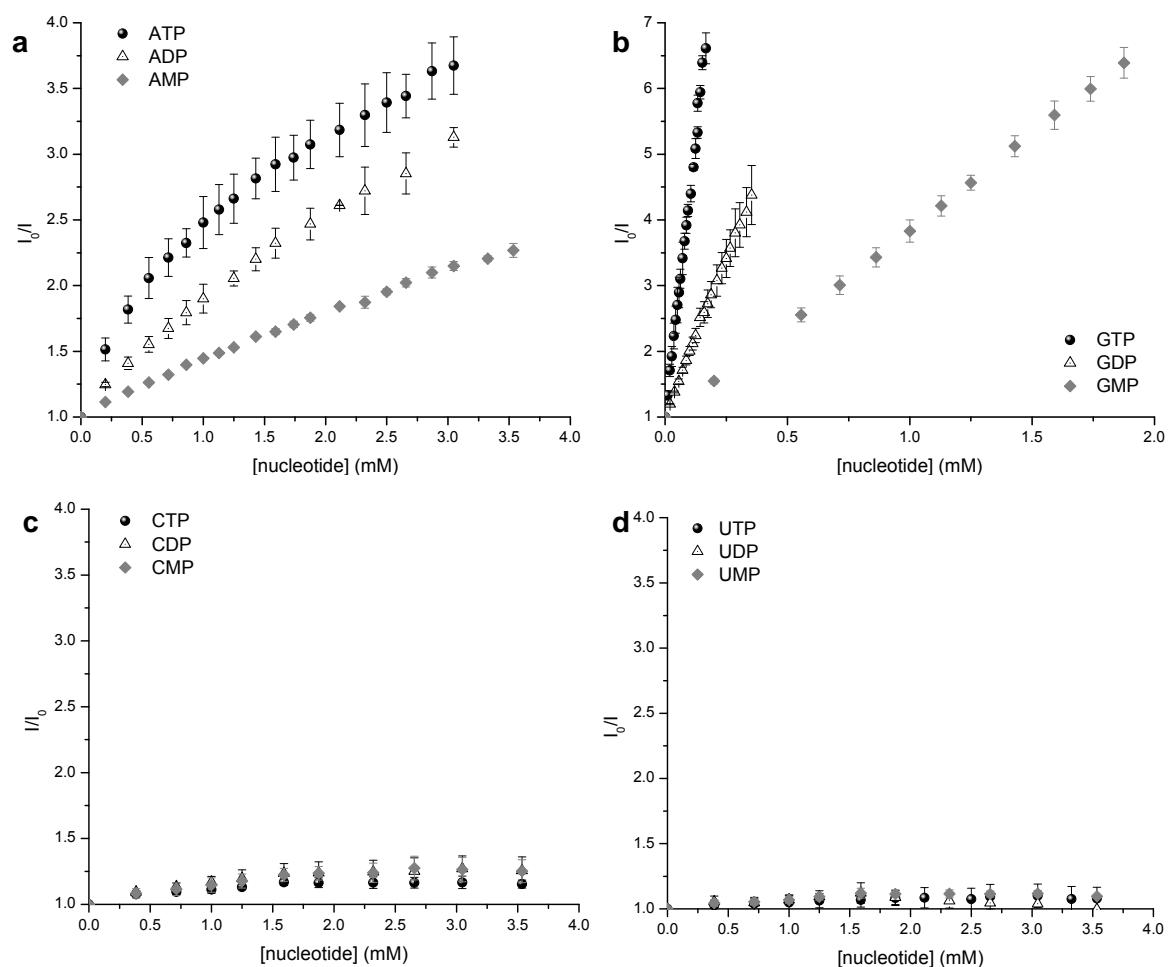


Figure S13. Stern-Volmer plot of the time-delayed luminescence quenching of Tb-DOTAm-Phen by a) adenosine, b) guanosine, c) cytosine and d) uridine nucleotides. Experimental conditions: excitation at 346 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, $[Tb\text{-DOTAm-Phen}] = 10 \mu\text{M}$, water, $[\text{Tris}] = 10 \text{ mM}$, pH 7.0, $T = 20^\circ\text{C}$.

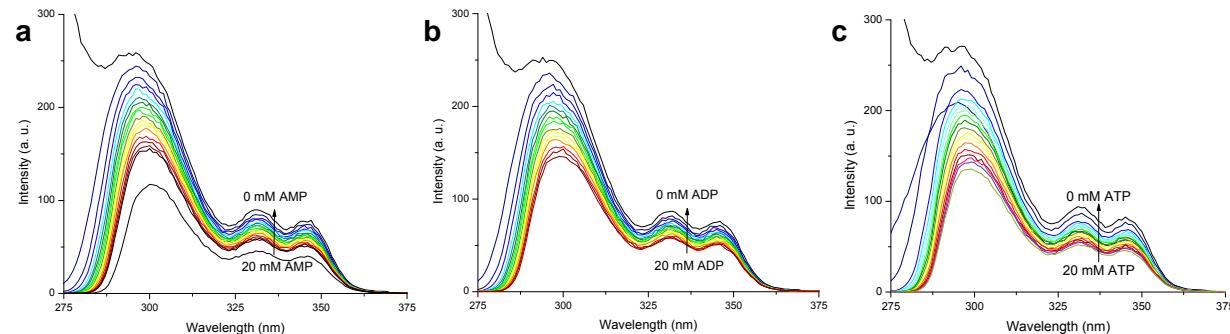


Figure S14. Time-delayed excitation spectra of a) Eu-DOTA-Phen•AMP, b) Eu-DOTA-Phen•ADP and c) Eu-DOTA-Phen•ATP titrations. Experimental conditions: emission at 545 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

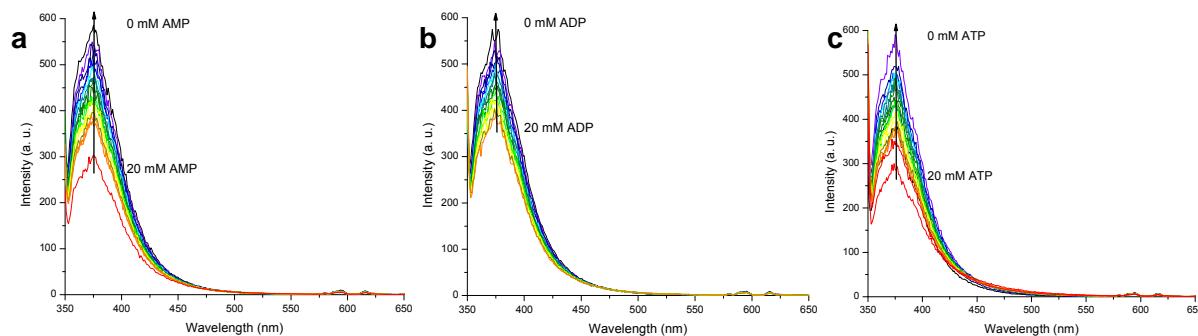


Figure S15. Fluorescence spectra of a) Eu-DOTA-Phen•AMP, b) Eu-DOTA-Phen•ADP and c) Eu-DOTA-Phen•ATP titrations. Experimental conditions: excitation at 346 nm, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

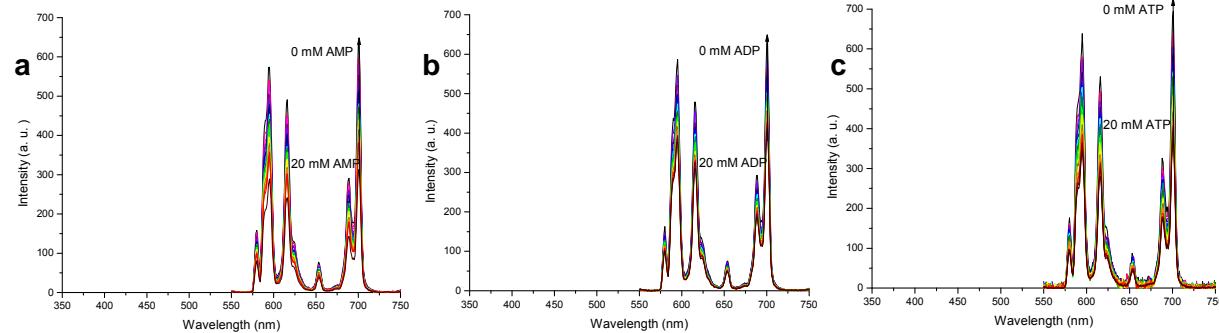


Figure S16. Time-delayed luminescence spectra of a) Eu-DOTA-Phen•AMP, b) Eu-DOTA-Phen•ADP and c) Eu-DOTA-Phen•ATP titrations. Experimental conditions: excitation at 346 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

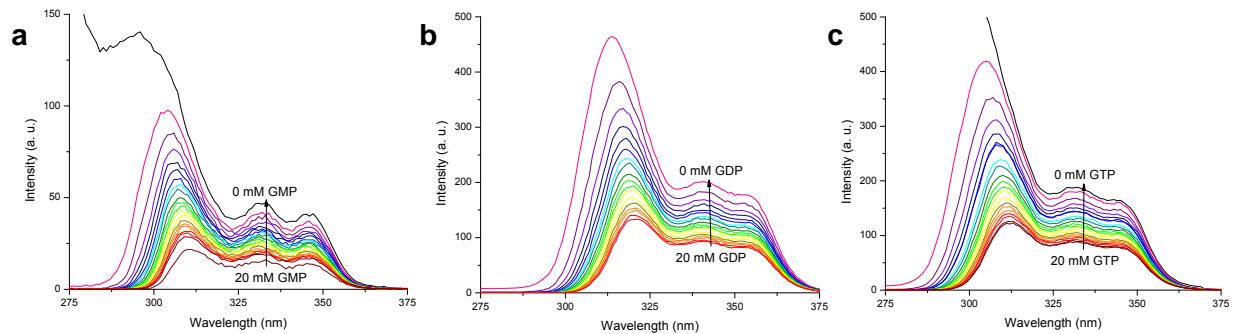


Figure S17. Time-delayed excitation spectra of a) Eu-DOTA-Phen•GMP, b) Eu-DOTA-Phen•GDP and c) Eu-DOTA-Phen•GTP titrations. Experimental conditions: emission at 545 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

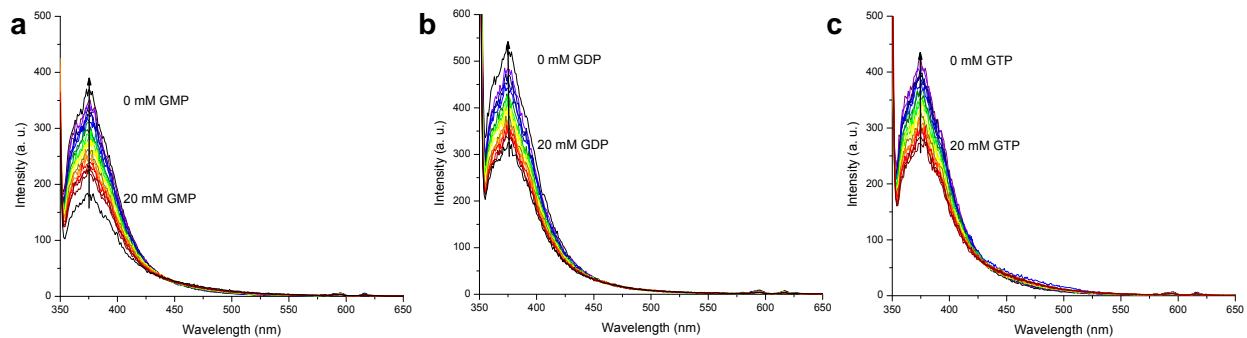


Figure S18. Fluorescence spectra of a) Eu-DOTA-Phen•GMP, b) Eu-DOTA-Phen•GDP and c) Eu-DOTA-Phen•GTP titrations. Experimental conditions: excitation at 346 nm, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

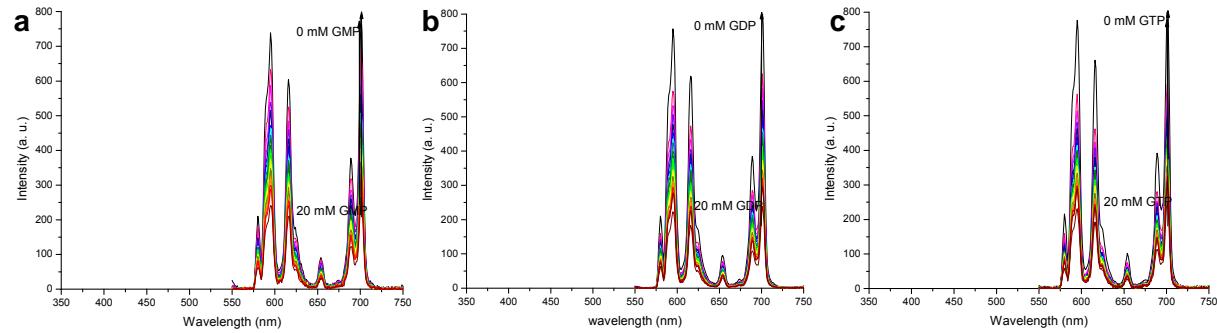


Figure S19. Time-delayed luminescence spectra of a) Eu-DOTA-Phen•GMP, b) Eu-DOTA-Phen•GDP and c) Eu-DOTA-Phen•GTP titrations. Experimental conditions: excitation at 346 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

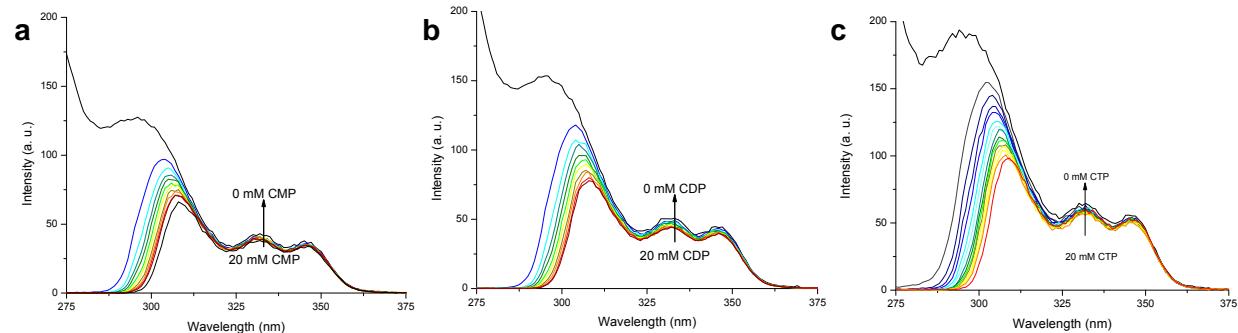


Figure S20. Time-delayed excitation spectra of a) Eu-DOTA-Phen•CMP, b) Eu-DOTA-Phen•CDP and c) Eu-DOTA-Phen•CTP titrations. Experimental conditions: emission at 545 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

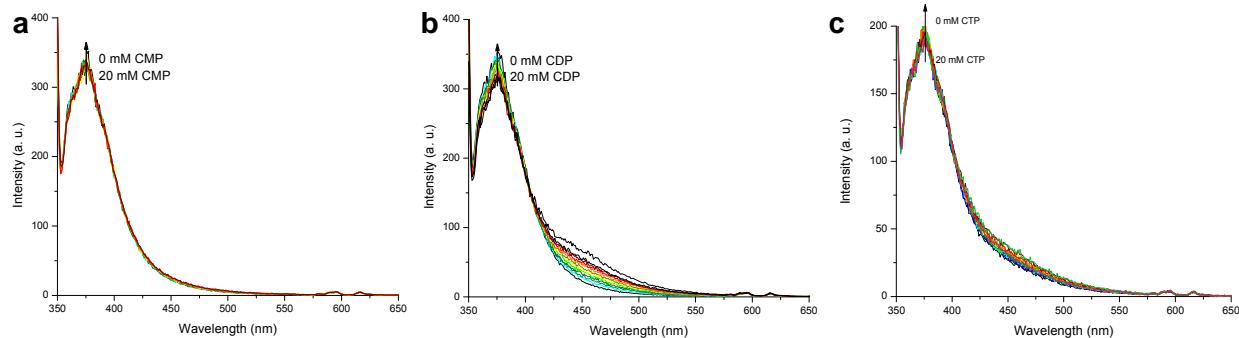


Figure S21. Fluorescence spectra of a) Eu-DOTA-Phen•CMP, b) Eu-DOTA-Phen•CDP and c) Eu-DOTA-Phen•CTP titrations. Experimental conditions: excitation at 346 nm, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

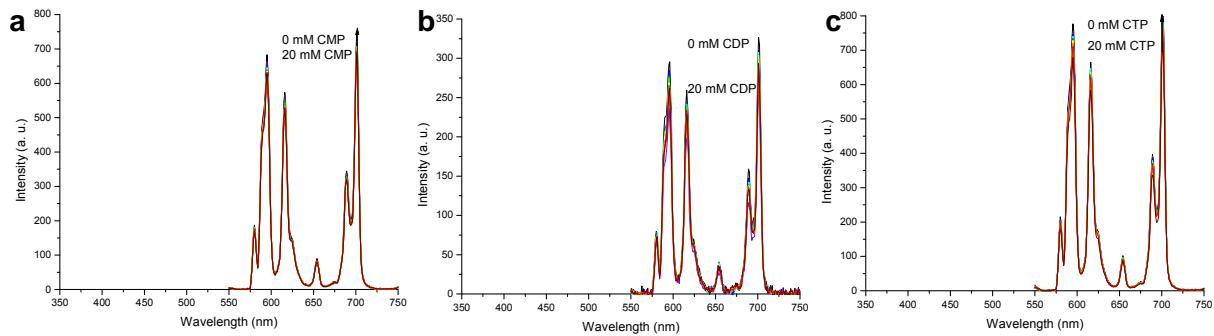


Figure S22. Time-delayed luminescence spectra of a) Eu-DOTA-Phen•CMP, b) Eu-DOTA-Phen•CDP and c) Eu-DOTA-Phen•CTP titrations. Experimental conditions: excitation at 346 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

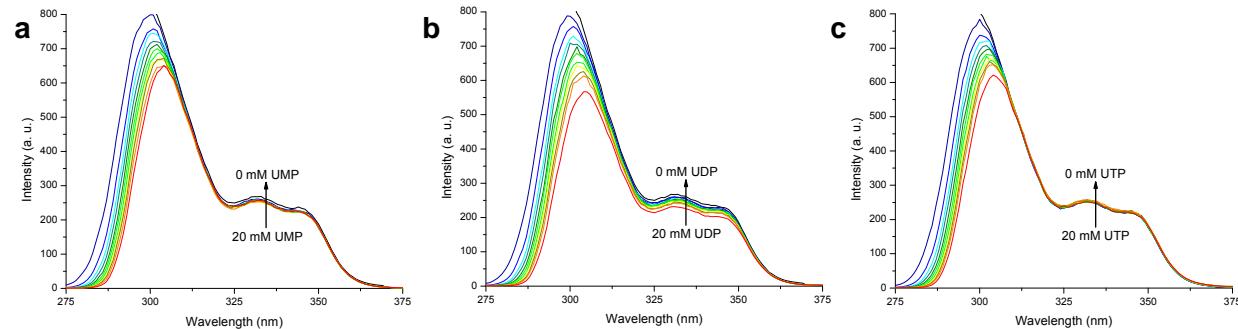


Figure S23. Time-delayed excitation spectra of a) Eu-DOTA-Phen•UMP, b) Eu-DOTA-Phen•UDP and c) Eu-DOTA-Phen•UTP titrations. Experimental conditions: emission at 545 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

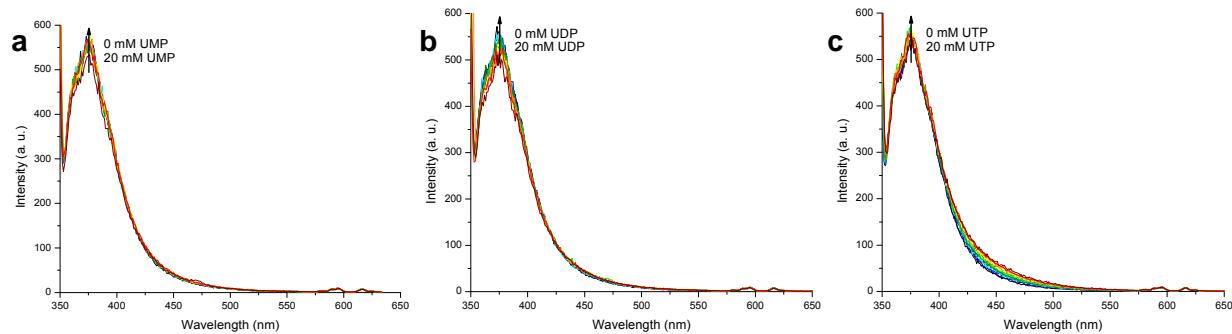


Figure S24. Fluorescence spectra of a) Eu-DOTA-Phen•UMP, b) Eu-DOTA-Phen•UDP and c) Eu-DOTA-Phen•UTP titrations. Experimental conditions: excitation at 346 nm, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

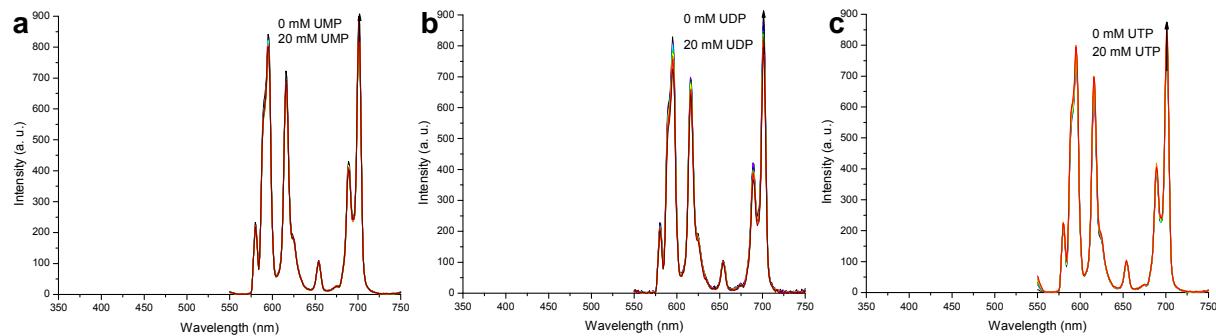


Figure S25. Time-delayed luminescence spectra of a) Eu-DOTA-Phen•UMP, b) Eu-DOTA-Phen•UDP and c) Eu-DOTA-Phen•UTP titrations. Experimental conditions: excitation at 346 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, [Eu-DOTA-Phen] = 10 μ M, water, [Tris] = 10 mM, pH 7.0, T = 20 °C.

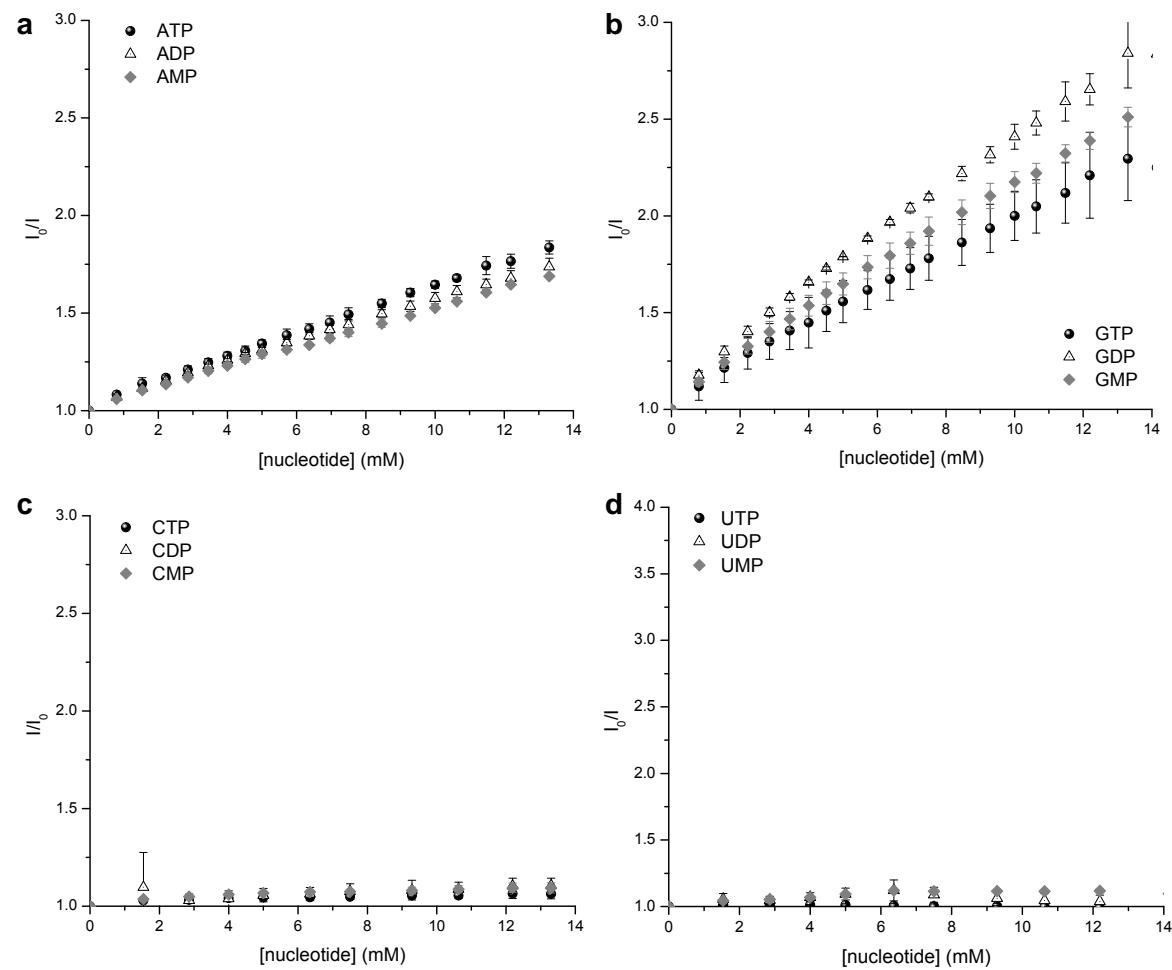


Figure S26. Stern-Volmer plot of the time-delayed luminescence quenching of Eu-DOTA-Phen by a) adenosine, b) guanosine, c) cytosine and d) uridine nucleotides. Experimental conditions: excitation at 346 nm, time-delay 0.1 ms, emission slit width = 5 nm, excitation slit width = 5 nm, $[\text{Eu-DOTA-Phen}] = 10 \mu\text{M}$, water, $[\text{Tris}] = 10 \text{ mM}$, pH 7.0, $T = 20^\circ\text{C}$.

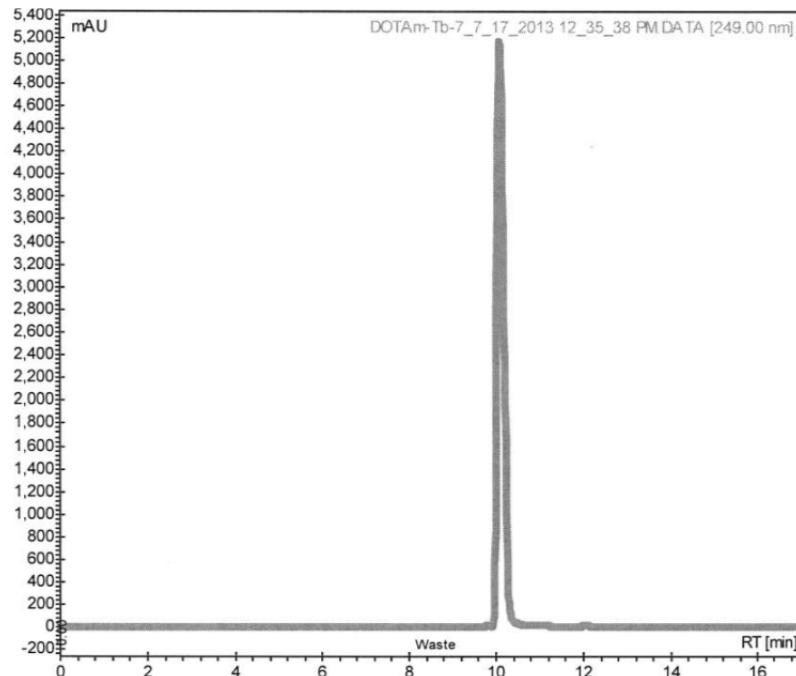


Figure S27. HPLC trace of Tb-DOTAm-Phen. Experimental conditions: Varian Microsorb 300-5 C18 250 mm x 4.6 mm column, 1.0 mL/min flow rate, solvent gradient: 100% 0.1% TFA (aq) to 40% 0.1% TFA (aq)/60% CH₃CN in 10 min, to 100% CH₃CN in 13 min.

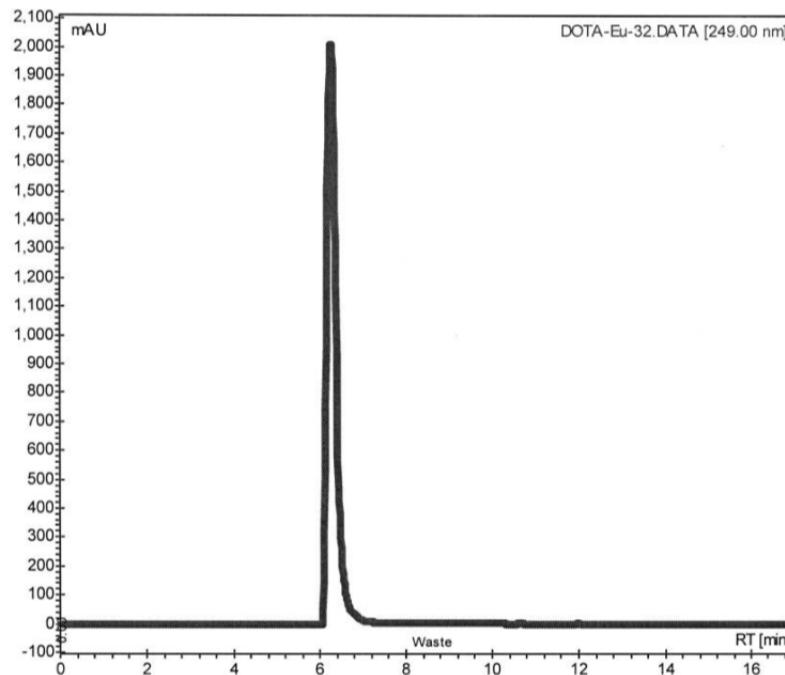


Figure S28. HPLC trace of Eu-DOTA-Phen. Experimental conditions: Varian Microsorb 300-5 C18 250 mm x 4.6 mm column, 1.0 mL/min flow rate, solvent gradient: 95% mQ water/5% CH₃CN to 40% mQ water/60% CH₃CN in 10 min, to 100% CH₃CN in 13 min.