Lanthanide luminescent switches: Modulation of the luminescence of bis-macrocyclic based Tb(III) conjugates in water by H^+, Na^+ and K^+

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Figure 1. Absorption pH titration of 14.

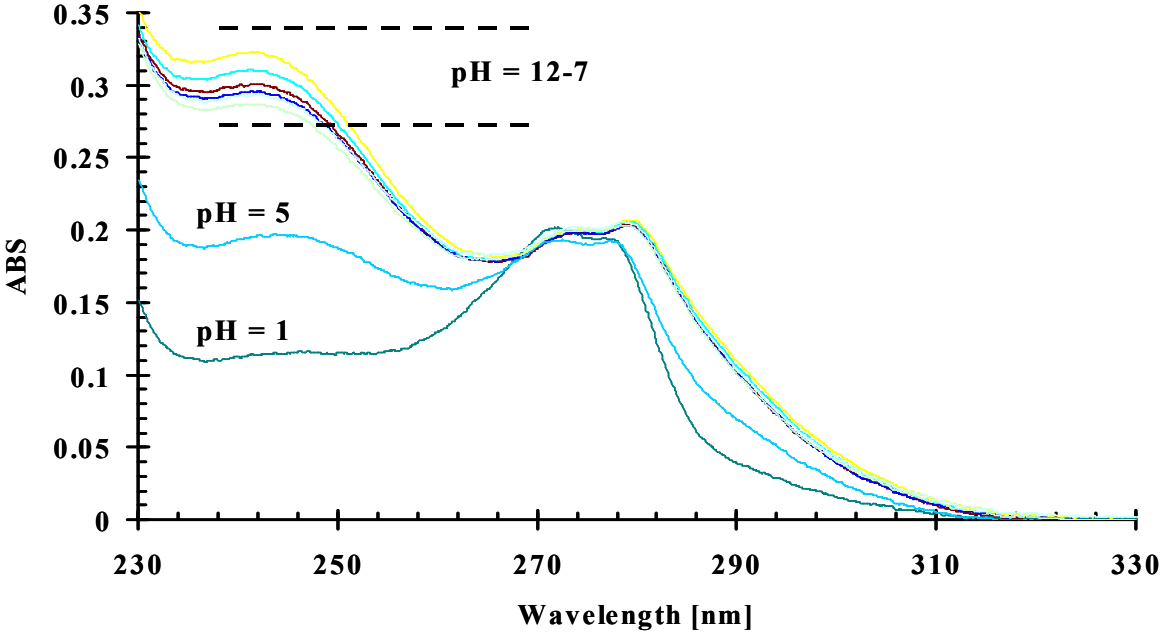


Figure 2. Absorption pH vs. Intensity profile of 14.

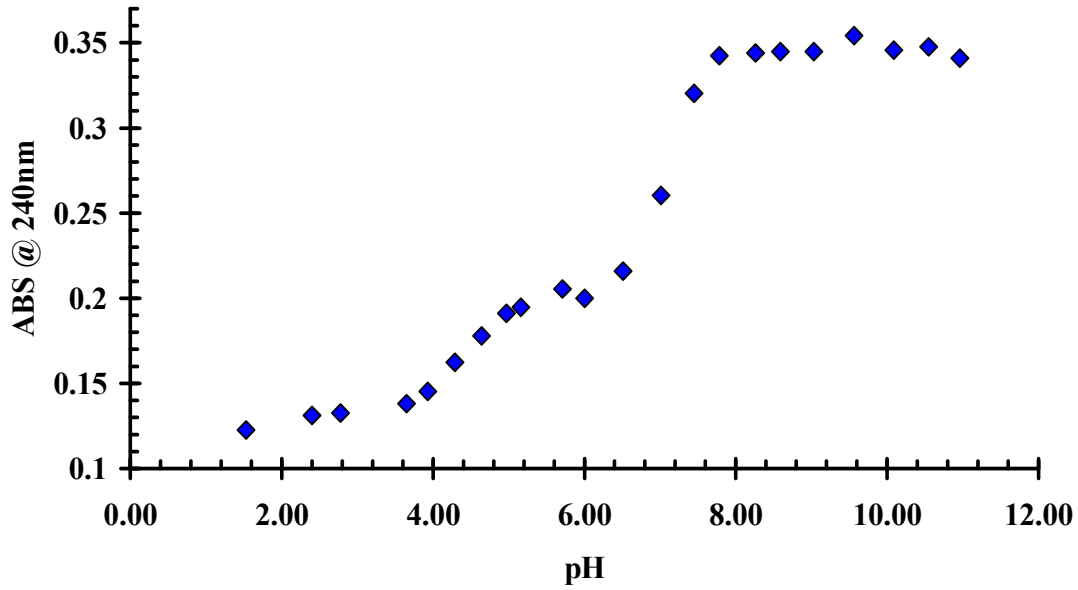


Figure 3. Absorption Potassium titration of 14.

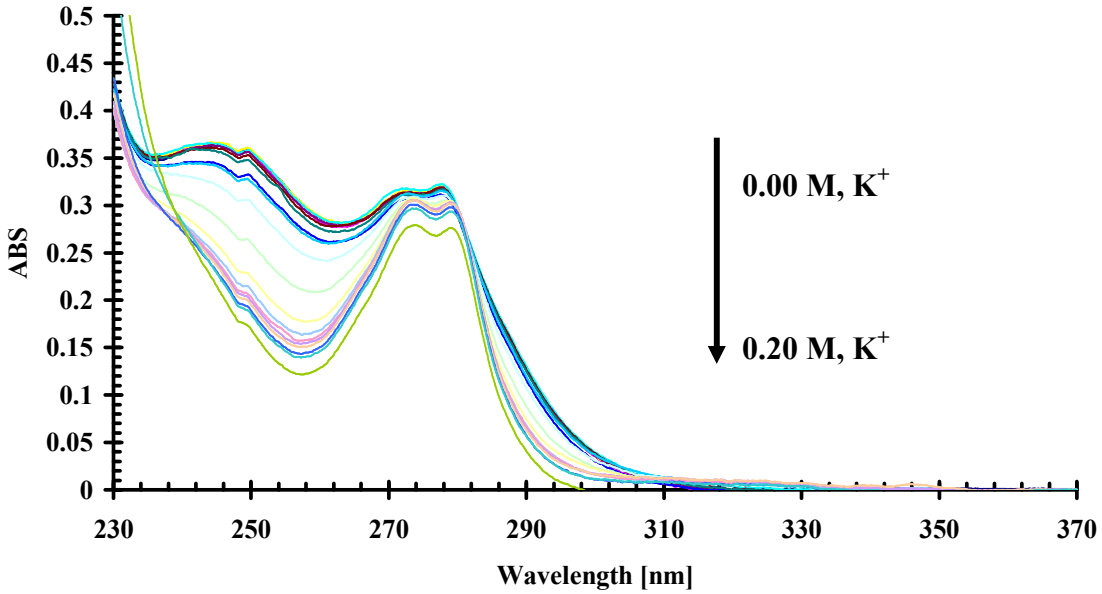


Figure 4. Absorption pK vs. Intensity profile of 14.

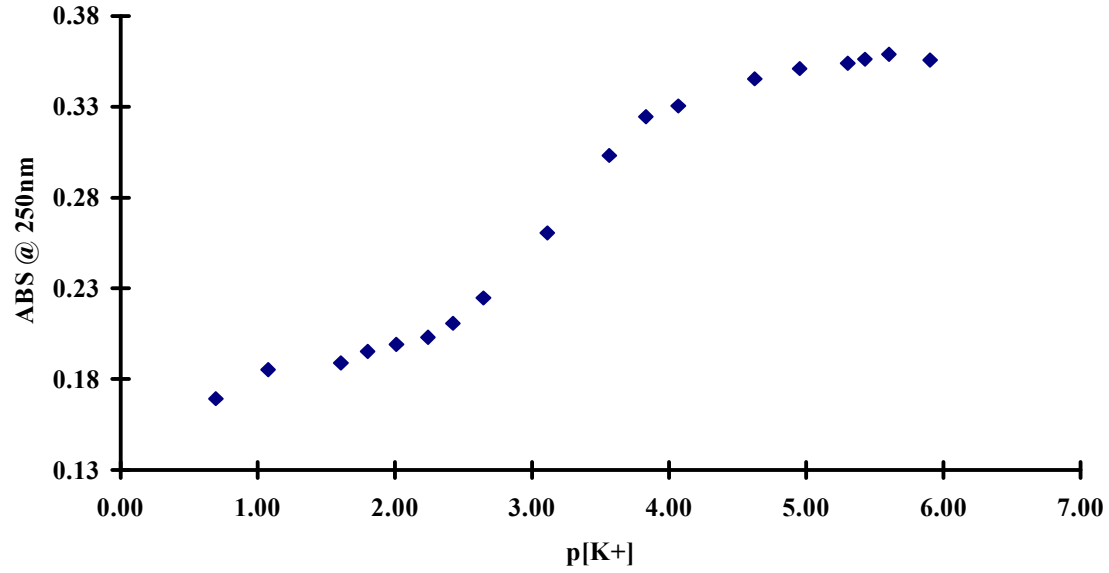


Figure 5. Ground state pH profile of Tb.2

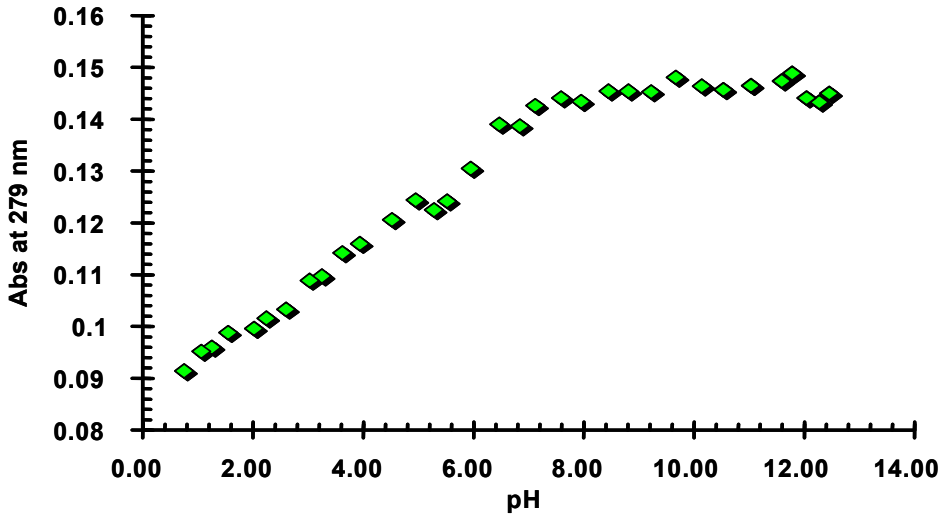


Figure 6. Ground state pH profile of Tb.3

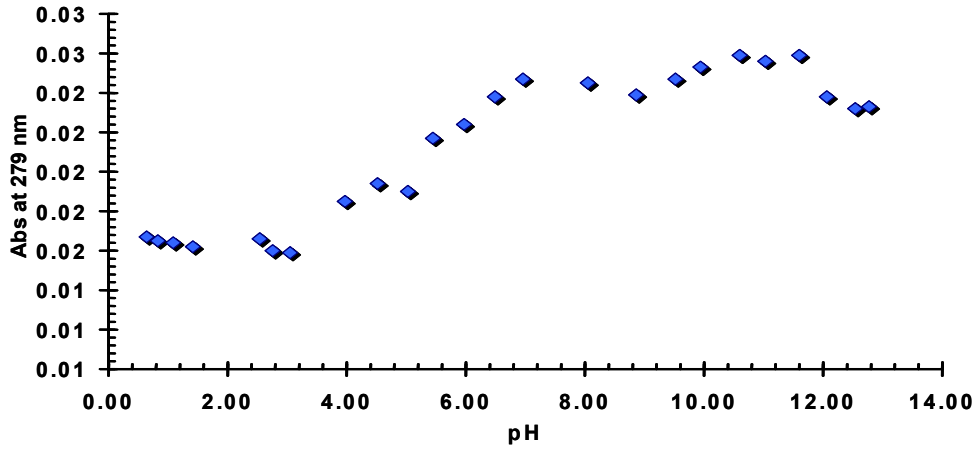


Figure 7. Ground state pH profile of Tb.4

Figure 8. Singlet Excited State pH profile of Tb.2

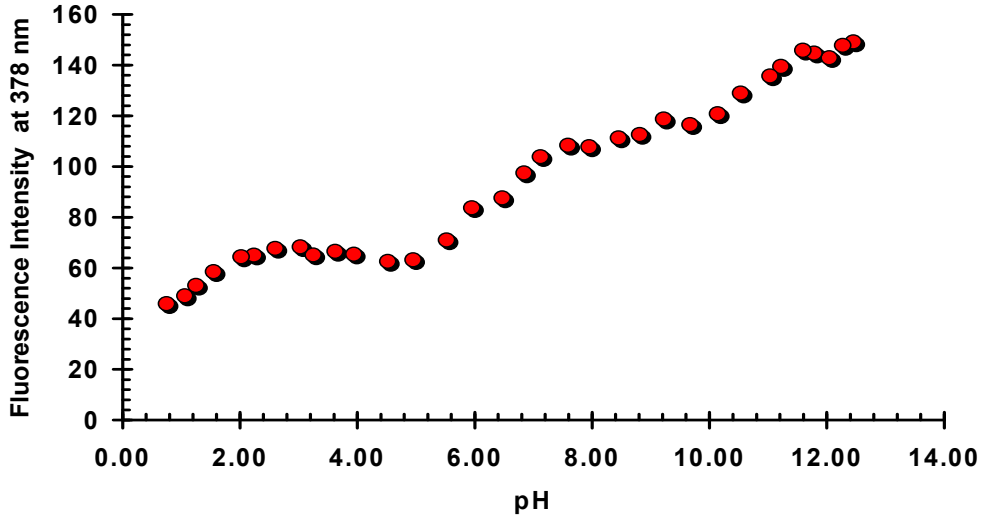


Figure 9. Singlet Excited State pH profile of Tb.3

Figure 10. Singlet Excited State pH profile of Tb.4

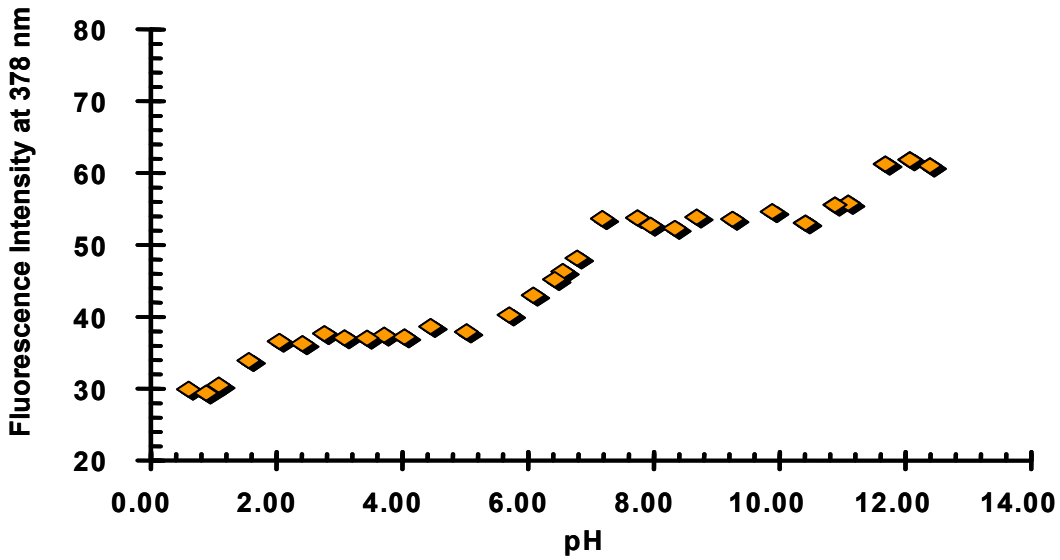


Figure 11. Singlet Excited State pK Titration of Tb.2

Figure 12. Singlet Excited State pNa Titration of Tb.3

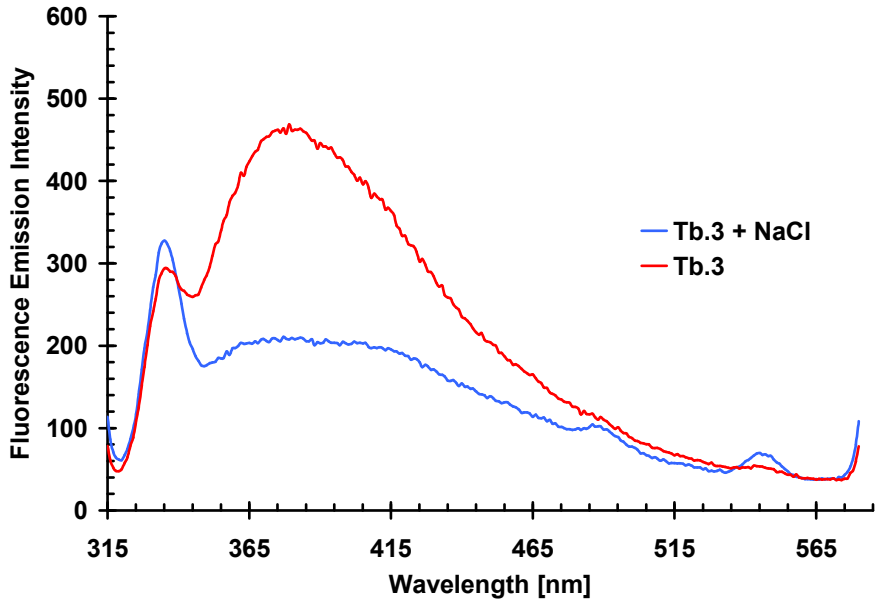


Figure 13. Singlet Excited State pK Titration of Tb.4

Figure 14. Singlet Excited State pNa Titration of Eu.1

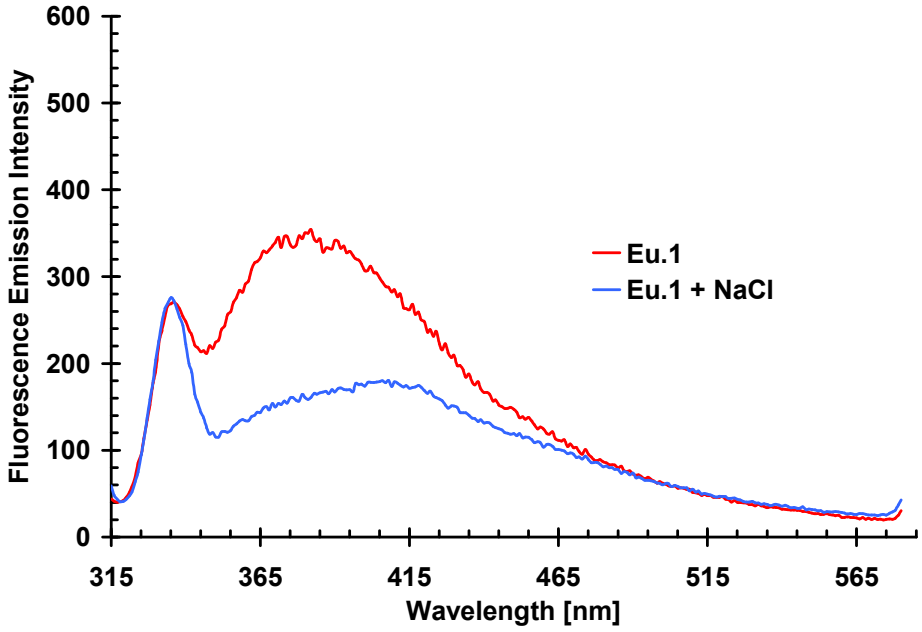
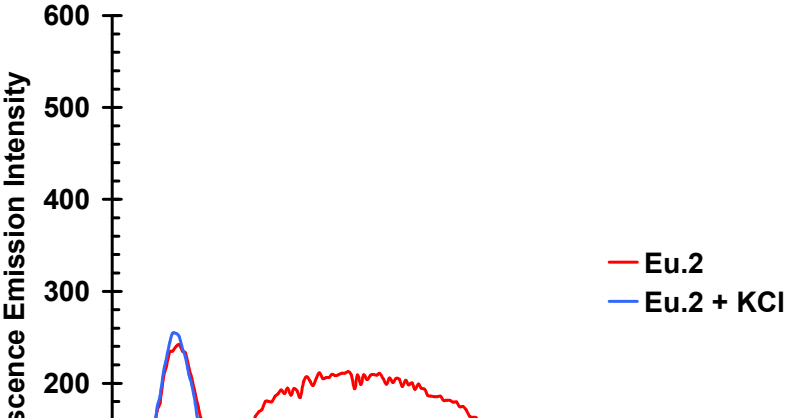


Figure 15. Singlet Excited State pK Titration of Eu.2



Lanthanide luminescence temperature investigations

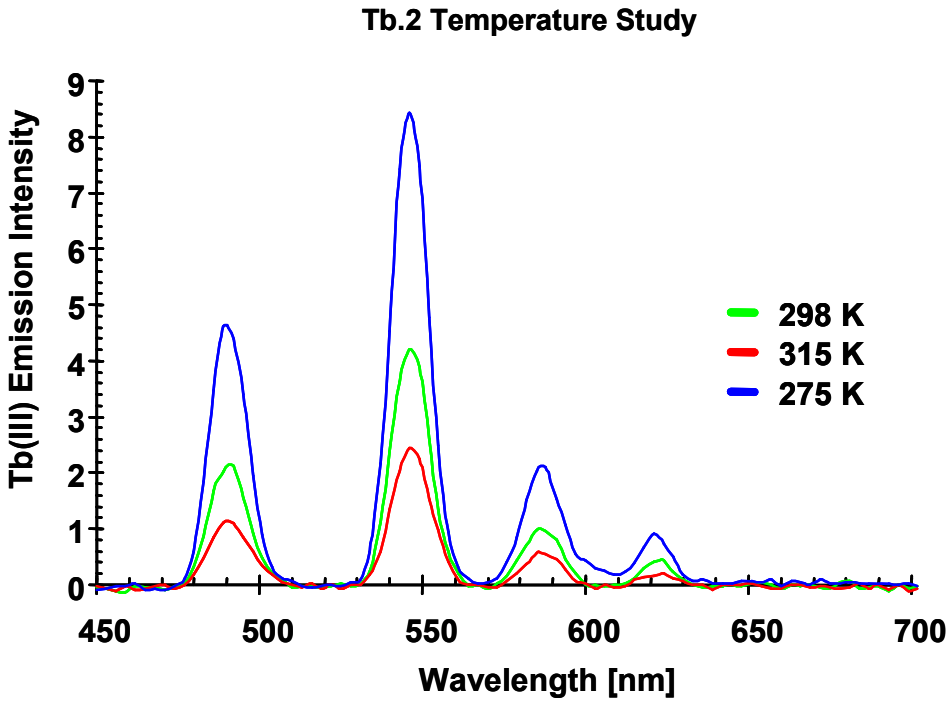
Ln(III) Luminescence studies were carried out on solutions of **Tb.2** .

The results shown were collected on a Varian Carey Eclipse Fluorescence Spectrophotometer with settings as detailed below:

Solutions were titrated using Chloride salts.

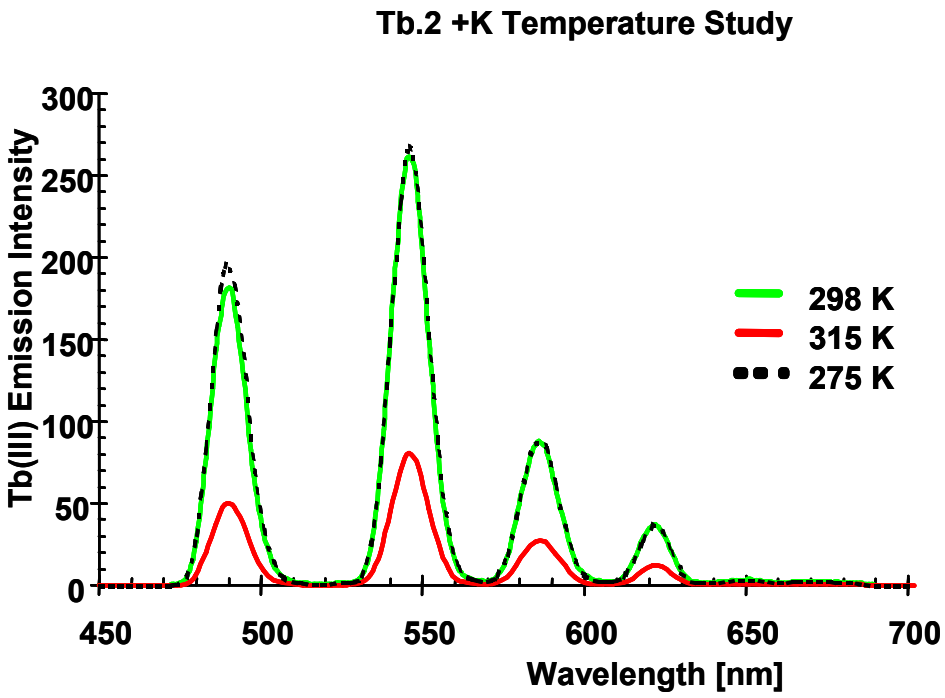
Temperature studies were carried out using a MGW Lauda C6 water bath.

Figure 16. Lanthanide Luminescent Temperature study of Tb.2



16 was a sample of the free sensor, **Tb.2**. (**Note:**Low intensity of the emission observed) As the temperature was decreased from 315K (42°C), then to 298K (25°C) and finally to 275K (2°C) an increase in the luminescent intensity of the Tb(III) emission was observed. Each change in temperature resulted in a two-fold increase in the emission intensity observed.

Figure 17. Lanthanide Luminescent Temperature study of Tb.2+K^+



17 was a sample of the K+ bound sensor, **Tb.2**. (**Note:**High intensity of the emission observed) As the temperature was decreased from 315K (42°C), then to 298K (25°C) and finally to 275K (2°C) an increase in the luminescent intensity of the Tb(III) emission was observed. The intensity increase at 298K and 275K were identical and represent a three-fold increase in the emission intensity observed.

Figure 18. Lanthanide Luminescent Degassing study of Tb.2

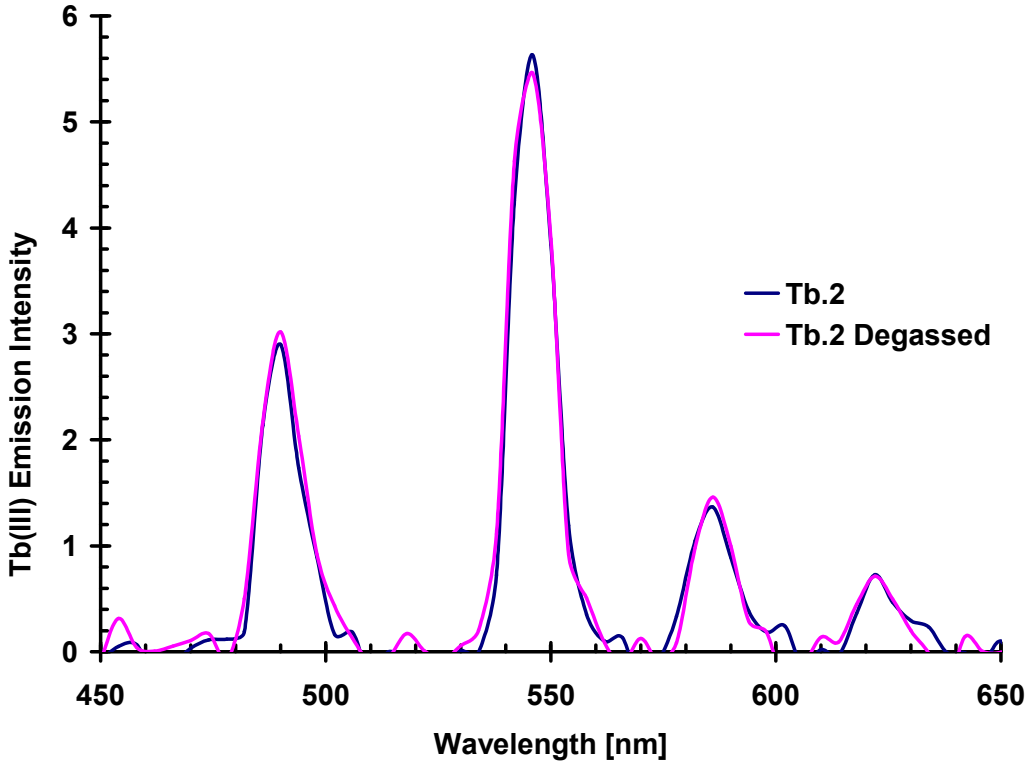


Figure 19. Lanthanide Luminescent Degassing study of Tb.2 + K^+

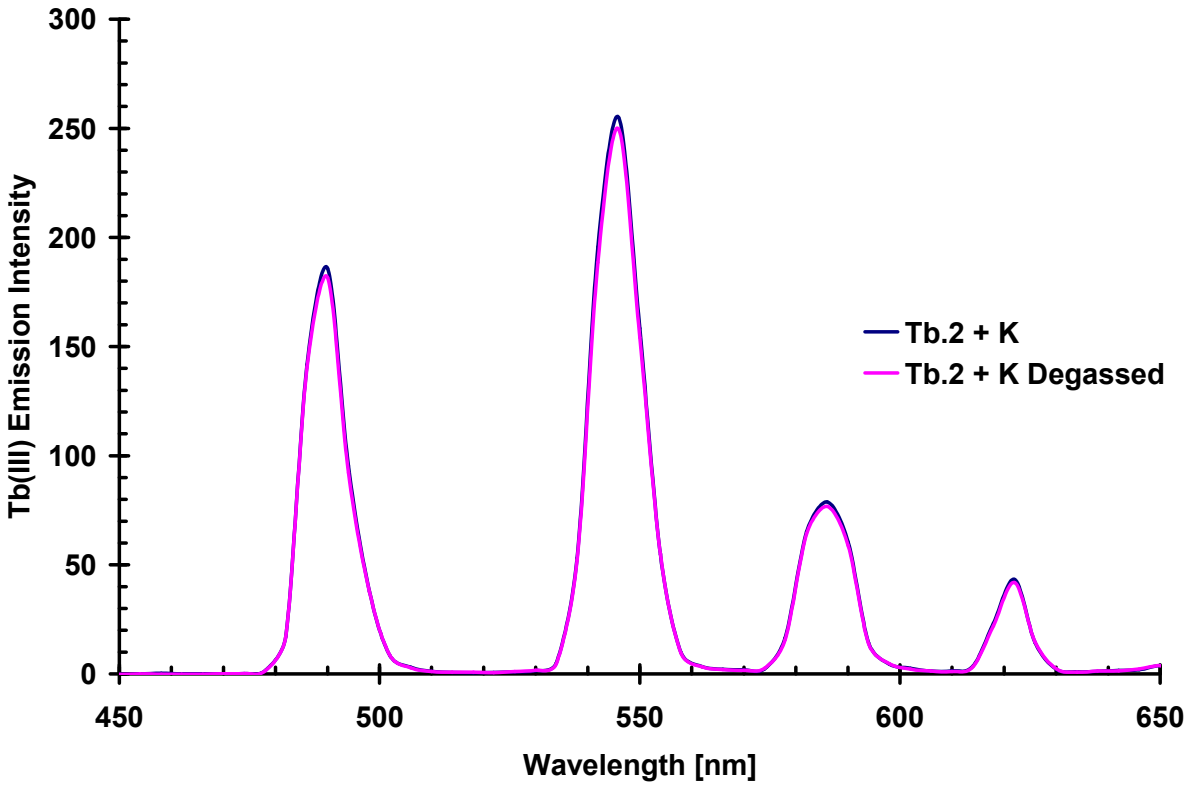


Figure 20. The changes in the Tb(III) emission of Tb.3 as a function of pM, where M = Na^+, K^+ and Li^+.

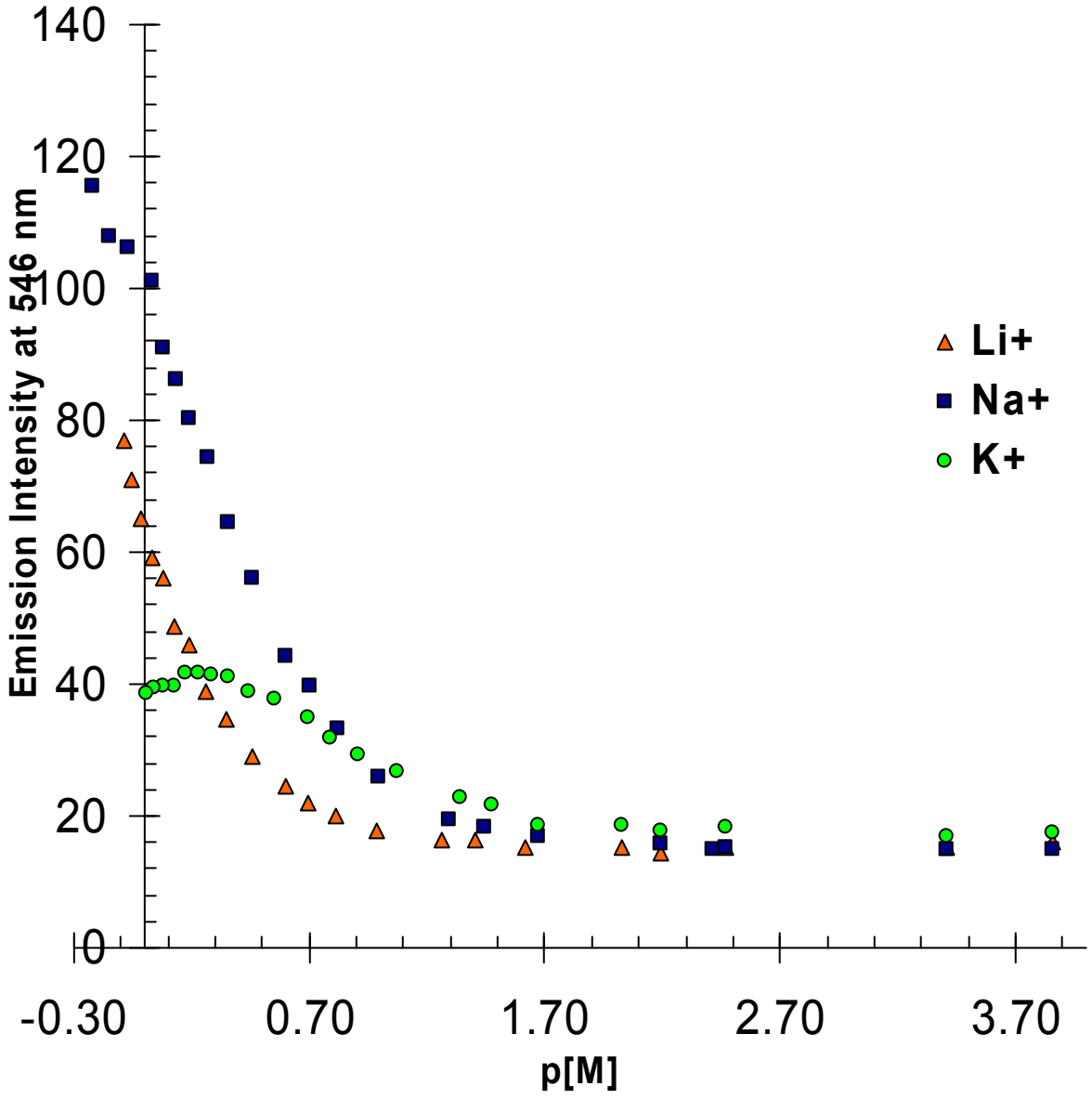


Figure 21. The changes in the Tb(III) emission of Tb.4 as a function of pM, where M = Na^+, K^+ , Ca^{2+}, Mg^{2+}, and Li^+.

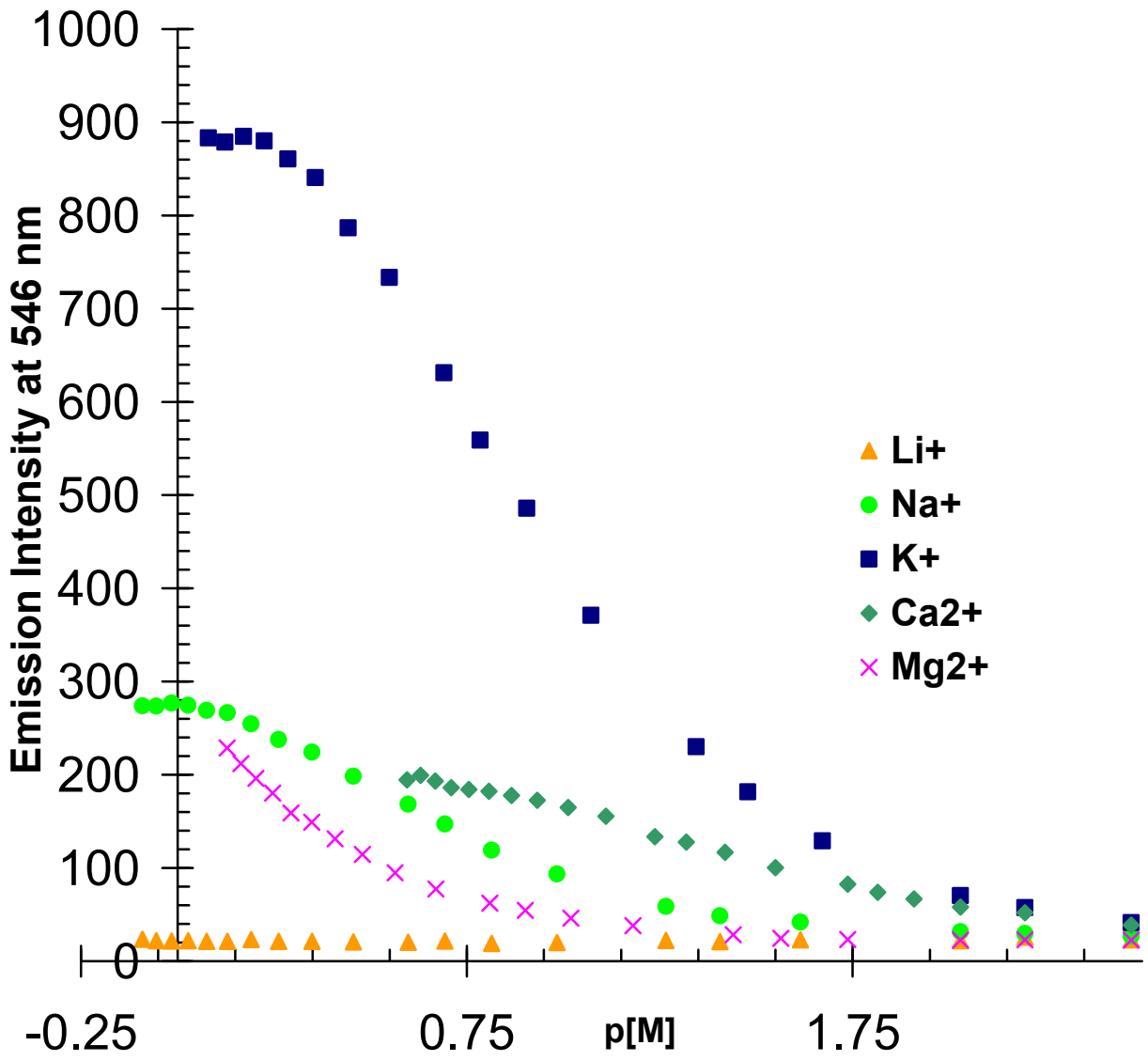


Figure 22. The X-ray crystal structure of 14 and the corresponding K^+ complex of 14 (previously published in *J. Chem. Soc., Perkin Trans. 1*, 2002, 1954-1962), showing the cooperative binding of K^+ by the aniline moieties and the two methoxy moieties.