Amino Acid Appended Gadolinium Complexes in Actuating Affinity and Selectivity for Anions in Aqueous Media

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Phosphate rich agricultural run offs raise significant environmental concerns. In addition, phosphate, which is high in the Hofmeister series with high hydration energy, is difficult to target both selectively and with high affinity in water. Although advances in supramolecular anion chemistry have been made recently, there is still a paucity of receptors that can recognize one anion over other competing anions selectively in water. Apart from high levels of affinity for phosphate, selectivity and stability are also key features that affect phosphate binding. Highly dilute natural aqueous media would pose a great exigency towards the viability of phosphate binding. Earlier trials succeeded in selective phosphate sensing with maltolate based-gadolinium(III) complexes. Added hydrogen bonding networks offered by amino acids are beneficial not only in the stabilization of the complex, but also create the ideal geometry in complementing the inbound phosphate. Thus, we have designed and synthesized a series of 4 tripodal tris-bidentate gadolinium(III) complexes by integrating amino acids in between the TREN backbone and maltolate cheating moiety. Among the charged complexes, TREN-Lys-MAM showed high sensitivity for phosphate, whereas glutamic acid analogue of the complex was the least responsive to all the tested anions. Stability studies of these complexes were evaluated by competition against DTPA-BMA. Europium(III) analogues of these complexes were also synthesized to evaluate the anion binding modes at metal center by studying Eu(III) based photoluminescence lifetime measurements.