



# Lanthanide Binding Capabilities of Sequence-Controlled Block Co-polymers with Di(phenylalanine)

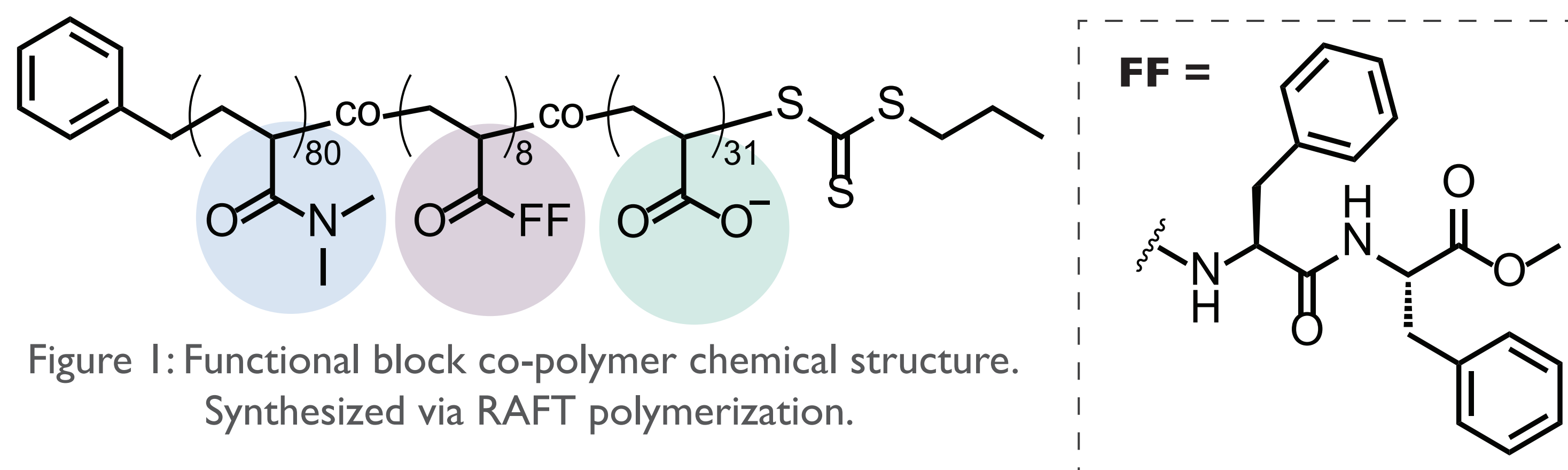
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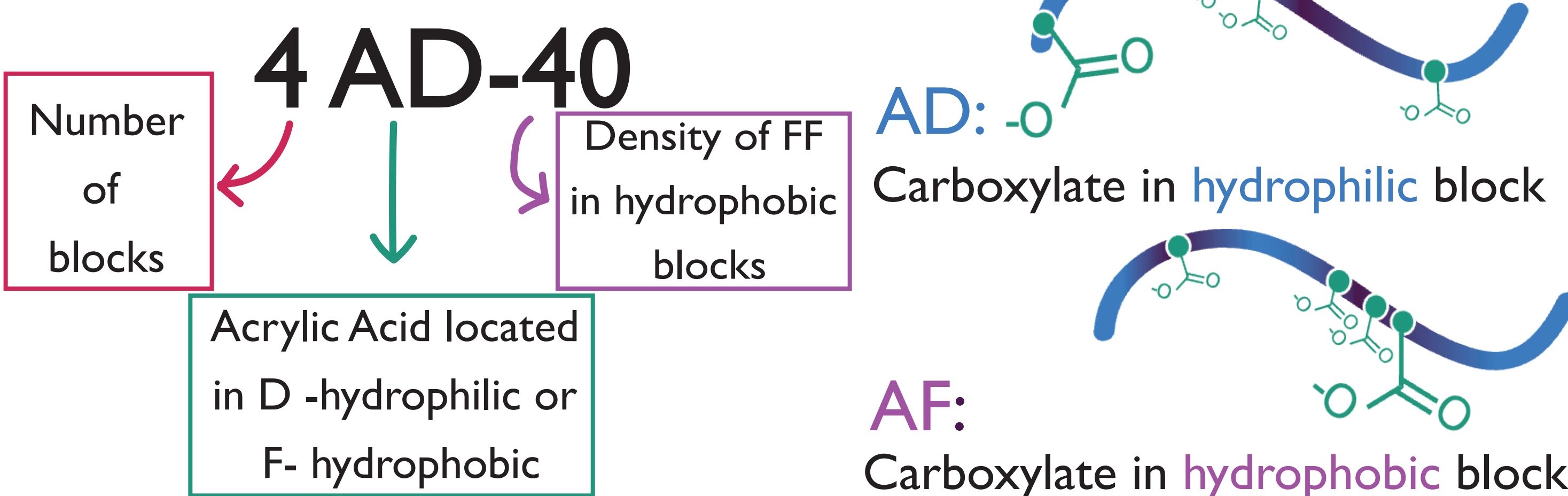
## Introduction

Synthetic polymers can be synthesized to appear and act similar to biopolymers like proteins, though they lack their finely tuned structures and functions found in nature. Our lab developed di(phenylalanine) acrylamide (FF) to impart amphiphilic polymers with biomimetic local and global structures that mimic those of proteins.<sup>1</sup> The sequences of these polymers are created and adapted via block co-polymerization to tune the structures built by FF. With a series of compositionally identical and structurally distinct copolymers, I aim to demonstrate the structure-function relationship of polymers to binding rare earth elements (REEs).<sup>2</sup> REEs are crucial to many industries but are energy demanding to purify due to their similar chemical properties. We developed a luminescence based assay to observe the binding of REEs to our polymers.

## Polymer Synthesis



Hydrophilic Monomer: Dimethyl acrylamide (DMA)  
Hydrophobic Monomer: Di(phenylalanine) acrylamide (FF)  
Functional Monomer: Acrylic acid\* (AA)  
\* Acrylic acid accessed via deprotection of tert-butyl acrylate in HFIP and HCl



## LRET Assay

Luminescence resonance energy transfer (LRET) is a phenomenon where the light is absorbed by an antenna molecule, transferred to an acceptor molecule, and then emitted at a specific wavelength.<sup>3</sup> In this case, LRET reports on the binding of the REE Terbium ( $Tb^{3+}$ ) to the functional units in our block copolymers.<sup>4</sup>

$Tb^{3+}$  is indirectly excited by FF which excites at 255 nm. FF transfers energy to nearby chelated terbium ions, which luminesce at 545 nm. The  $Tb^{3+}$  ion does not excite noticeably if it is not chelated to the polymer, making this assay especially sensitive for the polymer system.

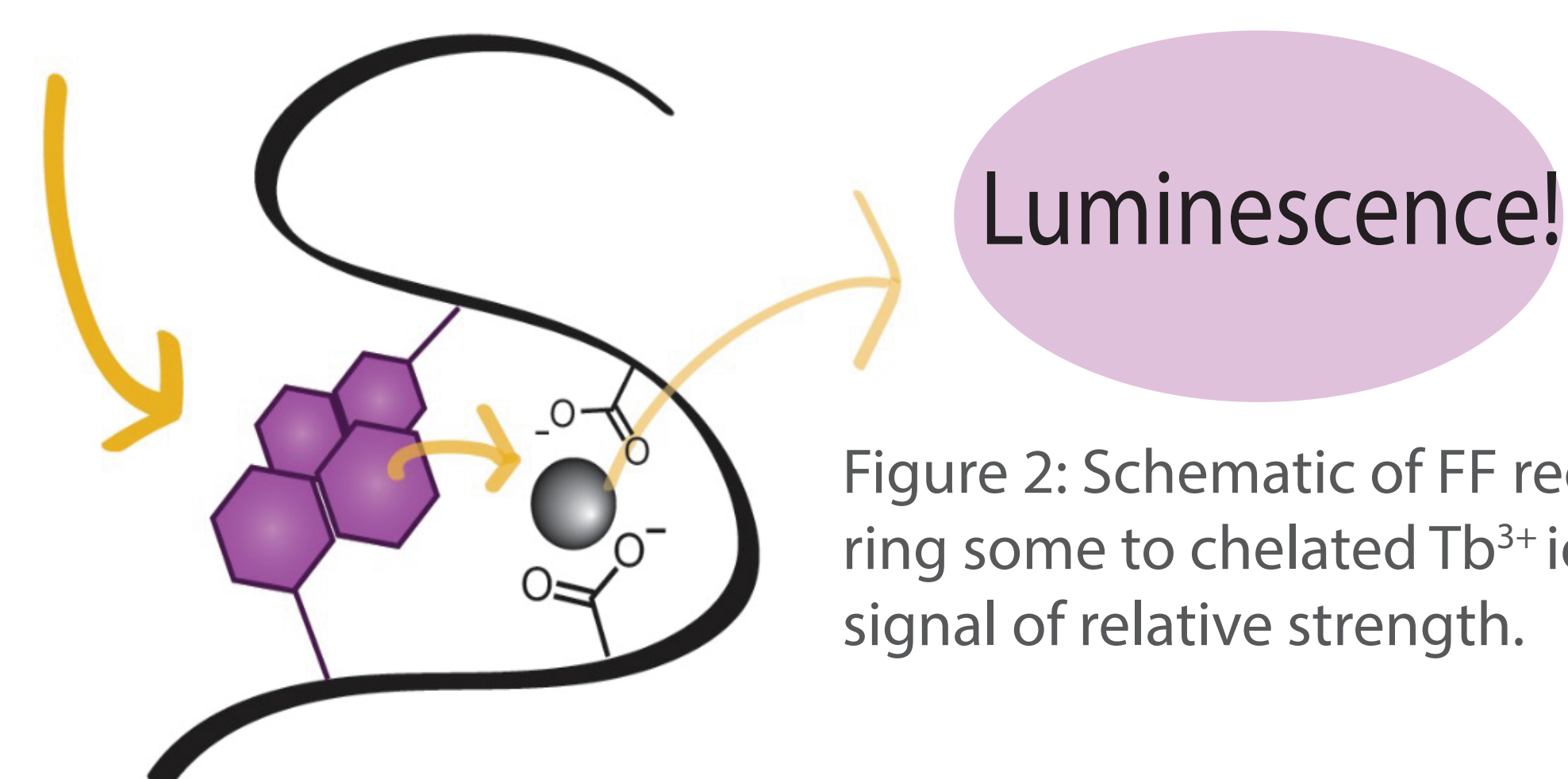


Figure 2: Schematic of FF receiving energy, transferring some to chelated  $Tb^{3+}$  ions, and then showing a signal of relative strength.

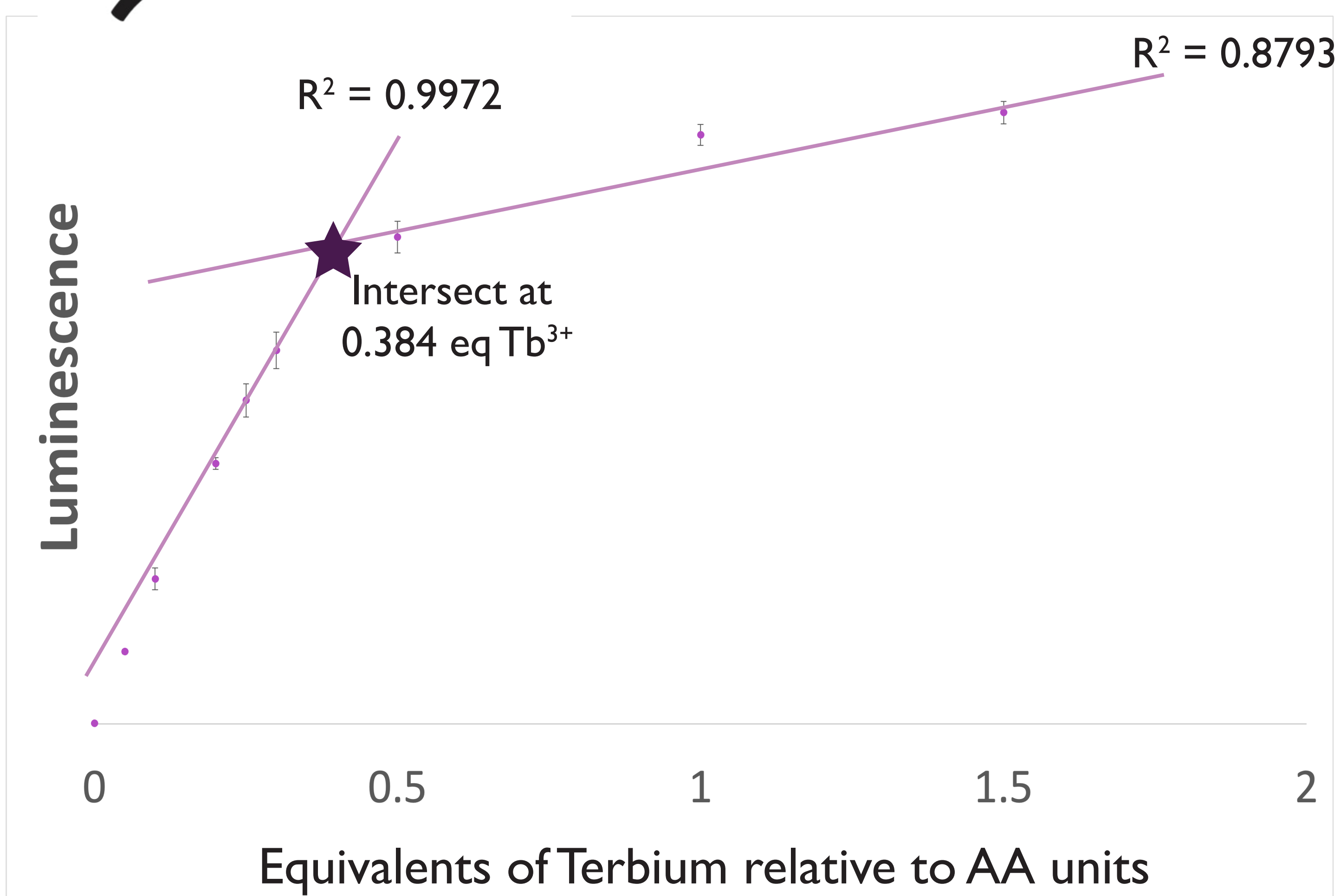


Figure 3: Luminescence of functional statistical polymer at multiple  $Tb^{3+}$  concentrations. The intersection point suggests a 3: 1  $Tb^{3+}$  ion to AA functional unit ratio of density to be optimal as the rate of luminescence increase begins to decay after this point.

## Relative Binding Affinity

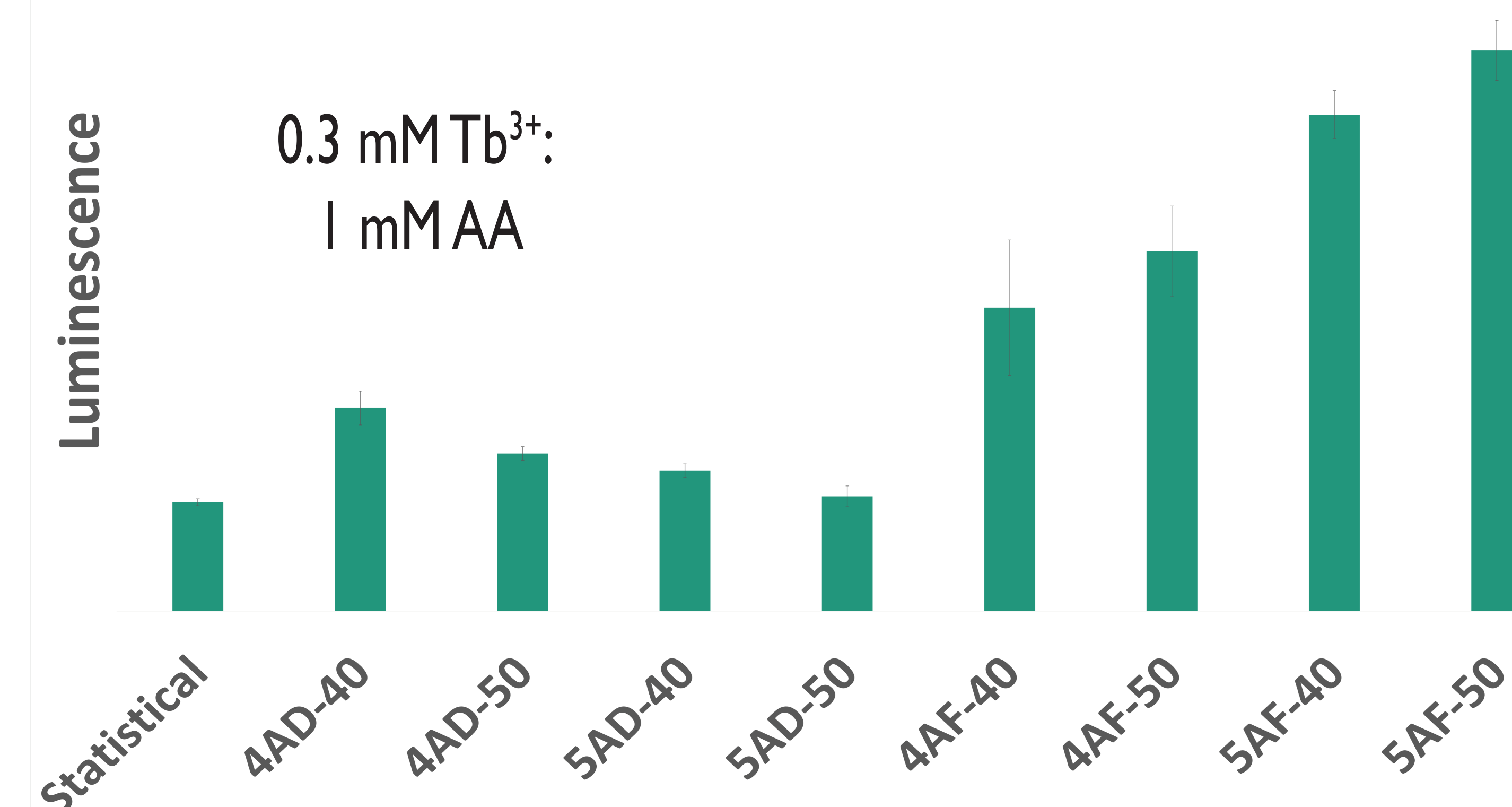
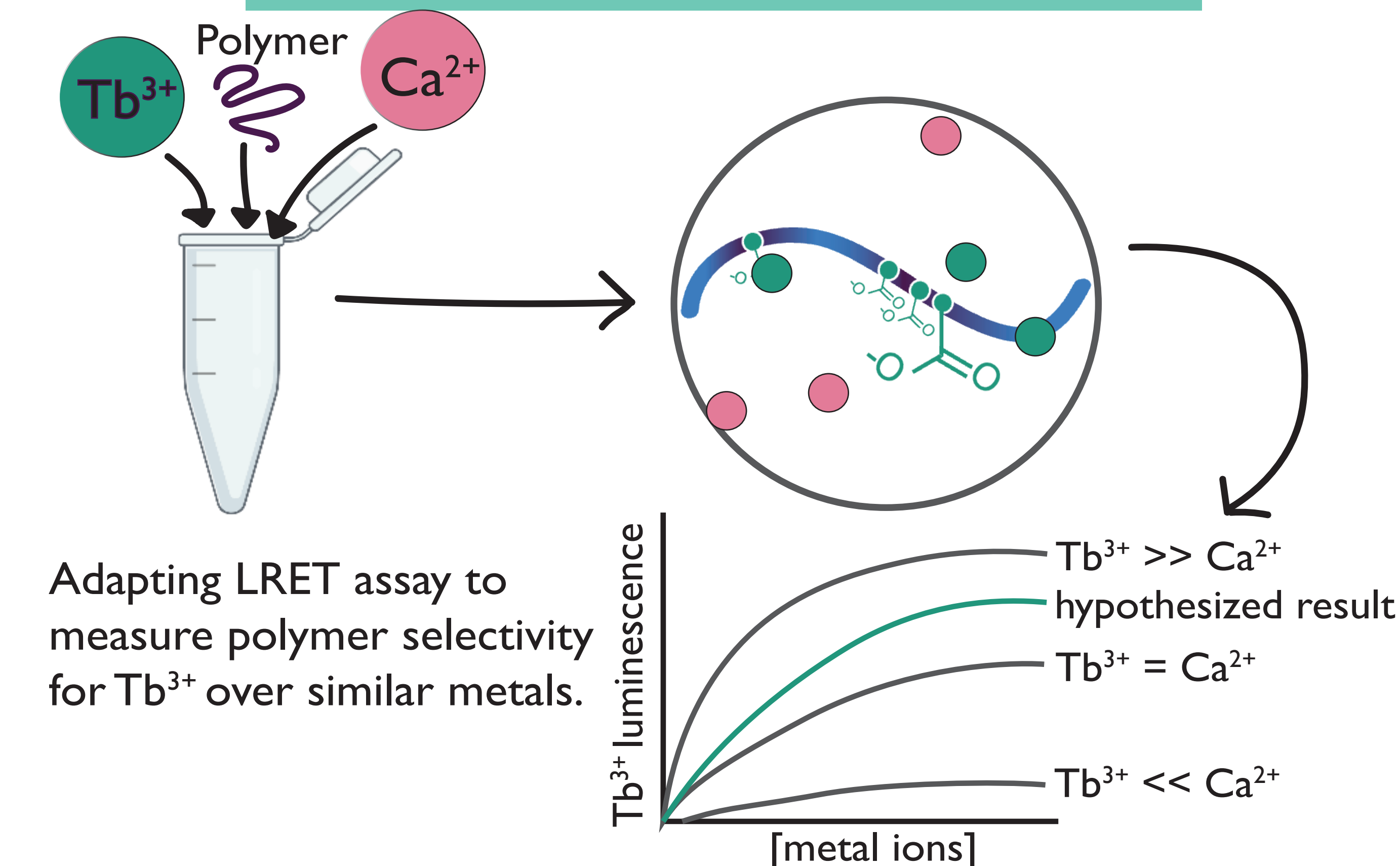


Figure 4: Luminescence data for series of tetra- and pentablock co-polymers.

- ✓ Hypothesis I: Increased binding with functional hydrophobic block
- ~ Hypothesis II: Increased binding with more blocks
- ~ Hypothesis III: Increased binding with increasing FF density

## Future Directions



1. Warren, J.; Dykeman-Birmingham, P.; and Abigail S. Knight. Controlling Amphiphilic Polymer Folding beyond the Primary Structure with Protein-Mimetic Di(Phenylalanine). Journal of the American Chemical Society 2021 143 (33) 13228-13234. DOI: 10.1021/jacs.1c05659  
2. Ćija, D; Urgel, J; Seitsonen, A; Auwärter, W; Barth, J. Lanthanide-Directed Assembly of Interfacial Coordination Architectures-From Complex Networks to Functional Nanosystems. Acc Chem Res. 2018, 51 (2), 365-375. DOI: 10.1021  
3. Dolino, D; Ramaswamy, S; Jayaraman, V. Luminescence resonance energy transfer to study conformational changes in membrane proteins expressed in mammalian cells. J Vis Exp. 2014 (91) DOI: 10.3791/51895.  
4. Bünzli, J. and Piguet, C. Taking advantage of luminescent lanthanide ions. Chem. Soc. Rev., 2005, 34, 1048-1077. DOI: 10.1039/SPECIAL THANKS TO THE U.S. DEPARTMENT OF ENERGY FOR FUNDING THIS RESEARCH