

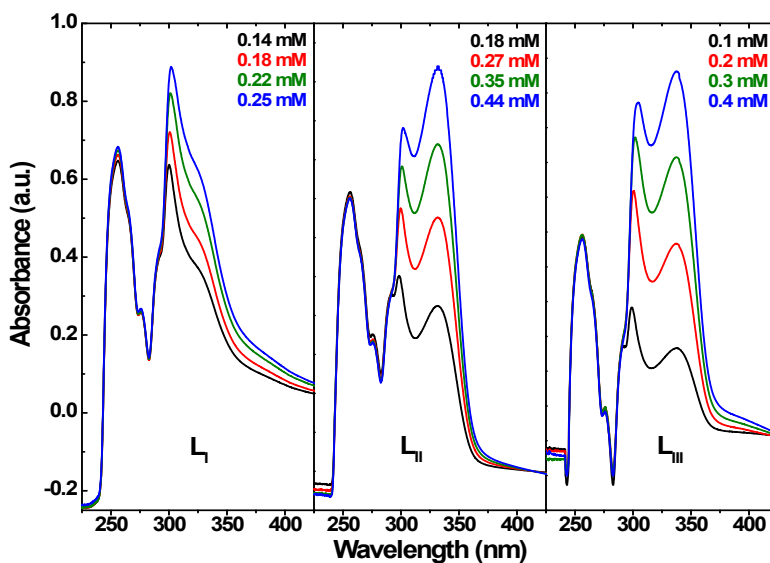
## Supporting Information

### **Binding of pyrazine-functionalized calix[4]arene ligands with lanthanides in an ionic liquid: Thermodynamics and coordination modes**

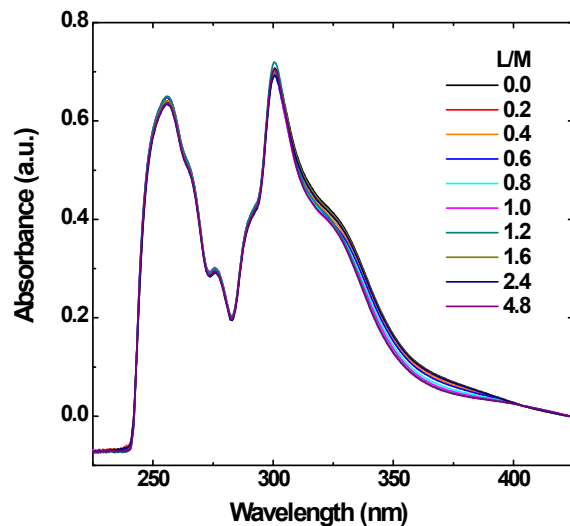
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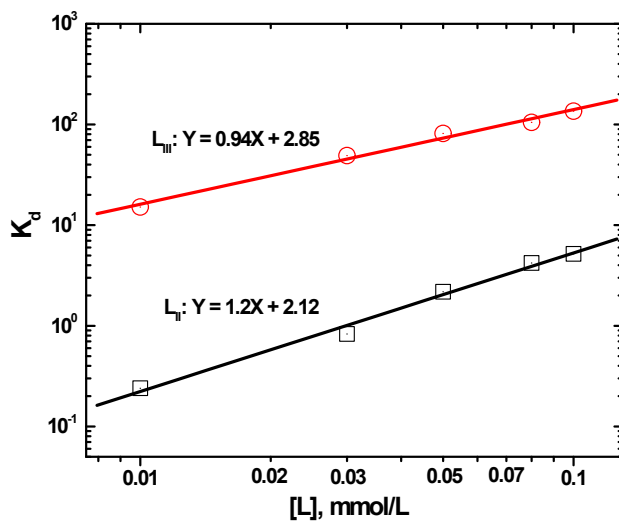
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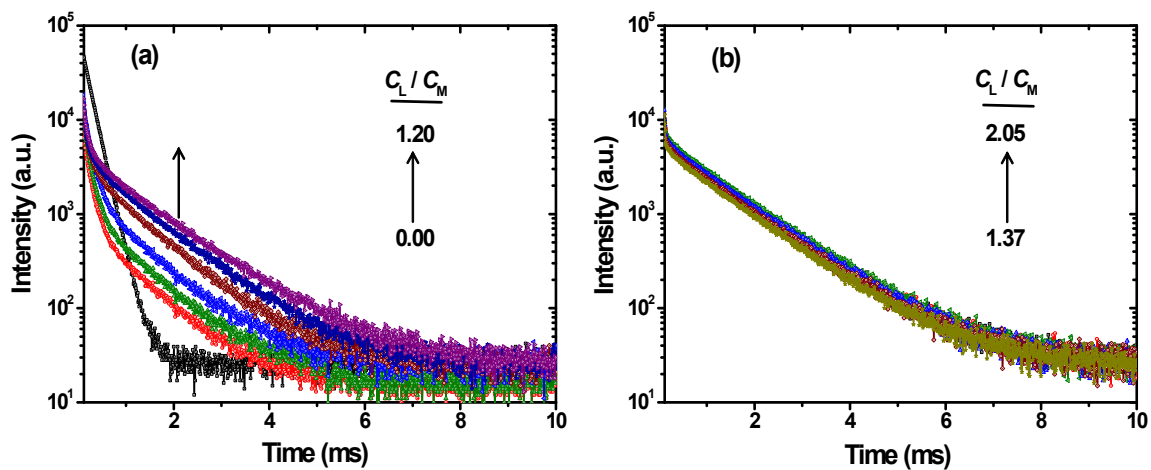
**Figure S1.** Absorption spectra of ligands  $L_{I-III}$  with increasing ligand concentration. The absorbance band between 285 – 400 nm followed Beer's Law, whereas the absorption band at 256 nm was not affected by the ligand concentration.



**Figure S2.** Spectrophotometric titration of  $L_I$  with  $\text{Eu}(\text{Tf}_2\text{N})_3$ . Cuvette solution: 0.18 mmol/L ligand (0.8 mL); Titrant: 3.8 mmol/L  $\text{Eu}(\text{Tf}_2\text{N})_3$  added in the range of 0.01 – 1.0 mL. L/M ratio refers to  $C_L/C_{Eu}$  in solution.



**Figure S3.** Variation of distribution coefficient ( $K_d$ ) as a function of ligand concentration. Organic phase:  $L_{II}$  or  $L_{III}$  in  $\text{BumimTf}_2\text{N}$ ; Aqueous phase: 1 mol/L  $\text{HNO}_3$ ; Temperature: 25 °C.



**Figure S4.** Luminescence decay of Eu(III) at varying  $C_L/C_{Eu}$  ratios. Excitation wavelength:  $(395 \pm 5)$  nm; Emission wavelength:  $(612 \pm 5)$  nm. Cuvette solution: 15 mmol/L  $\text{Eu}(\text{Tf}_2\text{N})_3$  (1.5 mL); Titrant: 15.3 mmol/L  $\text{L}_{II}$ .