

Design of Luminescent Materials Based on Dinuclear Lanthanide Complexes: A Molecular Modeling Approach

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Complexes of trivalent lanthanide are being extensively studied because of their wide applications based on their special luminescent and magnetic properties. Dinuclear structures are promising designing platforms because the ion-ion and ligand-ligand, in addition to the ion-ligand, interactions can be tuned to provide unusual and new properties. However, the syntheses of dinuclear lanthanide complexes are very difficult, especially of heteronuclear ones, and molecular modeling tools can aid in their design and predict some of their properties. Thus, two dinuclear complexes $[\text{Ln}(1)\text{-Ln}(2)]_{\text{asy}}$ and $[\text{Eu-Tb}]_{\text{sym}}$, depicted in Figure 1, with different chemical environments were investigated by quantum chemical methods. Complexes $[\text{Ln}(1)\text{-Ln}(2)]_{\text{asy}}$ have asymmetric environments for each site, whereas the $[\text{Eu-Tb}]_{\text{sym}}$ complex has symmetric environments both sites.

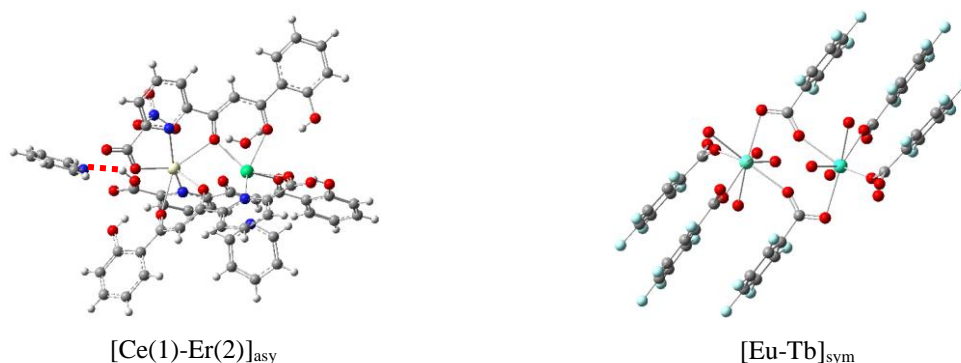


Figure 1: Structures of the $[\text{Ln}(1)\text{-Ln}(2)]_{\text{asy}}$ (left) and $[\text{Eu-Tb}]_{\text{sym}}$ (right) complexes.

These structures were successfully modeled with the B3LYP/MWB_x method using the Gaussian09 program. We obtained an energy difference in the 60 to 70 kJ mol⁻¹ for discriminating between the $[\text{Ln}(1)\text{-Ln}(2)]_{\text{asy}}$ and $[\text{Ln}(2)\text{-Ln}(1)]_{\text{asy}}$ asymmetric heteronuclear complexes. This discrimination energy has been attributed to the different sizes of cavities formed by the ligands that fit lanthanides with distinct ionic radii. However, we also found that the cavities were able to adjust according to the lanthanide radius and that this observed selectivity may have a strong contribution from the softness/hardness of each cavity. Whereas the entropy difference between the symmetric hetero $[\text{Eu-Tb}]_{\text{sym}}$ and homonuclear ($[\text{Eu-Eu}]_{\text{sym}}$ and $[\text{Tb-Tb}]_{\text{sym}}$) complexes has a significant contribution in explaining the selectivity toward the heterodimeric $[\text{Eu-Tb}]_{\text{sym}}$ structure. These results are relevant for formulating designing principles of lanthanide dimeric complexes synthesis.

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