

Self-assembly induced luminescence of Eu^{3+} -complexes for bioimaging application

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The unique properties of rare earth (RE) complexes including ligand-sensitized energy transfer, fingerprint-like emissions and long-lived emissions, make them promising materials for many applications, such

as optical encoding, luminescence imaging/sensing and time-resolved luminescence detection. In particular, the use of RE luminescent materials for in vitro and in vivo imaging can easily eliminate the autofluorescence of organisms and any interference from background fluorescence. However, most RE complexes have poor solubility and stability in aqueous solution, and their luminescence can be easily quenched by nearby X-H ($X = O, N, C$) oscillators, which limits their further applications in aqueous solutions and bioimaging. Consequently, improving luminescence performance as well as dispersibility has become a key issue to expand the application of RE complexes. Till now, extensive efforts have been devoted to increasing the luminescence intensity of RE complexes, such as increasing structural rigidity, adjusting coordination numbers, replacing ligand C-H bonds with C-F bonds and changing the electron-donating or electron-withdrawing characteristics of substituents.

Recently, assembly-induced emission materials, such as room temperature phosphorescence materials and aggregation-induced emission luminogens have become research hotspots. Compared to these emitting materials, RE complexes possess a relatively complicated sensitized [luminescence](#) mechanism. In the sensitization processes of RE complexes, the energy transfer from the excited triplet state of the ligands to the excited state of the RE ions is the main cause of emission. Therefore, increasing the possibility of intersystem crossing to the ligand triplet excited state and reducing the non-radiative decay would be beneficial to the luminescence of RE complexes.

Recent studies have shown that supramolecular assembly can build highly water-dispersible nanostructures through non-covalent intermolecular force, which would allow the RE complexes to be applied in more areas. However, it is difficult to predict the assembly and to control the particle size distribution by simply dispersing RE complexes into host matrices. As known, self-assembly driven by [intermolecular](#)

[forces](#), such as hydrophobic—hydrophobic, hydrogen bonding, and aromatic π - π stacking, has a high degree of orientation and predictability, and is a powerful strategy for synthesizing nanostructures with precise sizes and shapes. At the same time, such intermolecular interaction forces can change the intermolecular distance, limit the rotation of the ligand molecules, and regulate the [energy transfer](#) from the ligands to the central RE ions.

Here, a new strategy was proposed to obtain size-controlled Eu^{3+} -[complex](#) nanoparticles (Eu-NPs) with self-assembly induced luminescence (SAIL) characteristics without encapsulation or hybridization. The amphiphilic Eu^{3+} -complex possessing carbazole derivative ligands, with highly π - π conjugated electron structure, could self-assemble into Eu-NPs with excellent water dispersibility and controllable particle size in aqueous solution. Researchers envisaged that adjusting the molecular polarity of the ligands and transferring the RE complexes from the organic phase to the water phase could cause the RE complexes to assemble into NPs with good water-dispersibility. By studying the changes in luminescence lifetimes and quantum yields in [aqueous solution](#), they found that [self-assembly](#) could effectively shield the water molecules in the luminescent center and thus reduce the quenching effect of the water molecules from the vibration of the O-H bond. And when the molecules are self-assembled together, they restrain each other and the movement within the molecules is restricted.

This will greatly limit the intramolecular rotation or vibration of Eu^{3+} -complexes, thus resulting in the enhancement of luminescence in aqueous conditions. Also, this system could be used for bioimaging application for the detection of temperature and HClO by steady-state fluorescence and time-resolved assay. In this sense, the SAIL activity of the self-assembled RE complexes system proposed here has ushered the trend for the development of RE light conversion systems and their integration in bioimaging and therapy applications.

More information: Ping-Ru Su et al, Self-assembly induced luminescence of Eu^{3+} -complexes and application in bioimaging, *National Science Review* (2021). [DOI: 10.1093/nsr/nwab016](https://doi.org/10.1093/nsr/nwab016)

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