Supporting Information

Design and Synthesis of an Eu-based β-diketone Sensor for the Highly Selective Detection of Al^{3+} Ions

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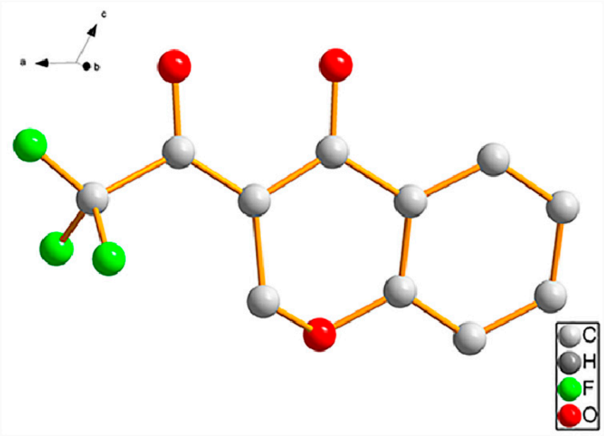


Figure S1. Molecular structure of ligand 4-TFC.

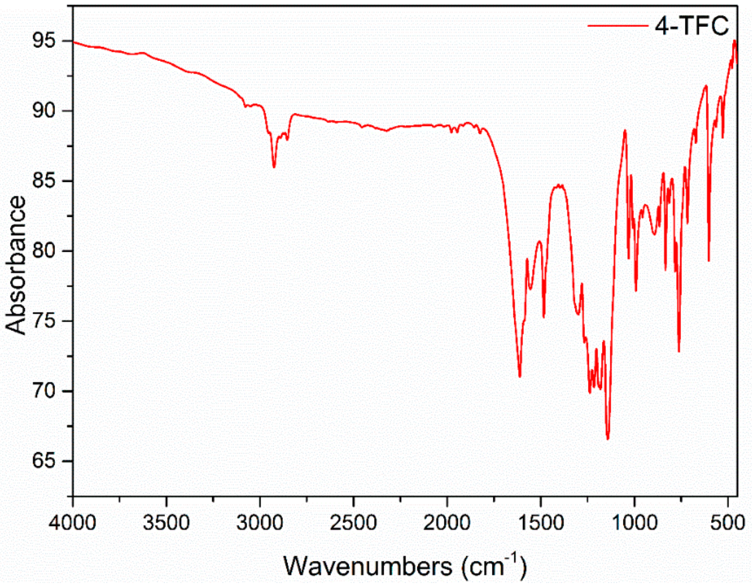
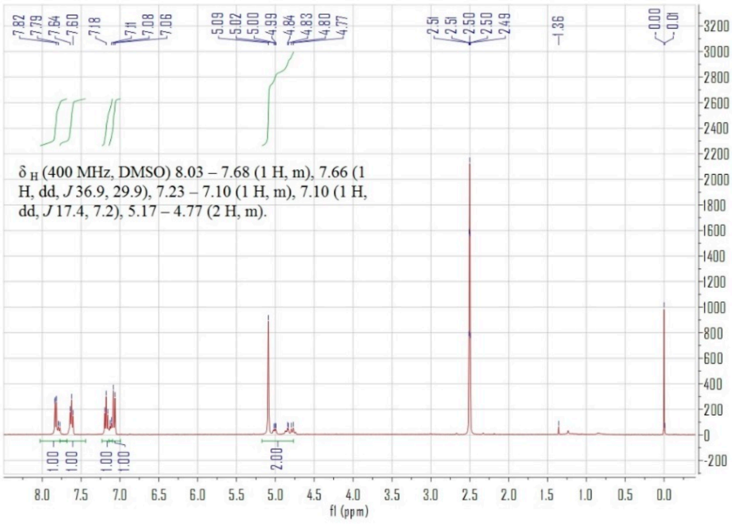


Figure S2. IR of the ligand 4-TFC.



δ_H (400 MHz, DMSO) 8.03 – 7.68 (1 H, m), 7.66 (1 H, dd, *J* 36.9, 29.9), 7.23 – 7.10 (1 H, m), 7.10 (1 H, dd, *J* 17.4, 7.2), 5.17 – 4.77 (2 H, m).

Figure S3. HNMR of the ligand 4-TFC.

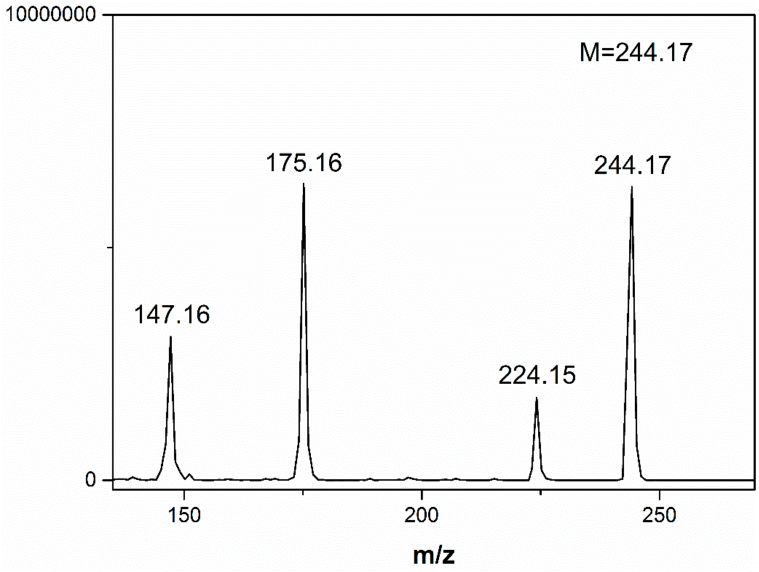


Figure S4. Expanded regions of the ESI-TOF of 4-TFC.

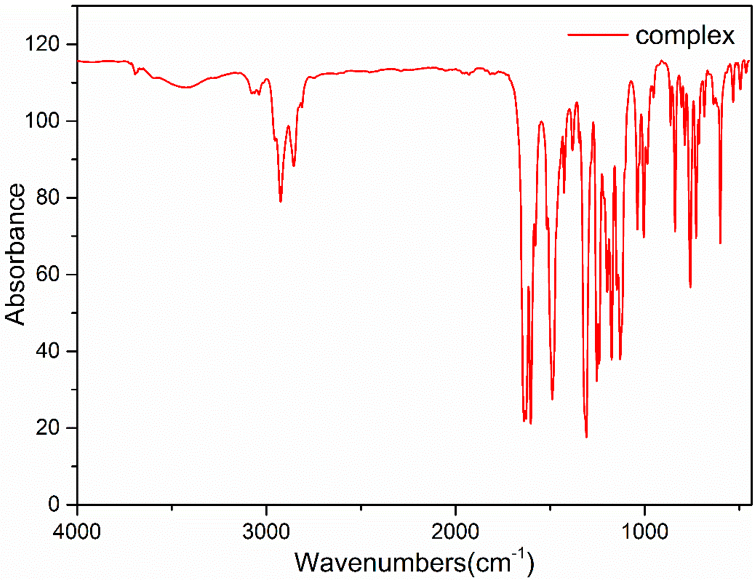


Figure S5. IR of the Eu(4-TFC)$_3$(phen) complex.

Thermalgravimetric Analysis

Thermal gravimetric analysis (TGA) was performed to investigate the thermal stability of the crystalline sample by heating it from 50 to 750 °C at a rate of 10 °C·min^{-1} under a nitrogen gas atmosphere. As shown in Figure S6, the TGA curves of complex 1 exhibit two main weight loss steps until the decomposition of the framework. Between 50 °C to 200 °C, a weight loss of 2.0% occurs, which is related to the loss of solvent molecules and water in the air. In the range of 200–490 °C, a weight loss of 64.4% occurs, corresponding to the 4-TFC ligands (calcd 66.2%) gradual decomposition. After that, from 490 °C to about 600 °C, a weight loss of 17.0% is related to the loss of one 1,10-phen molecule (calcd 19.0%). The final mass residues were almost 16.8%, which is due to the generation of Eu_2O_3, (calcd 16.8%).

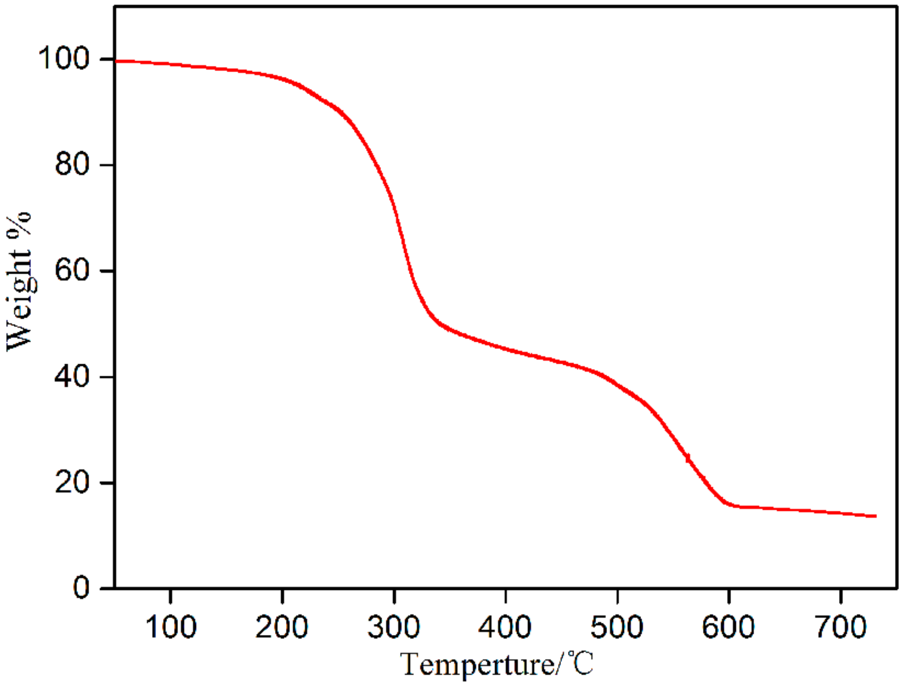
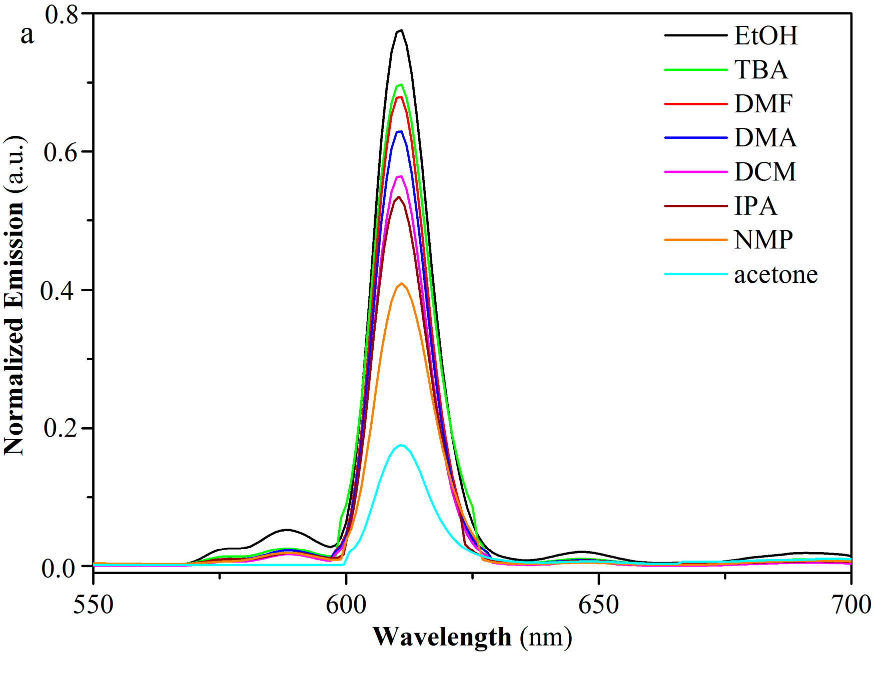


Figure S6. Thermal gravimetric of the Eu(4-TFC)$_3$(phen) complex.

Sensing Properties of Organic Small Molecules

Adverse organic small molecule pollutants can induce apoptotic cell death in various cell lines and have a harmful impact on the environment. From these, the luminance of europium-based, promising novel sensing complexes has been widely studied by fluorescence spectroscopy and has been employed to recognize organic small molecule pollutants in biosystems and environments where we live. One can notice that the complexes are quite suitable for detecting small molecules through the change of obvious luminescent signals caused by these pollutants. Although these ligands have a complicated structure, they tend to give predictable results in different organic solvents. To further explore their potential function, solvent-dependent luminescence studies on the complex were conducted for the sensing of various small organic molecules such as acetone, isopropanol (IPA), dichloromethane (DCM), DMF, ethanol (EtOH), Tert- butyl alcohol (TBA), Dimethyl adipate (DMA), and N-methyl pyrrolidinone (NMP). These studies can help us to understand the luminescence properties of the complex in different solvents. As shown in Figure S7, no obvious responses were observed in the luminescent upon addition of the above species. However, the addition of acetone could quench the luminescence effectively. This phenomenon might due to the competitive coordination of the carbonyl from acetone which could be attributed to the fact that Eu^{3+} ions reacted with acetone to form new ligands so that they cannot effectively transfer the intramolecular energy to the central ion. All of these results indicate that complex 1 displayed remarkable specificity toward acetone and could serve as a sensitive naked-eye indicator for acetone under 365 nm.



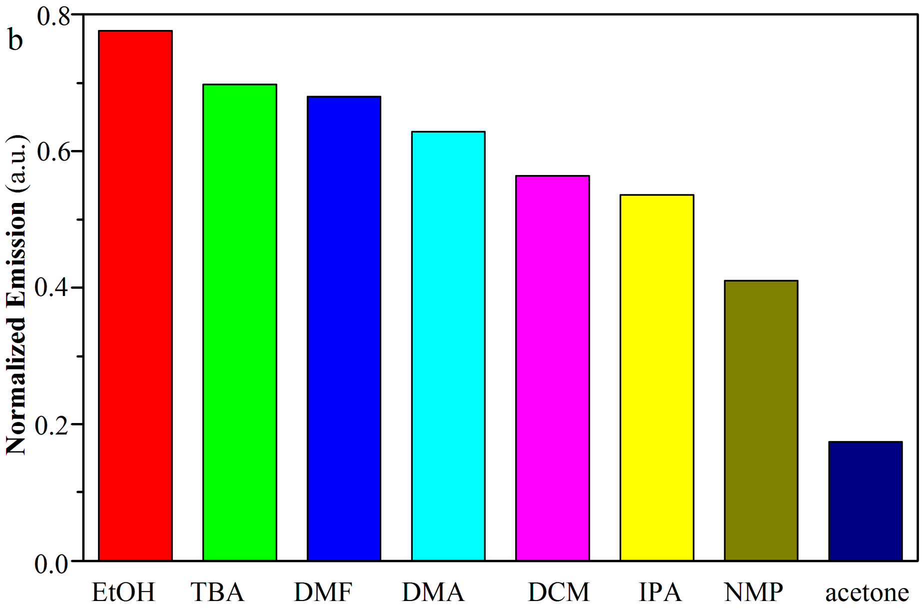


Fig. S7 (a) Luminescence spectra of complex 1 and (b) the corresponding luminescence intensity of complex 1 with various organic pure solvents in DMF solutions (c = 1 × 10^{-2} mol L^{-1}).

Mechanism of Luminescence Lighting and Quenching Response

For the purpose of making the most efficient energy transfer, the triplet state energy level of the ligand should be less than the $^5D_1$ level (19100 cm^{-1}) of the Eu^{3+} ion. At the same time, the triplet state energy level of the ligand should be more than the $^5D_0$ level (17500 cm^{-1}). Moreover, when the energy difference is about 1100 cm^{-1} to 1300 cm^{-1}, the strongest fluorescence emission peak will occur. In order to elucidate the energy transfer processes in the europium complex, it is essential to predict the energy levels of the relevant electronic states. In addition, the singlet and triplet energy levels of 4-TFC and phen are estimated according to their wavelengths of UV−Vis absorption spectra and the characteristic emission peaks of the corresponding phosphorescence spectra. Additionally, the internal conversion from the higher excited states to the lower excited states such as $^5D_3 \rightarrow {}^5D_2 \rightarrow {}^5D_1 \rightarrow {}^5D_0$ becomes feasible. Consequently, most europium complexes show the characteristic ligand-field splitting emission bands at 579 nm ($^5D_0 \rightarrow {}^7F_0$), 588–596 nm ($^5D_0 \rightarrow {}^7F_1$), 612–614 nm ($^5D_0 \rightarrow {}^7F_2$), 651–645 nm ($^5D_0 \rightarrow {}^7F_3$), and 693–702 nm ($^5D_0 \rightarrow {}^7F_4$). Thus, the key factor which can affect the luminescence properties of europium complexes is the energy level's match of the triplet state of the ligands to the $^5D_0$ of the Eu^{3+} ion. In the β-diketone luminescent complex, fluorescence can be significantly improved when combined with auxiliary ligands such as phen and bipyridine. Since an auxiliary ligand does not act as a receptor for energy and does not destroy the fluorescence of the original complex, but plays an important role in preventing the ligand from entering the interior of the complex, it accordingly inhibits the fluorescence quenching. This effect is called a "synergistic effect," as it not only can improve the fluorescence efficiency, but also maximize the coordination number of metal ions and facilitate the complex to reach a more stable state. In addition, the higher degree of conjugation of the auxiliary ligand, the lower the excitation energy of the formed complexes needed, and the higher luminous efficiency of the complex will be accessible.

As described above, the luminescence intensity of lanthanide complexes due to the "antenna effect" can be explained by the electron transfer effect from ligands to metal centers. Keeping this in mind, we then speculated that the luminescence quenching might be up to the competitive coordination of Eu^{3+} between the carbonyl group from acetone and 4-TFC ligands, which may interfere with the essential energy transfer and thus quench the luminescence of Eu^{3+}. Another point may be that the weak interaction between phen and europium cations results in part because the bonds between Eu^{3+} and N atoms, which are replaced by the carbonyl group and reduce the ligands' antenna efficiency. Acetone is an organic alkali in a Lewis acid-base reaction for the electron-donating carbonyl group, and the oxygen atom has lone-pair electrons which can move to the europium cations and disturb the original Eu-O and Eu-N bonds, which in turn decreases the intramolecular energy transfer efficiency and reduces the luminescent intensity.

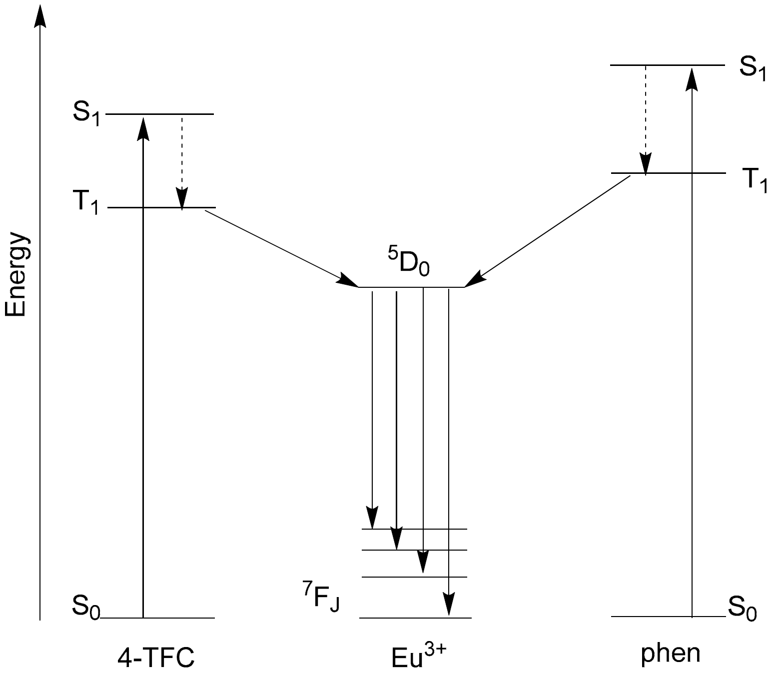
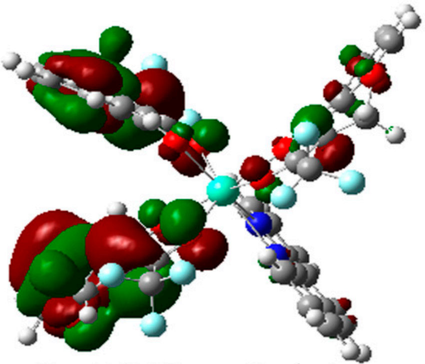
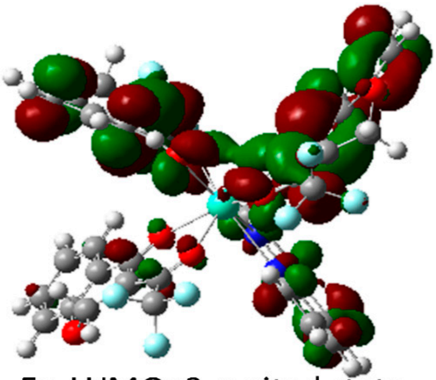


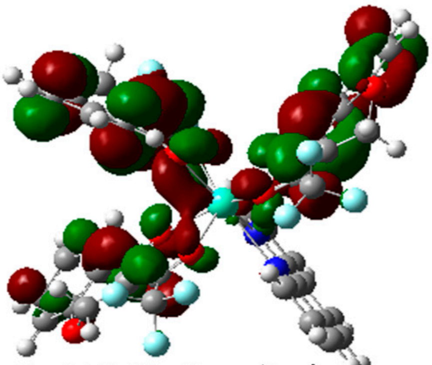
Figure S8. Schematic energy level diagram and energy transfer process for complex 1. S1, first excited singlet state; T1, first excited triplet state.



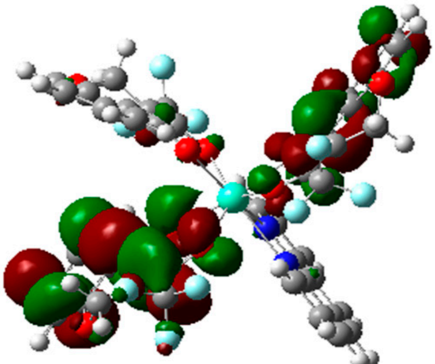
Eu-LUMO-excited state



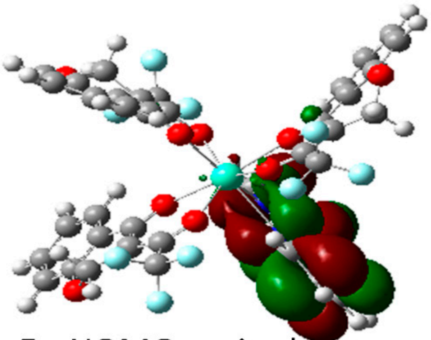
Eu-LUMO+3-excited state



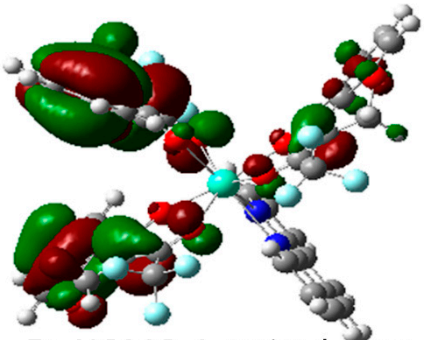
Eu-LUMO+2-excited state



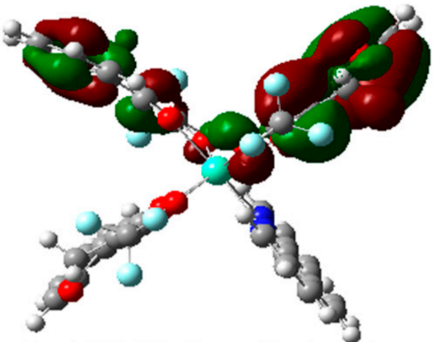
Eu-LUMO+4-excited state



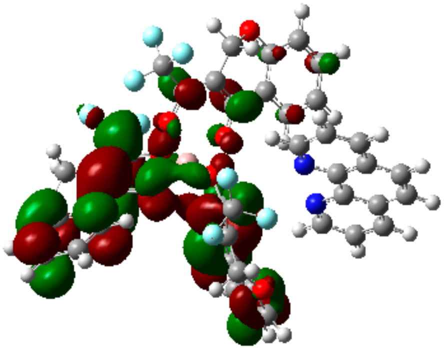
Eu-HOMO-excited state



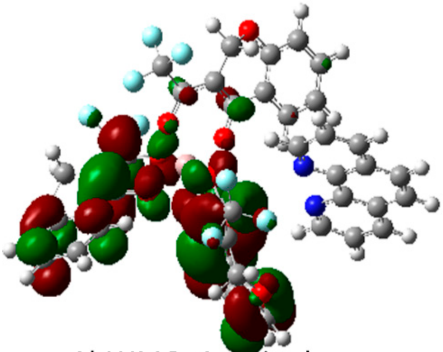
Eu-HOMO-1-excited state



Eu-HOMO-2-excited state

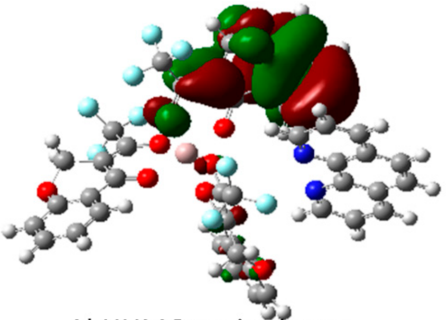


Al-LUMO-excited state

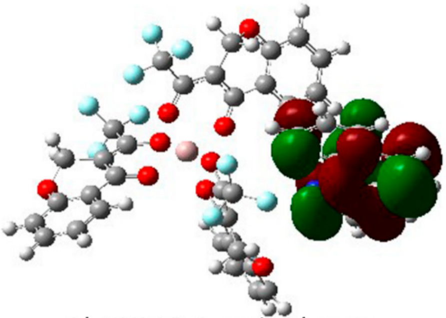


Al-LUMO+1-excited state

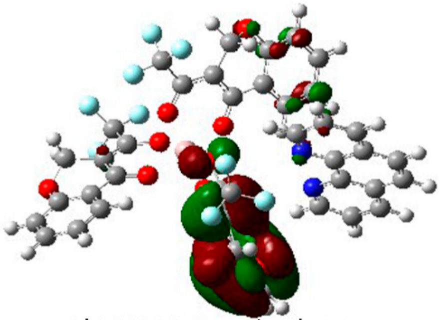
Al-LUMO+2-excited state



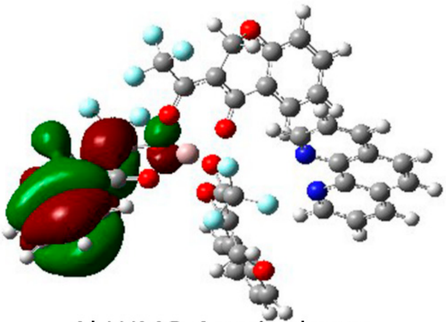
Al-HUMO-excited state



Al-HUMO-1-excited state



Al-HUMO-3-excited state



Al-LUMO-4-excited state

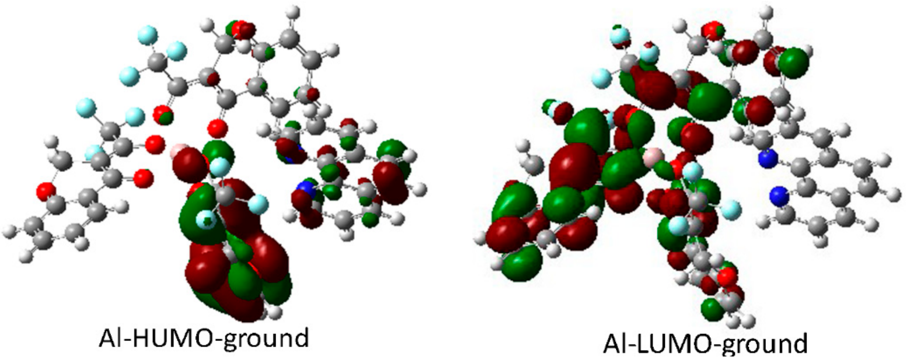


Figure S9. The results of the theoretical calculations for the absorption properties of the complexes.

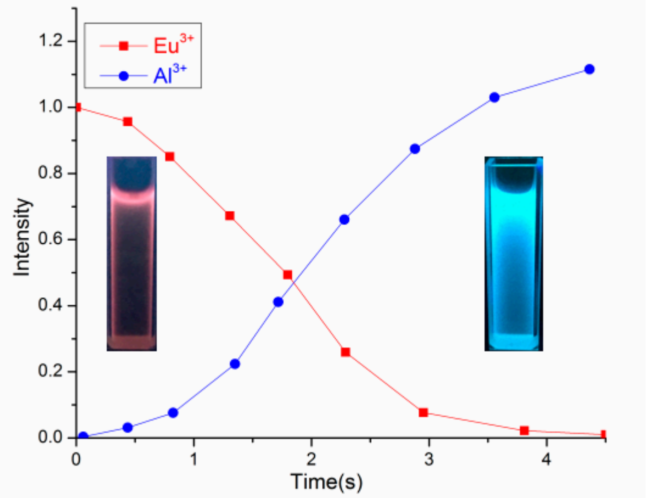


Figure S10. Effect of Al^{3+} concentration on fluorescence intensity in the presence of Eu^{3+}.