Theoretical study on absorption properties of nitroxide diradicals

Ryota Nakamura[1], Yasuteru Shigeta*[1,2], Katsuki Okuno[1], Shuichi Suzuki[3], Masatoshi Kozaki, Keiji Okada[3], Miki Hasegawa[4], and Masayoshi Nakano[1]

[1] *Graduate School of Engineering Science, Osaka University, Toyonaka, 560-8531, Japan.*

[2]*CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, 332-0012, Japan.*

[3] *Graduate School of Science, Osaka City University, 3-3-138 Sugimoto Sumiyoshi-ku, Osaka 558-8585, Japan.*

[4]*College of Science and Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, 252-5258, Japan.*

Abstract

Some lanthanide complexes are known to exhibit specific luminescence from the central lanthanide ion originating in the energy transfer from the organic ligands to the central lanthanide ion. Most of studies adopted closed-shell ligands as a photoabsorber. In recent years, Suzuki established the synthesis method of diradical molecules, which have two identical or different nitroxide radicals, i.e. IN-IN, IN-NO, and NN-NO (IN: imino nitroxide, NO: nitroxide, NN: nitronyl nitroxide) [1]. Hasegawa first found that IN-IN and IN-NO coexistent with Eu or Tb ion show highly efficient lanthanide-ion-specific photoemission [2]. To control the absorption wavelength and intensity, it is essential to know information on the excited states of these diradical organic ligands. In this study, we theoretically elucidate the relationship between their electronic structures and absorption in solution. Singlet and triplet states of three diradical molecules, IN-IN, IN-NO, and NN-NO, were optimized at UB3LYP/6-311G(2d, 2p) level of approximation with the polarizable continuum solvation model (PCM) for describing solvent effects in acetonitrile, and corresponding excitation energies were evaluated by time-dependent density functional theory. It is found that IN-IN and IN-NO have two conformations for each spin state, i.e. totally four different states, while NN-NO has only one conformer, i.e., two different ones. Using all possible conformers, the statistical averages of UV/Vis spectra are found to well reproduce experimental absorption wavelength, though a peak in a long wavelength region is slightly underestimated.

References

[1] S. Suzuki, T. Furui, M. Kuratsu, M. Kozaki, D. Shimoi, K. Sato, T. Takui, K. Okada, *J. Am. Chem. Soc.* **132**, 15908-15910 (2010). [2] M. Hasegawa et al. in preparation.