



Relativistic and TD-DFT study of the substituent effects on the optical and electronic structure properties of Europium (III) macrocyclic complexes

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ABSTRACT

The ability of the lanthanide (III) ions to promote the Schiff-base condensation of appropriate diamine and dicarbonyl precursors, resulting in the formation of metal complexes of otherwise inaccessible macrocyclic ligands, is by now well established, and the topic was recently reviewed.^{1,2} Most efforts to date have focused on symmetric macrocycles consisting of two identical aromatic head units (pyridines, furans, or phenols) symmetrically connected through imine linkages to identical aliphatic side chains.³ The complexes of the 18-member, six nitrogen donor ligands have received special attention because of can be used in several medical applications as radiopharmaceuticals in radioimmunotherapy, as a contrast-enhancing agents in magnetic resonance, as luminescent labels in luminescence immunoassay, as luminophores, as luminescent probes, etc.¹⁻⁵ From all applications mentioned before, we have special interest in study macrocyclic complex with ortho-diimine side chains and pyridine head units, because we expected that these complexes have more intense ligand-mediated luminescence. Therefore, we have investigated systematically the optical and the electronic structure properties of Eu(III) hexa-aza macrocycle complexes and its derivatives functionalized with some donor and attractor organic groups using relativistic-DFT methodologies. This study was carried out using the ADF package with the two-component ZORA Hamiltonian incorporating relativistic effects. All geometries were obtained at scalar relativistic level using the general gradient approximation (GGA) with the density functional proposed by Perdew-Burke-Ernzerhof (PBE) using Triple- ζ Slater basis set with two polarization functions (STO-TZ2P) for all systems. Energy decomposition analysis (EDA) proposed by Morokuma and implemented by Ziegler was used to study the bonding interaction between the macrocycle and europium ion. Electronic excitations were obtained at TD-DFT theory level using the SAOP/ALDA potential model methodology.

REFERENCES

1. De Cola, L.; Smailes, D. L.; Vallarino, L. M. *Inorganic Chemistry* **1986**, 25, 1729.
2. Fonda, K. K.; Smailes, D. L.; Vallarino, L. M.; Bombieri, G.; Benetollo, F.; Polo, A.; de Cola, L. *Polyhedron* **1993**, 12, 549.
3. Fenton, D. E.; Vigato, P. A. *Chemical Society Reviews* **1988**, 17, 69.
4. Alexander, V. *Chemical Reviews* **1995**, 95, 273.
5. te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *Journal of Computational Chemistry* **2001**, 22, 931.

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