

“ON-OFF” switching of europium complex luminescence coupled with ligand redox process

Masafumi Yano,^{*a} Keisuke Matsuhira,^a Masakazu Tatsumi,^a Yukiyasu Kashiwagi,^b Masami Nakamoto,^b Munetaka Oyama,^c Kei Ohkubo,^d Shunich Fukuzumi,^{d,e} Hitomi Misaki,^f and Hiroshi Tsukube^f

^a *Faculty of Chemistry, Material and Bioengineering, Kansai University, 3-3-35 Yamate-cho, Suita, 564-8680, Japan. Fax: +81-6-6330-3770; Tel: +81-6-6368-0751; E-mail: myano@kansai-u.ac.jp*

^b *Osaka Municipal Technical Research Institute, 1-6-50 Morinomiya, Joto-ku, Osaka 536-8553, Japan.*

^c *Graduate School of Engineering, Kyoto University, Nishikyo-ku, 615-8520, Kyoto, Japan.*

^d *Department of Material and Life Science Graduate School of Engineering, Osaka University and ALCA (JST), 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan.*

^e *Department of Bioinspired Science, Ewha Womans University, Seoul, 120-750, Korea.*

^f *Department of Chemistry, Graduate School of Science and CREST(JST), Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan*

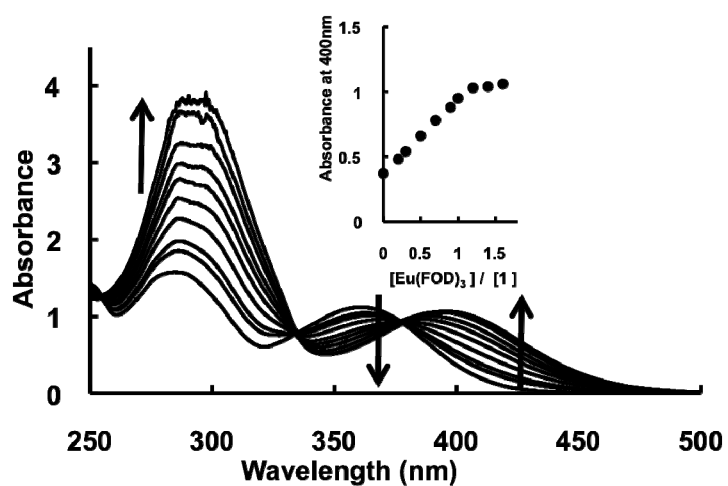


Fig. S1 UV spectral changes and titration curve for complexation between **1** and $\text{Eu}(\text{FOD})_3$ in CH_3CN . $[\mathbf{1}] = 5.0 \times 10^{-5} \text{ M}$.

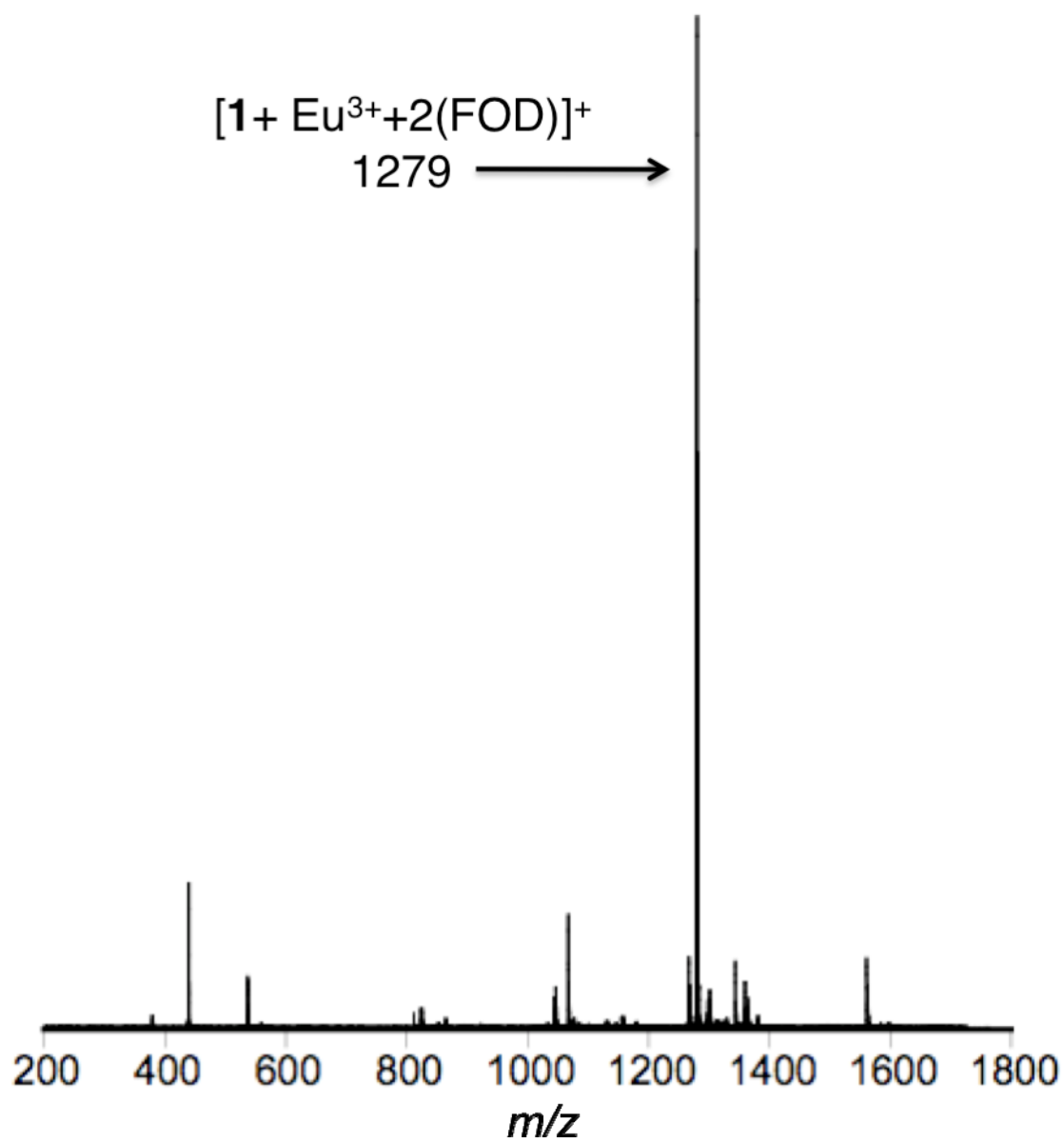


Fig. S2 ESI-MS spectrum of $1 \cdot \text{Eu}(\text{FOD})_3$ in acetonitrile.

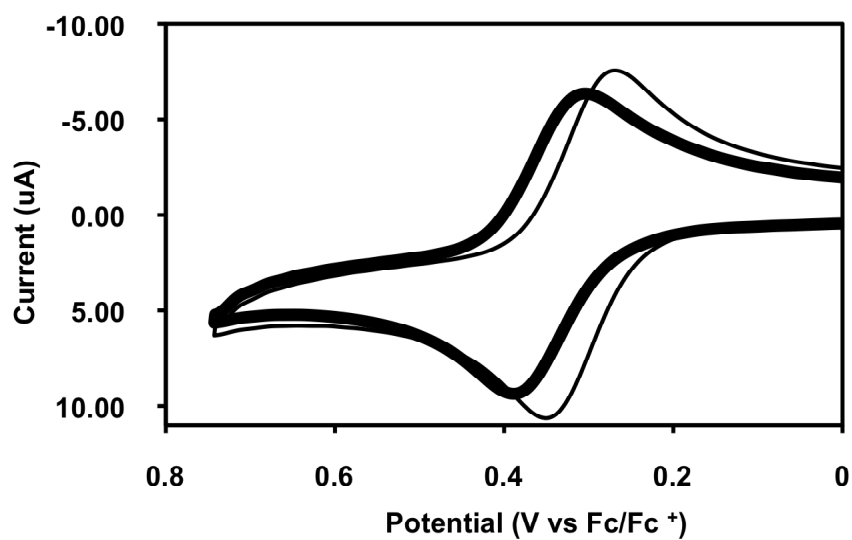


Fig. S3 Cyclic voltammograms of **1** (plain) and **1**•Eu(FOD)₃ (bold) in *n*-butyronitrile at room temperature. [**1**]=[**1**•Eu(FOD)₃] = 1.0 x 10⁻⁴ M.

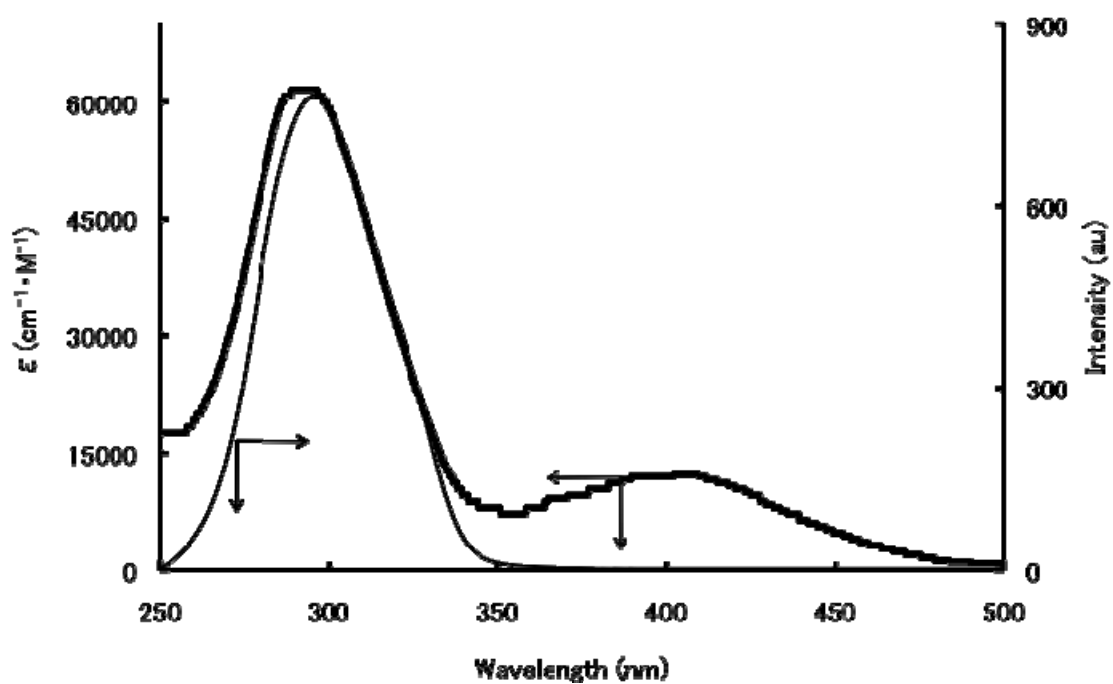


Fig. S4 Excitation ($\lambda_{em}=615\text{nm}$) (plain) and absorption (bold) spectra of **1**•Eu(FOD)₃ in acetonitrile at room temperature. [**1**•Eu(FOD)₃] = 5×10^{-6} M.

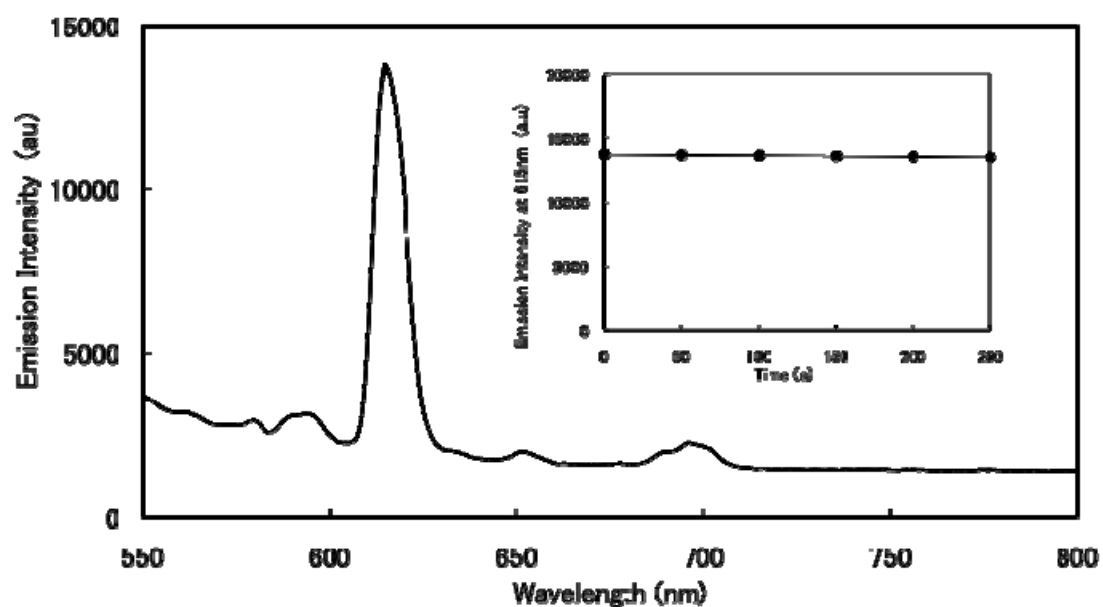


Fig. S5 Emission spectral change of $2\bullet\text{Eu}(\text{FOD})_3$ in deaerated acetonitrile containing NBu_4PF_6 (0.1 M) upon oxidation at 1.0 V vs. Fc/Fc^+ . Excitation at 290 nm. Inset: Emission intensity change at 615nm of the $2\bullet\text{Eu}(\text{FOD})$ solution.

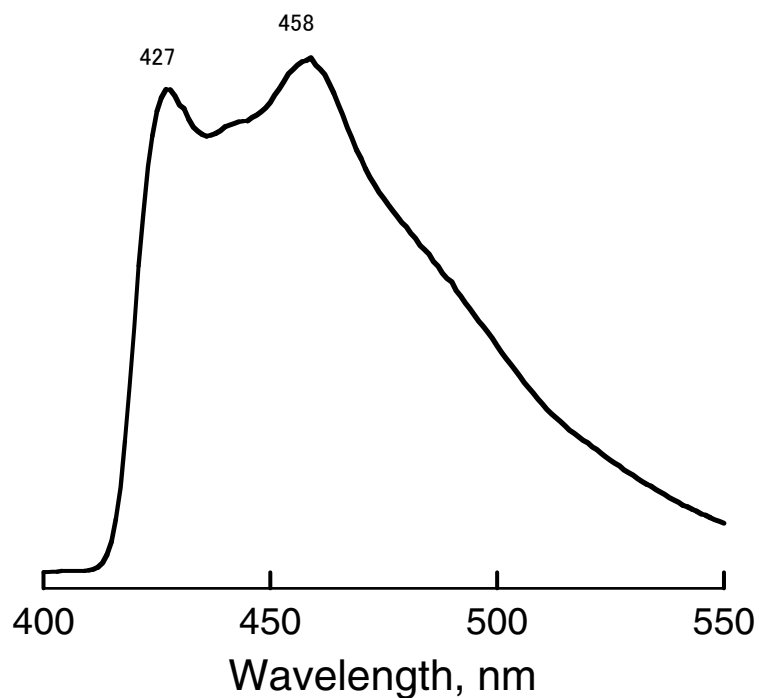


Fig. S6. Emission spectrum of 4, 4'-dimethoxytriphenylamine in deaerated EPA/ethyl iodide (3:1 v/v) glass at 77 K. EPA =5:5:2 diethyl ether / isopentane / ethanol. Excitation wavelength = 370 nm.