

Communication

Eu^{III}-1-Naphthoate Complex with N-Donor Ligand as a New White Luminescent Single Molecular Material

Yu Kyung Eom, Silvanose Biju and Hwan Kyu Kim*

Global GET-Future Lab. and Department of Advanced Materials Chemistry, Korea University, Sejong 339-700, Korea.

ABSTRACT: Two novel antenna complexes of Eu^{III} with 1-naphthoic acid (NA) as primary ligand and two aromatic N-donor ligands namely N-hexyl-N-(pyridin-2-yl) pyridin-2-amine (**1**) and 4-((dipyridin-2-ylamino)methyl)benzoic acid (**2**) have been synthesized and characterized by various spectroscopic techniques. The room-temperature (298 K) photoluminescence spectrum of Eu^{III} complexes composed of typical line like emissions, assigned to transitions between the first excited state ⁵D₀ to the ⁷F_J (J = 0-4), resulting in red emission along with the residual emission from the 1-naphthoic acid moiety in the blue region. The determined CIE color coordinate value for the complex **2** is (x = 0.36, y = 0.34), which is in white region.

One of the main challenges faced by modern day lighting technology is the production of efficient white light emitting materials. These are essential for the applications such as full color displays and for backlighting liquid crystal displays,^{1,2} whereas in some other places pure colors are necessary.³ Hence, white emission should ideally be composed of three (blue, green, and red) primary colors and cover the whole visible range, at the same time the emitter should have the ability to emit the primary colors simultaneously with equal intensities to produce white light and the pure colors separately in a tunable way.⁴ This goal is achieved by mixing various primary colors from different emitting materials.⁵ Another approach for the generation of white light sources is to use a single component emitter, with greater stability, reproducibility, no phase separation, and simpler fabrication processes.⁶ However, most of the organic dyes used usually possess broad spectrum covering entire visible region. Hence these organic dyes are not best suited for this purpose.

In contrast, Ln^{III} ions which exhibit excellent sharp and long lived luminescence properties, bonded to

suitable antenna molecules have attracted considerable interest towards the development of white emitting materials.⁷ With precisely selected Ln^{III} ions such as (Eu^{III}, Sm^{III}, Pr^{III} -red), (Tb^{III}, Er^{III} -green) and (Tm^{III}, Ce^{III} -blue), it is possible to obtain white light with high color purity.⁸ Moreover, there is considerable interest for the development of single molecular materials containing Dy^{III} ion, which can emit white light.⁹ In recent past many Eu^{III} containing single molecular materials with carefully designed ligand system which allows partial energy transfer between organic fluorophore to central metal ions are known to emit white light.⁷ To this end we have designed a new Eu^{III} complex with 1-naphthoic acid as primary ligand and 4-((dipyridin-2-ylamino)methyl)benzoic acid as ancillary ligand (**2**). Its photophysical properties were compared with a known Eu^{III}-1-naphthoate complex (**1**).

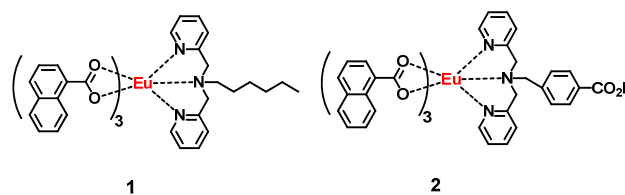


Figure 1. Molecular structures for the Eu^{III} complexes **1-2**.

The Eu^{III} complexes **1-2** were synthesized according to a reported procedure.¹⁰ The detailed synthesis and experimental procedures are given in experimental section and molecular structures of **1-2** are presented in **Figure 1**. Fourier transform IR spectroscopic studies and elemental analysis results shown that the Eu^{III} ion is reacted with three 1-naphthoic acid molecules and one tridentate N-donor ligands, resulting nine coordinated anhydrous complexes.

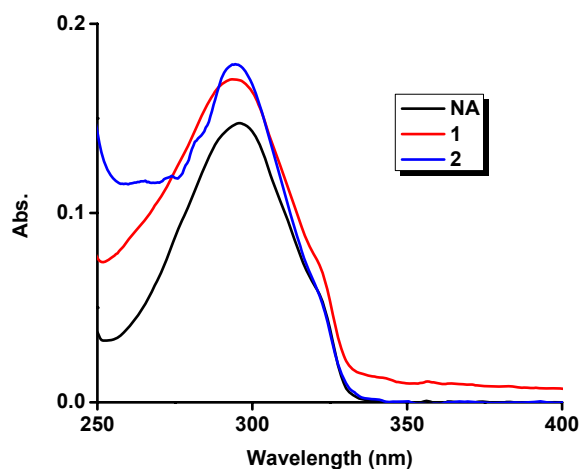


Figure 1. UV-Vis absorption spectra of 1-naphthoic acid (NA; $c = 3 \times 10^{-5}$) and Eu³⁺ complexes **1-2** ($c = 1 \times 10^{-5}$) in THF.

The UV-Vis absorption spectra of the primary ligand 1-naphthoic acid (NA) and Eu^{III} complexes **1-2** were recorded in THF and were gathered in Figure 1. All the spectra were identical in their shape and peak position, but the calculated ϵ values shows large differences. The obtained ϵ values for **1-2** (Table 1) are almost three times higher than NA. This is in good agreement with the presence of three NA molecules per Eu^{III} complexes. Exciting at the ligand centered band at 300 nm, Eu^{III} complexes **1-2** shows emission in the region 320-720 nm (Figure 2).

Table 1. Photophysical data for Eu^{III} complexes **1-2** and 1-Naphthoic acid.

	$\lambda_{\text{abs max}}$ /nm	ϵ /M ⁻¹ cm ⁻¹	$\lambda_{\text{em max}}$ /nm	τ /μs
NA	295	4992 ± 28	350	
1	295	17175 ± 1460	351	615
2	295	16096 ± 1224	354	216 ± 1

The emission spectra of **1-2** displays characteristically sharp peaks in the 575-725 nm region, which are associated with the $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ transitions of the Eu^{III} ion.¹¹ The five peaks that are anticipated for the $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ transitions are well resolved, and the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_{3,4}$ transition is very intense, pointing to a highly polarizable chemical environment around the Eu^{III} ion.¹² The presence of only one line for the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition strongly indicates the existence of only one coordination site for the Eu^{III} cations, as this transition

occurs between nondegenerated levels. The intensity ratios $R = I(^5\text{D}_0 \rightarrow ^7\text{F}_2)/I(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ for Eu^{III} complexes **1-2** are in the range 6-7. The large value of R and the noticeable intensity of the forbidden $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition indicate the absence of inversion centre at the Eu^{III} sites.¹¹

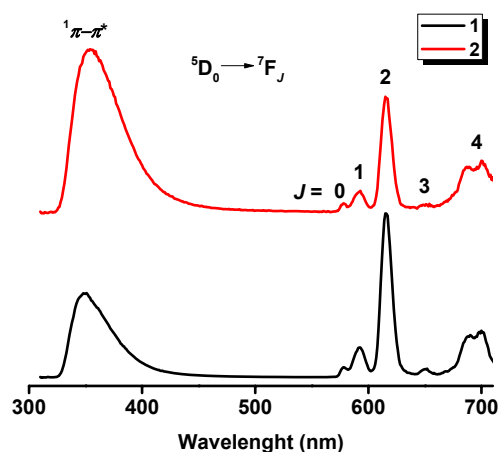


Figure 2. Emission spectra of Eu^{III} complexes **1-2** in solid state at 298K.

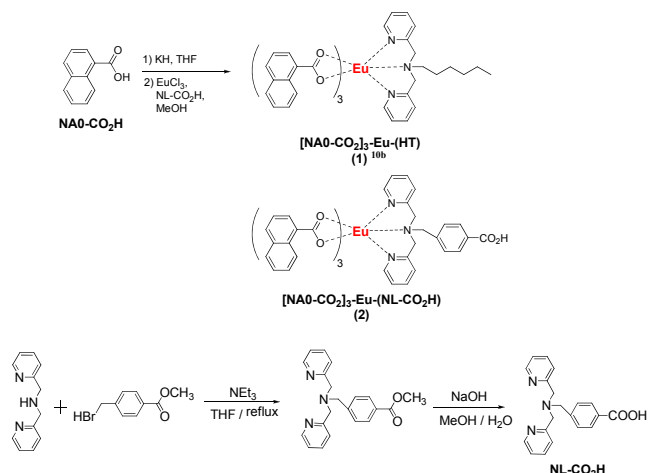
In addition to the above mentioned ff transitions in the red region, the emission spectra of **1-2** shows broad emissions in the shorter wavelength (blue) region (320-420 nm). These are much broader than the ff transitions of Eu^{III} ion and hence it is reasonable to assume that, the emission is caused by the organic moieties in complexes **1-2**. The residual emission shown by complexes **1-2** is similar in shape and position of maxima, but there is a large difference in their intensities. In complex **1**, the relative intensity of residual emission is only 50% of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{III} ion, indicating sizable energy transfer between the organic ligands and central Eu^{III} ion. On contrary the residual emission shown by **2** is greater in intensity than the Eu^{III} emission; this is in accordance with the less efficient energy transfer in complex **2**. The low energy transfer efficiency of **2** than **1** may be attributed to the nonradiative back energy transfer from the triplet state of 4-((dipyridin-2-ylamino)methyl)benzoic acid to 1-naphthoic acid. The $^5\text{D}_0$ lifetime values for complexes **1-2** were computed from the luminescence decay profile at room temperature by fitting with a monoexponential curve. The obtained values (Table 1) confirm that more nonradiative decay channels were available in **2** than **1**. Thus the intense blue emission from the organic chromophore present in **2** combine with the less efficient red emission from central Eu^{III} ion results in bright white emission. The CIE colour coordinates

calculated are ($x = 0.34$, $y = 0.36$) which represents pure white.⁷

In conclusion we have designed two new antenna complexes of Eu^{III} ion with 1-naphthoic acid by replacing the solvent molecules in the first coordination sphere with N-hexyl-N-(pyridin-2-yl)pyridin-2-amine or 4-((dipyridin-2-ylamino)methyl)benzoic acid. The complex **2** shows highly efficient white luminescence. Thus complex **2** in the present study may find potential application in the field of optoelectronics as a single molecular white emitter. Furthermore, the carboxylate group present in the nitrogen donor 4-((dipyridin-2-ylamino)methyl)benzoic acid will help this white emitting material to bind surface of TiO_2 and hence may improve the performance of DSSC. Further work in this direction is under progress in our laboratory.

Experimental procedures

General. All reagents are from Aldrich and were used as received except tetrahydrofuran (THF) which was freshly distilled from sodium-benzophenone under N_2 . 4-(4-(4-(2-Ethylhexyloxy)phenyl)naphthalen-1-yl)benzoic acid and $[\text{NAO-CO}_2]_3\text{-Eu}(\text{HT})$ were synthesized as reported.¹⁰ ^1H NMR spectra were recorded on Varian Oxford 300 MHz and chemical shifts are reported in ppm with respect to tetramethylsilane as internal standard. Infrared spectra were measured on KBr pellets using a Jasco FT/IR-4200 Spectrometer. Steady-state and time-resolved photoluminescence spectra were measured on a Fluorolog FL-3-22 spectrofluorimeter from Horiba-Jobin-Yvon Ltd. equipped with a 450W Xe-lamp and monochromator. Visible emission spectra were detected with a Hamamatsu R928 photomultiplier



Scheme 1. Synthesis procedure for Eu^{III} complexes **1-2** and 4-((bis(pyridin-2-ylmethyl)amino)methyl)benzoic acid

4-((Bis(pyridin-2-ylmethyl)amino)methyl)benzoic acid (NL-CO₂H): NEt_3 (1.4 mL, 10.04 mmol) was added to a solution of bis(2-picolyl)amine (1.18 mL, 10.04 mmol) and methyl p-(bromomethyl) benzoate (2.3 g, 10.04 mmol) in THF (80 mL), and the mixture was refluxed for 1.5 h. The mixture was allowed to reach room temperature and filtered to remove a white precipitate. After removal of the solvent, the oily residue was dissolved in Et_2O (80 mL) and filtered to remove a red solid. Evaporation of the solvent yielded 2 g (83%) of an orange oil, which was used as such in the next step. A solution of NaOH (0.8 g, 20 mmol) in 5 mL of H_2O was added to a solution of methyl 4-((bis(pyridin-2-ylmethyl)amino)methyl) benzoate (1.4 g, 4.0 mmol) in MeOH (20 mL), and the mixture was stirred for 2 h at room temperature. The pH was neutralized with 2 M HCl , followed by removal of the solvent under reduced pressure. The white residue was triturated with CHCl_3 (200 mL), followed by filtration to remove NaCl . The CHCl_3 solution was dried with MgSO_4 . Removal of the solvent under reduced pressure afforded a yellow oil, to which CH_3CN (30 mL) was added, followed by stirring. After approximately 30 min., a white precipitate formed. The solution was stored at 0°C for 2 h, to effect further precipitation and the white solid was then isolated by filtration and dried in vacuo. Yield 0.6 g (53%). Anal. Calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_2$ Exact Mass = 333.3, IR (KBr) $\text{cm}^{-1} = 1698$ (m) $\nu_{\text{C=O}}$. ^1H NMR (CDCl_3 , 300 MHz) δ 12.82 (s, 1H), 8.49 (d, 2H, $J = 4.2$ Hz), 7.91 (d, 2H, $J = 8.4$ Hz), 7.77 (t, 2H, $J = 7.6$ Hz), 7.55 (d, 2H, $J = 9.0$ Hz), 7.54 (d, 2H, $J = 7.8$ Hz), 7.24 (m, 4H), 3.71 (s, 6H), ^{13}C NMR (CDCl_3 , 226.4 MHz) δ 169.3 (C=O), 159.7, 148.3, 143.8, 137.5, 131.0, 128.7, 123.5, 122.7, 122.5, 59.7, 58.6.

Synthesis of $\text{Eu}(\text{III})$ complexes.

$\text{Eu}(\text{III})$ -cored complex was synthesized using synthetic methods previously developed by our group.^{10a} A mixture of **1** (3.0 equiv.), and KH (3.0 equiv.) was stirred in freshly distilled THF at room temperature for overnight until there was no more H_2 gas to generate. After the completion of salts, the methanol solution of anhydrous EuCl_3 (1.0 equiv.) and appropriated **2** (1.1 equiv.) added to the reaction solution, and then stirred for 2 days. The resulting solution was filtered and the solvents were removed. The resultant solid was washed sequentially with methanol, hexane and diethyl ether, yielding a white solid. Yield 54%. IR (KBr): $\text{cm}^{-1} = 3401$ ($-\text{OH}$), 1699 (C=O). Anal. Calcd. For $\text{C}_{53}\text{H}_{40}\text{EuN}_3\text{O}_8$ and C, 63.73; H, 4.04; N, 4.21; O, 12.81; Eu, 15.21. Found:

C, 63.58; H, 3.98; N, 4.19; O, 12.75; Eu, 15.17.

ACKNOWLEDGEMENT

This research was supported by the Human Resources Development Program (No. 20124010203190) of the Korean Institute of Energy Technology Evaluation and Planning (KETEP) Grant funded by the Korean Government of Knowledge Economy.

KEYWORDS: Lanthanide, Luminescence, White Emission, Antenna Molecule, *ff* Transitions

Received April 2, 2013; Accepted April 15, 2013

REFERENCES AND NOTES

1. C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker, K. Meerholz, *Nature* **2003**, *421*, 829 – 833.
2. J. Kido, M. Kimura, K. Nagai, *Science* **1995**, *267*, 1332 – 1334.
3. C.-T. Chen, *Chem. Mater.* **2004**, *16*, 4389 – 4400.
4. (a) R. Abbel, C. Grenier, M. J. Pouderoijen, J.W. Stouwdam, P. E. L. G. Leclere, R. P. Sijbesma, E. W. Meijer, A. P. H. J. Schenning, *J. Am. Chem. Soc.* **2009**, *131*, 833 – 843; (b) J. Luo, X. Li, Q. Hou, J. Peng, W. Yang, Y. Cao, *Adv. Mater.* **2007**, *19*, 1113 – 1117.
5. (a) H. Su, H. Chen, F. Fang, C. Liu, C. Wu, K. Wong, Y. Liu, S. Peng, *J. Am. Chem. Soc.* **2008**, *130*, 3413 – 3419; (b) X. Yu, H. Kwok, W.-Y. Wong, G. Zhou, *Chem. Mater.* **2006**, *18*, 5097– 5103.
6. (a) J. Liu, Y. Cheng, Z. Xie, Y. Geng, L. Wang, X. Jing, *Adv. Mater.* **2008**, *20*, 1357 – 1362; (b) J. Liu, Z. Xie, Y. Cheng, Y. Geng, L. Wang, X. Jing, F. Wang, *Adv. Mater.* **2007**, *19*, 531 – 535; (c) Y. Yang, M. Lowry, C. M. Schowalter, S. O. Fakayode, J. O. Escobedo, X. Xu, H. Zhang, T. J. Jensen, F. P. Fronczek, I. M. Warner, R. M. Strongin, *J. Am. Chem. Soc.* **2006**, *128*, 14081 –14092.
7. G. He, D. Guo, C. He, X. Zhang, X. Zhao, C. Duan, *Angew. Chem.* **2009**, *121*, 6248 –6251.
8. S. V. Eliseeva, J. -C. G. Bünzli, *Chem. Soc. Rev.*, **2010**, *39*, 189–227.
9. Z. -F. Li, L. Zhou, J. -B. Yu, H. -J. Zhang, R. -P. Deng, Z. -P. Peng, Z. -Y. Guo, *J. Phys. Chem. C* **2007**, *111*, 2295–2300.
10. (a) Oh, J. H.; Song, H. M.; Eom, Y. K.; Ryu, J. H.; Ju, M. J.; Kim, H. K. *Bull. Korean Chem. Soc.* **2011**, *32*, 2743–2750. (b) Baek, N. S.; Kim, Y. H.; Lee, D. H.; Seo, K. D.; Kim, H. K. *Bull. Korean Chem. Soc.* **2009**, *30*, 1553–1558; (c) Kim, Y. H.; Baek, N. S.; Kim, H. K. *ChemPhysChem* **2006**, *7*, 213–221; (d) Baek, N. S.; Kim, Y. H.; Roh, S. -G.; Kwak, B. K.; Kim, H. K. *Adv. Funct. Mater.* **2006**, *16*, 1873–1882; (e) Oh, J. B.; Nah, M. K.; Kim, Y. H.; Kang, M. S.; Ka, J. -W.; Kim, H. K. *Adv. Funct. Mater.* **2007**, *17*, 413–424.
11. K. Binnemans, *Chem. Rev.* **2009**, *109*, 4283–4374.
12. (a) D. B. Ambili Raj, S. Biju, M. L. P. Reddy, *Inorg. Chem.* **2008**, *47*, 8091–8100, (b) D. B. Ambili Raj, S. Biju, M. L. P. Reddy, *Dalton Trans.* **2009**, *36*, 7519–7528. (c) D. B. Ambili Raj, S. Biju, M. L. P. Reddy, *J. Mater. Chem.* **2009**, *19*, 7976–7983. (d) V. Divya, S. Biju, R. Luxmi Varma, M. L. P. Reddy, *J. Mater. Chem.* **2010**, *20*, 5220–5227.