**Eu^{3+} complex of ligand4’-(4-carboxyphenyl)-2,2’:6’,2''-terpyridine as fluorosensor of heavy metals**

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**Abstract.** Ligand 4’-(4-carboxyphenyl)-2,2’:6’,2''-terpyridine (2-Hcptpy) has been synthesized by modification of Kröhnke method. The synthesize was performed using aldol condensation reaction. The white precipitate was collected and produced 62% yield (1.062 gr). Ligand 2-Hcptpy has been characterized by FTIR, Elemental analyzer, H-NMR, UV-vis, and UV-DRS spectrometer. It was then reacted with lanthanide group (Eu^{3+}) to form a complex by hydrothermal process. The result of Eu^{3+} complex was 0.352 gr. of white yellowish precipitate. The application of this research is for the fluorosensor of heavy metals (Pb^{2+}dan Cd^{2+}). The data of fluorescence showed two types of fluorescence, either turn on or turn off fluorosensor. Ligand 2-Hcptpy has an on-off type with the addition of Pb^{2+} and Cd^{2+}, while complex Eu^{3+} has two types of fluorosensor. The complex showed turn on-off and turn on-off by addition of Pb^{2+} and type of turn off by addition of Cd^{2+}. Either ligand or complex, showed fluorescence intensity by adding heavy metals up to concentration 5x10^{-8} M.

**Keywords:** Fluorosensor, Hcptpy, lanthanide, heavy metals.

**1. Introduction**

The lanthanides are unique among other elements. It has shielding effect by 4f orbitals resulting in the spectroscopic properties. The result of having a narrow-line emission is a wide range wavelength of the emission bands that do not overlap noticeably, and long life-time fluorescent to distinguish the background of fluorescence [1-3]. The complex compound between lanthanides and fluorophore organic ligand could form a fluorosensor. These properties attract some interests, for example to detect some metals or to apply as labeling agent, and also potential for heterogeneous catalysis [4-6].

Free lanthanide ions follow Laporte rule, thus it has a low extinction coefficient. The organic ligands which have fully π-π* transitions are able to pull through the lowlight absorbance of lanthanide [7-9]. Some organic ligands with functional group such carboxylic acid has the ability to work as sensitizer for lanthanide ions. Thus organic ligand with functional group could exhibit higher fluorescent stabilities than other sensitizers. The complex compound formed between sensitizer and lanthanide ions have been widely studied as fluorescence [4].

The organic ligand with functional group of carboxylic acid has been developed for several applications. Its fascinating structure lead some interests in **bifunctional function**, such as to act as bridge or chelating group to form building blocks by forming some linkage between carbonyl and metal ions, while the organic ligand of terpyridyl group can act as linker to extend network such as forming polymerization. To fulfill good connection of electron transport between the donor and acceptor is supported by the Hcptpy itself which has a large π-conjugated system [10].
2. Materials and methods

The 2-Hcptpy ligand and Eu$^{3+}$ complex were prepared according to the literature [10] with some modification. The ligand was prepared using aldol condensation by Kröhnke method while the lanthanide complex by hydrothermal processes. All chemicals were obtained from commercial sources without further purification. The chemicals used were 2-acetylpyridine (Sigma-Aldrich), 4-carboxybenzaldehyde (Sigma-Aldrich), KOH (Merck), NH$_3$.H$_2$O (Merck), Ethanol p.a (Merck), Methanol p.a (Merck), HCl (Merck), Eu$_2$O$_3$ (Merck), HNO$_3$ (Merck), Cd(NO$_3$)$_2$.4H$_2$O (Merck), and Pb(NO$_3$)$_2$ (Merck). While the instrumentation used to determine the structure and molecular structure of ligand and complex was Elemental TrueSpec LECO. $^1$H NMR spectra were recorded at room temperature using JEOL 500 MHz apparatus with tetramethylsilane (TMS) as reference and DMSO as solvent. Infrared spectra were obtained from KBr pellets on Shimadzu 8400-S in the range of 400-4000 cm$^{-1}$, while the emission spectra fluorescence were recorded on a Hitachi F-2000 spectrophotometer.

2.1. Synthesis of ligand 2-Hcptpy

Ligand 2-Hcptpy was prepared according to the literature method with some modification by one-pot synthesis [4]. The reaction process used aldol condensation reaction between 2-acetylpyridine (1.21 g) and 4-carboxybenzaldehyde (0.75 g) in basic condition by using KOH (0.8 g) and NH$_3$.H$_2$O (20 mL) in 150 mL ethanol as solvent. The reaction mixture was stirred for 48 hours at room temperature for a while, then continued with the addition of HCl [aq., conc.] until slightly acidic (reached around pH 5). The result was light yellow precipitate then continued by washing it with mixture of ethanol and methanol by ratio of 1:1 until the precipitate changed into slightly white color. The precipitate was collected and dried in vacuum. The result was 1.09 g (62%). Based on the data, following are the result found for C$_{22}$H$_{15}$N$_3$O$_2$ (353.11 g/mol); C, 74.37; H, 5.39; N, 11.96. IR (KBr, cm$^{-1}$): 3061 (w), 1696 (s), 1579 (s), 1462 (m), 1363 (w), 1267 (s), 857 (w), 759 (w), 681 (w). $^1$H-NMR (500 MHz, DMSO-d$_6$). $\delta$: 8.76 (s, 1H), 8.68 (t, 3H), 8.17 (d, 2H), 7.76 (d, 2H), 7.56 (d, 2H).

2.2. Synthesis of Eu$^{3+}$ complex

Complex of Eu$^{3+}$ was prepared according to the literature method with some modification by hydrothermal process [5]. The reaction consist of Ln(NO$_3$)$_3$.6H$_2$O (1 mmol), 2-Hcptpy (1 mmol), and NaOH (1 mmol) in 100 mL deionized water at 150°C for 72 h. After cooling to room temperature at a rate 10°C/h, the separation process was performed by filtering the light brown precipitate and dried in vacuum until the humidity was lower than the initial condition. The result was 0.36 g. The data of elemental analyzer found for C$_{88}$H$_{57}$N$_{12}$O$_8$ (1561.07 g/mol) are C, 67.27; H, 6.73; N, 10.4. The IR spectra should be 3070 (m), 2560 (m), 2285 (m), 1960 (s), 1276 (s), 869 (s), 798 (s), 594 (m).

3. Results and discussion

3.1. Characterization of ligand and complex

The synthesis of 2-Hcptpy was used aldol condensation reaction by Kröhnke method with some modification. The reaction was done in one-pot synthesized with high yield percentage and simple preparation. Ligand of 2-hcptpy was characterized by infrared spectroscopy, H-NMR, elemental analyzer, and UV-DRS spectroscopy. The complexation process with Eu$^{3+}$ was adapted by hydrothermal process with some modification. The confirmation for the complexation reaction was performed by infrared spectra that showed the absence of the strong bands at around 1700 cm$^{-1}$. It indicated that the carbonyl group of ligand 2-Hcptpy were completely deprotonated. The other way to confirm the complexation successfully was by UV-DRS spectroscopy. The spectra showed band gap energy was decreased from ligand 2-Hcptpy to complex. Ligand 2-Hcptpy had a band gap of 2.89 eV, while Eu$^{3+}$ complex had 2.67 eV.
3.2. Fluorescence properties

The ligand and complex were used as fluorosensor of heavy metals. Both compounds were added with heavy metals in various concentrations (5x10^{-4} – 5x10^{-8}) M. It showed that either ligand or complex was given fluorescence response by heavy metals addition up to 5x10^{-8} M. The data of fluorescence intensity of ligand and complex are shown in figure 1. The detection mechanism of heavy metals was conducted by PET (Photoinduced Electron Transfer) process. Fluorescence intensity of ligand was 170 a.u. while Eu^{3+} complex was 130 a.u. The band gap of complex was decreased from its ligand with fluorescence intensity. The addition of heavy metals to ligand or complex produced a quenching effect by decreasing the fluorescence intensity and an enhancement effect by showing increasing fluorescence intensity.

4. Conclusions

The synthesis of ligand 2-Hcpty was done by Kröhnke method with some modification. The synthesis reaction was using aldol condensation with the yield of 62%. Eu^{3+} complex preparation was done by hydrothermal process with result of 0.35 gram. The confirmation of complexation was done by infrared spectra by showing the absence of carbonyl group at 1700 cm\(^{-1}\) and hydroxyl group at 3300 cm\(^{-1}\). The other characterization to confirm the complexation was performed by UV-DRS spectroscopy. It showed
that band gap energy from ligand and complex was decreased from 2.89 eV to 2.67 eV. The fluorescence properties of ligand and complex with the addition of heavy metals in various concentrations (5\times10^{-4} – 5\times10^{-8}) M showed a quenching effect of fluoresensor. The confirmation of quenching effect was showed by the decrease of fluorescence intensity before heavy metals was added into solution. The ligand showed a turn-off fluorosensor while Eu^{3+} complex showed a turn on and off fluorosensor.

**Acknowledgements**

This work was supported by university of Indonesia

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