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Transition metal complexes of 4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine as fluorosensor sodium ion

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Abstract. Ligand 4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine has been synthesized using Kröhnke method by aldol condensation reaction. The solid brown precipitate was collected and resulted 40% yield. The ligand was characterized by 1H-NMR spectrometer, IR spectrophotometer, elemental analyzer, UV-Vis spectrometer, and spectrofluorometer. The complexation of ligand was done by chelating method with transition metal (Cu²⁺, Zn²⁺). The complex compounds have been confirmed by UV-Vis spectrophotometer from absorbance spectrum data. The data showed a new peak at wavelength 236 nm for Cu²⁺ complex and 233 nm for Zn²⁺ complex. The application of ligand 4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine and complex compounds is as fluorosensor of sodium ion. The intensity of fluorescence was determined by spectrofluorometer. The addition of various concentrations of sodium ion into ligand and complex compounds (Cu²⁺, Zn²⁺) changed the intensity of fluorescence. The fluorescence data of ligand showed the on-off type while Cu and Zn complex showed the off-on type. The on-off type fluorescence was indicated by decreasing intensity and the off-on by increasing intensity. Both ligand and complex compound showed a wavelength shift when sodium ion was added into solution.

1. Introduction
Recently, the progress of fluorescence based on organic compound has been developed [1-3]. The recent research about fluorescence was used to detect some heavy metals [4]. Fluorescence is one of the types of luminescence which based on excited electromagnetic wavelength. When the substance absorbs some energy at a specific wavelength and releases energy in terms of light in short lifetime, it produces fluorescence that used as sensor.

Most organic compounds which have aromatic or heterocyclic system with π-conjugated system, for example derivatives pyridine, azatriphenylene, and terpyridine, show a higher possibility for a fluorescence characteristic [4]. Fluorescence detection in complex compound is considered to be effective for sensing, owing to the complex compounds’ longer lifetime than organic compound [5]. The longer lifetime is able to reduce the interference that comes from another compound, and therefore increases the fluorescence sensitivity [6].

In fluorescence mechanism, the ligand acts as fluorophore, therefore, the type of ligand affects the chemo sensor. The most common ligand used for chemo sensor are 2,2’:6’,2”-terpyridine and its derivatives, because terpyridine have high binding affinity [7, 8]. The photophysical properties of 2,2’:6’,2”-terpyridine are unique and have strong binding affinity to some metals. In order to achieve these goals, the terpyridine must be substituted to C-4’ position [7-9]. This research used ligand...
4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine that complexed with transition metals Cu$^{2+}$ and Zn$^{2+}$. The previous research about this ligand had been conducted by Bo et al. [10]. This ligand has phi-conjugated system that helps to form a good connection between donor and acceptor electron.

2. Materials and methods

2.1. Materials

The 4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine ligand was prepared according to the literature, with some modification, while Cu$^{2+}$ and Zn$^{2+}$ complex was done by chelating process. All chemicals were obtained from commercial sources without further purification. The chemicals used were 2-acetylpyridine from commercial sources without further purification. The chemicals used were 2-acetylpyridine (Sigma-Aldrich), 4-nitrobenzaldehyde (Sigma-Aldrich), KOH (Merck), NH$_3$.H$_2$O (Merck), Ethanol p.a (Merck), Methanol p.a (Merck), Cu(NO$_3$)$_2$.6H$_2$O (Merck), Zn(NO$_3$)$_2$.4H$_2$O (Merck), and NaCl (Merck). Elemental analysis (C, H, and N) were performed with an Elemental TruSpec LECO. $^1$H NMR spectra were recorded at room temperature using JEOL 500 MHz apparatus and tetramethylsilane (TMS) as reference and CDCl$_3$ as solvent. Infrared spectra were obtained from KBr pellets on Shimadzu 8400-S in the range 400-4000 cm$^{-1}$. Emission spectra were recorded on a Hitachi F-2000 spectrophotometer at room temperature.

2.2. Synthesis of the ligand 4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine [10]

Synthesis of ligand 4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine: solution of 2-acetylpyridine (5 g, 41.5 mmol) and nitrobenzaldehyde (3.17 g, 21 mmol) in methanol (175 mL) was stirred vigorously with 15% KOH aqueous solution (15 mL) and NH$_3$.H$_2$O (150 mL) concentrate for 3 days at room temperature. The dark brown precipitate was collected by vacuum filtration, washed with water until pH = 7 and dissolved in CH$_2$Cl$_2$. The organic fraction was washed with 1% NaHCO$_3$ aqueous solution, dried with anhydrous MgSO$_4$ and evaporated to give 2.933 g crude ligand 4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine (yield 40%). Analytic calculation for C$_{26}$H$_{14}$N$_2$O (354.11) are C, 71.11; H, 4.77; N, 15.09. The results are C, 74.37; H, 5.39; N, 11.96. IR (KBr, cm$^{-1}$): 1315 (s), 1500 (s), 1494 (m), 1401(m), 1388 (w), 1118 (m), 870 (w), 769 (w), 702 (w), 617 (w). $^1$H NMR (CDCl$_3$): $\delta$ (ppm) = 8.66 (d, 2H), 8.62 (s, 2H), 8.59 (d, 2H), 7.71 (td, 2H), 7.27 (dd, 2H), 6.73 (d, 2H). ESI-MS:m/z = 325.2 [MH$^+$].

3.3. Synthesis of Cu$^{2+}$ complex

Cu(NO$_3$)$_2$.6H$_2$O (0.234 g, 0.64 mmol) in methanol (15 mL) was poured to solution of 4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine (0.2 g, 0.64 mmol) in CH$_2$Cl$_2$ (10 mL). The color of the reaction mixture turned to brown immediately. After stirring for 24 h at room temperature, a brown dark green crystals. IR (KBr, cm$^{-1}$): 1315 (s), 1500 (s), 1494 (w), 1401(w), 1388 (w), 1118 (m), 870 (w), 769 (w), 702 (w), 617 (w).

3.4. Synthesis of Zn$^{2+}$ complex

Zn(NO$_3$)$_2$.4H$_2$O (0.146 g, 0.64 mmol) in methanol (15 mL) was added to solution of 4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine (0.2 g, 0.64 mmol) in CH$_2$Cl$_2$ (10 mL). The color of the reaction mixture turned to brown immediately. After stirring for 24 h at room temperature, a brown precipitate was obtained. The solid was then washed with cold methanol (5 mL) and cold diethyl ether (10 mL), and finally dried over silica gel. Recrystallization in warm DMF generated the cuprum complex, [Cu(4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine)(NO$_3$)$_2$], 0.14 g (64%), as pale brown crystals. IR (KBr, cm$^{-1}$): 1315 (s), 1500 (s), 1494 (w), 1401(w), 1388 (w), 1118 (m), 870 (w), 769 (w), 702 (w), 617 (w).

3. Results and discussion

3.1. Synthesis and characterization of ligand 4’-(p-nitrophenyl)-2,2’:6’,2”-terpyridine and complex Cu$^{2+}$ and Zn$^{2+}$

Based on the graph above, new peaks at wavelength 239 nm, 236 nm, 233 nm, and 230 nm were
observed respectively for Fe complex, Zn complex, Cu complex, and Ni complex. It caused by electron transition from its metals that have d-d orbital. The result was a shifting wavelength and decreasing molar absorptivity. The functional group of NO$_2$ caused a shifting wavelength to the blue shift. It happened because of the functional group does not have an electron lone pair.

3.2. Fluorescence properties

Both ligand and complexes ML(NO$_3$)$_2$ have concentration of 500 μM and dissolved in methanol-dichloromethane by ratio 3:1. While sodium solution concentration ranged from 1 to 100 μM. Before the fluorescence intensity of ligand and complexes were determined, the first step was scanning the wavelength to determine the wavelength number with the highest excitation and emission intensity of ligand and complexes. The scanning measurement was done in the range 220-600 nm. The fluorescence data was plotted between wavelength and emission intensity or excitation intensity (figure 1).

3.3. Mechanism detection of Na analyte was based on PET process

It could be interpreted that NO$_2$ was as receptor and terpyridine was ligand, while benzene as σ-linker. There were two interaction possibilities when analyte interacts with ligand or complexes compound. The possibilities were turn on or turn off process. Based on the data above, it showed that the addition of sodium ion caused a fluorescence intensity change and wavelength shift. The shift of wavelength was

![Figure 1. The fluorescence data of (a) ligand, (b) Cu and (c) Zn complexes by adding heavy metals in various concentrations.](image-url)
Figure 2. The fluorescence data of ligand and complex by adding heavy metals in various concentrations.

from 283 nm to 285 nm and fluorescence intensity decrease caused a quenching effect or turn off fluorescence.

Cu and Zn complex shifted the wavelength from 278 nm to 273 nm and 282 nm to 287 nm, respectively. Both complexes showed an increase of fluorescence intensity. Based on that data, it showed an enhancing fluorescence or turn on mechanism. By addition of 1 μM sodium ion, the response of fluorescence intensity was still observed (figure 2). Based on that data of fluorescence, it can be concluded that both ligand and complexes were sensitive for sodium ion detection.

4. Conclusions
Ligand 4’-(p-nitrophenyl)-2,2':6',2”-terpyridine had been synthesized using Kröhnke method by aldol condensation reaction. The solid brown precipitate was collected and resulted 40% yield. The fluorescence data of ligand showed the on-off type while Cu and Zn complex showed the off-on type. The on-off type fluorescence was indicated by decreasing intensity and the off-on by increasing intensity. Both ligand and complex compound shifted the wavelength when sodium ion was added into solution. By addition of 1 μM of sodium ion, the response of fluorescence intensity was still observed. Based on the data of fluorescence, it can be concluded that both ligand and complexes were sensitive to detect sodium ion.

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