Ligand 4’-(4-carboxyphenyl)-2,2’:6’,2”-terpyridine grafted with TiO₂ – complexation with the ions metal transition and application as fluorosensor for Na⁺ ion

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Abstract. Ligand 4’-(4-Carboxyphenyl)-2,2’:6’,2”-Terpyridine (Hcptpy) has been synthesized using reaction of aldol condensation. The result was white-yellowish precipitate with yield of 62%. The Ligand hcptpy was grafted with TiO₂ by mass ratio 0.15 : 1 (wt/wt). The Hcptpy-TiO₂ was reacted in complexation reaction with transition metals (Fe, Mn, Ni) by chelating method, with the best mole chelating ratio of 0.15 : 1 (mole/mole). The ligand Hcptpy, Hcptpy-TiO₂ and complex assembly M-Hcptpy-TiO₂ were characterized by CHN Analyzer, HNMR, FT-IR, UV-VIS, and UV-DRS. The application of this research was to apply it as fluorosensor for sodium metal ion in sodium chloride. The study was conducted by spectrofluorometer. Types of fluorescent for sodium metal ion detection are Chelation Quenching Effect (on-off signal) and the Chelation Enhanced Fluorescence effect (off-on signal). The type of on-off signal causes a quenching in fluorescence intensity, while the off-on signal causes an increase in fluorescence intensity. The result showed that Hcptpy-TiO₂, Ni-Hcptpy-TiO₂ were the off-on fluorescence type with the ability to respond the presence of sodium ion at concentration 3 x 10⁻¹⁰ M and 3 x 10⁻⁹ M, respectively. While Mn-Hcptpy-TiO₂ and Fe-Hcptpy-TiO₂ were the on-off signal type with the ability to respond the presence of sodium metal ion at concentration 3 x 10⁻⁸ M and 3 x 10⁻⁸ M, respectively. The process of sodium metal ions detection was carried out by substitution reaction of metal ion in complex with sodium metal ions.

Keywords: 4’-(4-carboxyphenyl)-2,2’:6’,2”-terpyridine (Hcptpy), semiconductor TiO₂, complex compound, fluorosensor, transition metals, complex assembly M-hcptpy-TiO₂

1. Introduction

The effective fluorescence sensor for metal ions is a system that interact with the presence signal of metals ions in solution by the changes of fluorescence properties, such as wavelength or emission intensity that different from free metals ions sensor. It consists of one or more fluorophore connected with active coordination species through spacer [1]. Fluorescent chemosensor usually can be found in organic compounds that has π-conjugate system [2]. It generates a better fluorescence in terms of selectivity and practical applications for sensing method [3]. The fluorescence probe based on complex compounds has advantages in sensing method, such as longer lifetime of fluorescence and also wider stokes shift than organic fluorophore [4]. Fluorescence probe for metal ions sensor could be an organic molecule that can interact with a metal ion, either active or inactive [5]. Li et al. [6] has synthesized ligand 4’-(4-carboxyphenyl)-3,2’:6’,3”-terpyridine (3-Hcptpy) and complex compound of 3-hcptpy
with zinc metal and the result showed a good intensity of fluorescence. Griffith et al. [7] reported that terpyridine has fluorescence properties in gel instead of sol form to detect sodium metal ions. The formed gel can give respond to the presence of sodium ions up to 98%-99.2%. Yang et al. [8] reported that the luminescence properties of complex compound Zn-Hcptpy have photofluorescence properties in solid state at room temperature condition.

The assembly of electron donor and acceptor plays a role in solar cell conversion. The synthesis of this assembly complex compound consists of TiO$_2$ nanoparticle as an electron acceptor, and the organic linker to absorb the visible light and also complex of Mn as an electron donor [9-11]. Alec C. Durrell et al. [12] reported that the effect of linker and anchoring to stabilize the assembly tpy-L-Anchor-TiO$_2$ as highly turn-on fluorescence type, for an example the assembly of Mn(II)-L-TiO$_2$ with sensitivity detection up to nanomolar detection. This research was to synthesize and characterize the hcptpy grafting-TiO$_2$ (Hcptpy-TiO$_2$) and M-Hcptpy-TiO$_2$ to obtain the role of TiO$_2$, diamagnetic metals and paramagnetic metals into complex assembly for electron transfer process and the fluorescence intensity shift, and to study the assembly ligand, hcptpy grafting TiO$_2$ and M-hcptpy-TiO$_2$ as fluorescent chemosensor for Na-metal ion.

2. Materials and methods

2.1. Materials

The preparation of ligand hcptpy was performed according to the literature with some modifications [6]. Synthesis of Hcptpy-TiO$_2$ and M-Hcptpy-TiO$_2$ were prepared by modification of solvent (wudu ding). All other chemicals used were obtained from commercial source without further purification, such Merck and Sigma Aldrich. TruSpec LE CO CHN Elemental analyzer was applied to determine the percentage of C, H, and N. $^1$H-NMR spectra were recorded at room temperature using JNM ECA 500 MHz. Infrared spectra were obtained from KBr pellet on Shimadzu IR 8400-S in the range 400-4000 cm$^{-1}$. Emission spectra were recorded by UV-Vis fluorescent (Shimadzu UV-1601, Shimadzu UV-2450) and Spectrofluorometer (Hitachi F-2000).

2.2. Synthesis of ligand 2-Hcptpy

Preparation: 2-acetylpyridine (1.21 g, 10 mmol) was added to the stirring solution of 4-carboxybenzaldehyde (0.75 g, 5 mmol), KOH (0.8 g, 14 mmol) and NH$_2$OH (20 mL) in 150 mL ethanol. The reaction mixture was stirred at room temperature whilst open to air for 48 h, until the colloid suspension is formed, indicated by the change of brown to yellow color. After that, the solution was adjusted to slightly acidic (pH 5) with the addition of HCl (aq., conc.). The light yellow precipitate product was filtered, recrystallized with a mixture of ethanol and methanol, and dried in vacuum to collect the colorless crystals. The results was 1.31 g (62%). Analysis for C, H, and N. $^1$H-NMR spectra were recorded at room temperature using JNM ECA 500 MHz. All other chemicals used were obtained from commercial source without further purification, such Merck and Sigma Aldrich. TruSpec LE CO CHN Elemental analyzer was applied to determine the percentage of C, H, and N. $^1$H-NMR spectra were recorded at room temperature using JNM ECA 500 MHz. Infrared spectra were obtained from KBr pellet on Shimadzu IR 8400-S in the range 400-4000 cm$^{-1}$. Emission spectra were recorded by UV-Vis fluorescent (Shimadzu UV-1601, Shimadzu UV-2450) and Spectrofluorometer (Hitachi F-2000).

2.3. Synthesis of Hcptpy-TiO$_2$ and M-Hcptpy-TiO$_2$

Hcptpy-TiO$_2$ was prepared by stirring degussa P25 TiO$_2$ (1 g, 12.5mmol) with mass variation of ligand Hcptpy [0.1 g (0.28 mmol), 0.15 g (0.42 mmol), 0.2 g (0.56 mmol), and 0.3 g (0.84 mmol)] in 75 mL of DCM in reflux at temperature 40°C for 6 h. The suspension was cooled and filtered, and the white solid was washed with DCM then dried in vacuum. The best mole ratio of Hcptpy-TiO$_2$ used for complexation with the transition metals (MnSO$_4$·H$_2$O, FeCl$_2$·4H$_2$O, Ni(NO$_3$)$_2$·3H$_2$O) were 1:1, 1:0.3, and 1:0.15, respectively. All the transition metal was dissolve with 20mL of mQ water then added with Hcptpy-TiO$_2$ in 20 mL of DCM and ethanol mixture (1:1), next stirred for 6 h at room temperature. The surface of complex assembly was denoted as M-Hcptpy-TiO$_2$. The solid suspension was filtered and washed with the mQ water and dried in vacuum.
2.4. Characterization of Hcptpy-TiO$_2$ and M-Hcptpy-TiO$_2$

The samples were measured by UV-Vis spectroscopy with solvent of diethylether: ethanol (1:1) which showed the best mass and mole ratio to be used in fluorescence studies. To characterize UV-DRS measurement, the samples were collected as dry material and measured with BaSO$_4$ pellet. The data of UV-DRS showed the energy gap of the complex assembly, while the data of FT-IR spectra showed the binding of carboxylate linker on Degussa P25 TiO$_2$, and also the interaction of transition metal ions with the ligand terpyridine.

2.5. Fluorescence studies

The excited and emission band of each sample were measured by Fluorescence Spectrophotometer Hitachi F-2700. The emission band of sample appeared at wavelength 470 nm, while excited spectra was recorded in the range 220-600 nm.

3. Results and discussion

3.1. Synthesis of ligand Hcptpy

Synthesis of Hcptpy with aldol condensation reaction method of 2-acetyl pyridine and 4-carboxybenzaldehyde in ethanol and methanol medium (figure 1). The potassium hydroxide was added as catalysis base to play the role in formation of enolate, while ammonium hydroxides was added to close the chain ring in terpyridine, thus 4-(4’-Carboxyphenyl)-2,2’:6’,2”-terpyridine compound was obtained.

3.2. Synthesis of Hcptpy-TiO$_2$

The Grafting process occurred because of the carbonyl group in ligand that act as an anchor forced to bind with TiO$_2$ through covalent and covalent coordination bonds (figure 2). The best ratio of mass for grafting was 1 : 0.15 (wt:wt). Spectra FTIR in figure 3a of shows a decrease of vibration intensity of C=O at 1700 cm$^{-1}$ and 2500 cm$^{-1}$ while spectrum UV-VIS in figure 3b shows an adsorption transition orbital of $\sigma\rightarrow\sigma^*$ at wavelength 290 nm. The synthesis reaction of Hcptpy-TiO$_2$ occurred by the formation of bidentate bonds of carboxylic to Ti. The formed Hcptpy-TiO$_2$ bond is able to enhance the probability of electrons moving from HOMO to LUMO when the ligand adsorbs UV light.

The UV-DRS spectra is shown in figure 4a and the resulted plot in figure 4b showed that energy gap after grafting with TiO$_2$ increased from 2.89 eV to 3.21 eV. These changes occurred due to interaction between the p-orbitals from anchored to the d-orbital of the free TiO$_2$. The interaction was mutually reinforced to generate an increase in energy gap.

![Figure 1. Scheme synthesis of Hcptpy](image-url)
Figure 2. Scheme Hcptpy grafting TiO<sub>2</sub>

Figure 3. (a) Spectra FTIR and (b) UV-VIS absorbance spectra of Hcptpy-TiO<sub>2</sub>

Figure 4. (a) UV-VIS DRS spectra and (b) energy gap of Hcptpy-TiO<sub>2</sub> (1 : 0.15)

3.3. Synthesis M-Hcptpy-TiO<sub>2</sub>

The formation of complex between terpyridine ligand and transition metal through chelating method. The formation of complex assembly through photoinducted electron transfer, which the metal ion acts as electrons donor and the ligand terpyridine as adsorber of UV light, while the carboxylic group as an anchor in transferring electron to TiO<sub>2</sub>. The TiO<sub>2</sub> acts as electron acceptor which also adsorbs the UV light (figure 5). The best mole ratio of complex formation was 1 : 0.15. Figure 6 shows the results of
FT-IR measurement, the ratio showed a low interaction bonding between metal and terpyridine at 1260 cm\(^{-1}\), and low site interaction bonding between carbonyl group and TiO\(_2\) at 2500 cm\(^{-1}\).

Figure 7 shows an electronic transition in d-d orbitals that affecting in a decrease of molar efficiency and wavelength shifting towards hypochromatic shift. The DRS spectra of complex assembly M-Hcptpy-TiO\(_2\) is shown in figure 8a. The decrease of the energy gap (figure 8b) of complex assembly M-Hcptpy-TiO\(_2\) caused by the chelation of metals, which had a weak bonding that caused decrease of gap energy.

3.4. Studies of complex assembly (Mn, Fe, Ni) M-Hcptpy-TiO\(_2\)

Photoinduced Electrons Transfer (PET) [1] in figure 9 occurred when the chromophore adsorbs the UV light, then the electron will be excited from HOMO to LUMO, therefore no electrons in the ground state. Electron in metals (Mn, Fe, Ni) will inject an electrons to HOMO in ligand terpyridine, and the electrons move to be anchored by energy and forces of scattering electrons. The electron injection process from an anchor to TiO\(_2\) will occur in interfacial electron system to conduct in TiO\(_2\) band.

When the electrons are scattering fast enough, the recombination of electrons occurs. The undesired recombination will occur. Photoinduced electrons transfer is activation process that involves an internal oxidation-reduction reaction between the excited state of fluorophore and another species that able to donate or accept an electron. The properties of excited state of the species are different from the ground state.
3.5. Fluorescence studies

Quenching effect in fluorescent happened when terpyridine adsorbs some UV light. The excitation process of chromophore ligand occurred from HOMO to LUMO. The electrons in LUMO has a short relaxation then continue emit to conduction band of paramagnetic metals. The result was magnetic resonance that triple state condition. An enhancement effect in fluorescent happened when the terpyridine adsorbs some UV light. The excitation process of chromophore ligand occurred from HOMO to LUMO. The electrons in LUMO has a short relaxation then continued emission to conduction band of diamagnetic metals. The results was magnetic resonance with singlet state condition.
3.6. Addition of Na\(^+\) ion to Hcptpy-TiO\(_2\) and Ni-Hcptpy-TiO\(_2\)

Figure 10a show the increase of fluorescent emission intensity. The Hcptpy-TiO\(_2\) (3 x 10\(^{-6}\) M), change from 157.2 a.u to 970 a.u (by addition of Na\(^+\) \(10^{-4}\) M) 83.8% and 788.9 a.u (by addition of Na\(^+\) \(10^{-6}\) M) 80%, at the wavelength 246.5 nm. It indicated that Na\(^+\) was able to interact with the N-atoms in the ligand. The posibility interaction was chelation process with off-on (turn-on) fluorescent type. While figure 10b shows the limited respond of Hcptpy-TiO\(_2\) to detect the presence of Na\(^+\) ions up to \(10^{-10}\) M by showing the increase of fluorescent intensity up to 62.6%. In figure 11b, the Ni-Hcptpy-TiO\(_2\) (3 x \(10^{-9}\) M) change from 53.48 a.u to 1088 a.u (by addition of Na\(^+\) \(10^{-4}\) M) 95.1% to 475.1 a.u (by addition of Na\(^+\) \(10^{-6}\) M) 88.7%, at wavelength 246.5 nm. The possible interaction of Ni\(^2+\) metal ion was substitution reaction in complex with the Na\(^+\) ions and the type of fluorescent was the off-on (turn-on) type. Figure 11b shows the limited response of Ni-Hcptpy-TiO\(_2\) to detect the presence of Na\(^+\) ions up to \(10^{-9}\)M with the decrease of fluorescent intensity at 46%.

3.7. Influence of Na\(^+\) ions addition in Mn-Hcptpy-TiO\(_2\) and Fe-Hcptpy-TiO\(_2\) assembly

Figure 12a shows the decrease of fluorescent emission intensity of Mn-Hcptpy-TiO\(_2\) (3 x \(10^{-6}\)M) change from 32.28 a.u to 30.32 a.u (by addition of Na\(^+\) \(10^{-4}\) M) 6.07% to 26.59 a.u (by addition of Na\(^+\) \(10^{-6}\) M) 17.6%, at 246.5 nm. It indicated that Na\(^+\) was able to interact with the N-atoms in the ligand. Figure 13a
Figure 12. Fluorescent emission intensity of Mn-Hcptpy-TiO$_2$ concentrate with the addition of Na$^+$ and (b) limited response of Mn-Hcptpy-TiO$_2$ to the presence of Na$^+$ ions.

Figure 13. Fluorescent emission intensity of Fe-Hcptpy-TiO$_2$ concentrate with the addition of Na$^+$ and (b) limited response of Fe-Hcptpy-TiO$_2$ to the presence of Na$^+$ ions.

shows the decrease in fluorescent emission intensity of Fe-Hcptpy-TiO$_2$ (3 x 10$^{-6}$ M) changed from 155.1 a.u to 25.88 a.u (by addition of Na$^+$ 10$^{-4}$ M) 83.3% to 28.5 a.u (by addition of Na$^+$ 10$^{-6}$ M) 81.6%, at the wavelength 246.5 nm. The possible interaction was the substitution process of Mn$^{2+}$ and Fe$^{2+}$ in complex with Na$^+$ ions, with on-off (turn-off) fluorescent type. Figure 12b shows the limited response of Mn-Hcptpy-TiO$_2$ to detect the presence of Na$^+$ ions up to 10$^{-8}$ M, with the decrease of fluorescent intensity at 67%, while Fe-Hcptpy-TiO$_2$ detected the presence of Na$^+$ ions up to 10$^{-8}$ M, with the decrease of fluorescent intensity at 90% (figure 13b).

4. Conclusions

The characteristics of complex assembly through PET process, the transition metal ions act as electron donor while ligand terpyridine as the UV light adsorber with the anchoring carboxylic group as linker to inject an electron from ligand to TiO$_2$. The TiO$_2$ act as electron acceptor, also to follow and assist the ligand to adsorb some UV light. The transfer process of an electron from transition metal to ligand is in accordance with charge transfer. The studies of fluorescent in assembly compounds have 2 types. The first type is Chelation Quenching Effect (decreased intensity fluorescent) (on-off signal) showed by Mn-Hcptpy-TiO$_2$ and Fe-Hcptpy-TiO$_2$ (paramagnetic metals) and the second type is Chelation Enhanced effect (off-on signal) showed by Hcptpy-TiO$_2$ and Ni-Hcptpy-TiO$_2$ which enhance the fluorescent intensity (diamagnetic metals). Generally all the complex assembly can detect Na$^+$ ion in some concentrations.
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