

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 (Hcpty) has been synthesized using reaction of aldol condensation. The result was white-yellowish precipitate with yield of 62%. The Ligand hcppty was grafted with TiO₂ by mass ratio 0.15 : 1 (wt/wt). The Hcpty-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 Hcpty, Hcpty-TiO₂ and complex assembly M-Hcpty-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 Hcpty-TiO₂, Ni-Hcpty-TiO₂ were the off-on fluorescence type with the ability to respond the presence of sodium ion at concentration 3×10^{-10} M and 3×10^{-9} M, respectively. While Mn-Hcpty-TiO₂ and Fe-Hcpty-TiO₂ were the on-off signal type with the ability to respond the presence of sodium metal ion at concentration 3×10^{-8} M and 3×10^{-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 (Hcpty), semiconductor TiO₂, complex compound, fluorosensor, transition metals, complex assembly M-hcpty-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 fluoressensor 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-Hcpty) and complex compound of 3-hcpty



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-Hcpty 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 TiO₂ 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-TiO₂ as highly turn-on fluorescence type, for an example the assembly of Mn(II)-L-TiO₂ with sensitivity detection up to nanomolar detection. This research was to synthesize and characterize the hcpty grafting-TiO₂ (Hcpty-TiO₂) and M-Hcpty-TiO₂ to obtain the role of TiO₂, diamagnetic metals and paramagnetic metals into complex assembly for electron transfer process and the fluorescence intensity shift, and to study the assembly ligand, hcpty grafting TiO₂ and M-hcpty-TiO₂ as fluorescent chemosensor for Na⁺ metal ion.

2. Materials and methods

2.1. Materials

The preparation of ligand hcpty was performed according to the literature with some modifications [6]. Synthesis of Hcpty-TiO₂ and M-Hcpty-TiO₂ were prepared by modification of solvent (*wendu ding*). All other chemicals used were obtained from commercial source without further purification, such Merck and Sigma Aldrich. TruSpec LECO CHN Elemental analyzer was applied to determine the percentage of C, H, and N. H¹-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-Hcpty

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 NH₄OH (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 C₂₂H₁₅N₃O₂ (353.11): C, 74.78; H, 4.28; N, 11.89 showed the result as follows C, 74.37; H, 5.39; N, 11.96%. IR (KBr, cm⁻¹): 3445(s), 1715(s), 1631(m), 1490(w), 1400(m), 1255(w), 1118(m), 870(w), 769(w), 702(w), 617(w). H¹ NMR (400 MHz, DMSO-d₆).

2.3. Synthesis of Hcpty-TiO₂ and M-Hcpty-TiO₂

Hcpty-TiO₂ was prepared by stirring degussa P25 TiO₂ (1 g, 12.5mmol) with mass variation of ligand Hcpty [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 Hcpty-TiO₂ used for complexation with the transition metals (MnSO₄·H₂O, FeCl₂·4H₂O, Ni(NO₃)₂·3H₂O) were 1:1, 1:0.3, and 1:0.15, respectively. All the transition metal was dissolved with 20mL of mQ water then added with Hcpty-TiO₂ 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-Hcpty-TiO₂. The solid suspension was filtered and washed with the mQ water and dried in vacuum.

2.4. Characterization of Hcpty-TiO₂ and M-Hcpty-TiO₂

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 BaSO₄ 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 TiO₂, 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 Hcpty

Synthesis of Hcpty 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 Hcpty-TiO₂

The Grafting process occurred because of the carbonyl group in ligand that act as an anchor forced to bind with TiO₂ 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 Hcpty-TiO₂ occurred by the formation of bidentate bonds of carboxylic to Ti. The formed Hcpty-TiO₂ 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 TiO₂ 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 TiO₂. The interaction was mutually reinforced to generate an increase in energy gap.

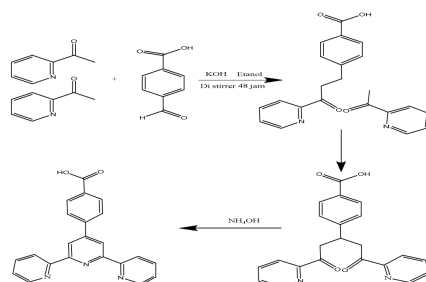
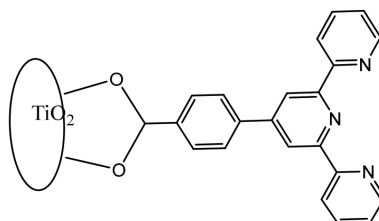
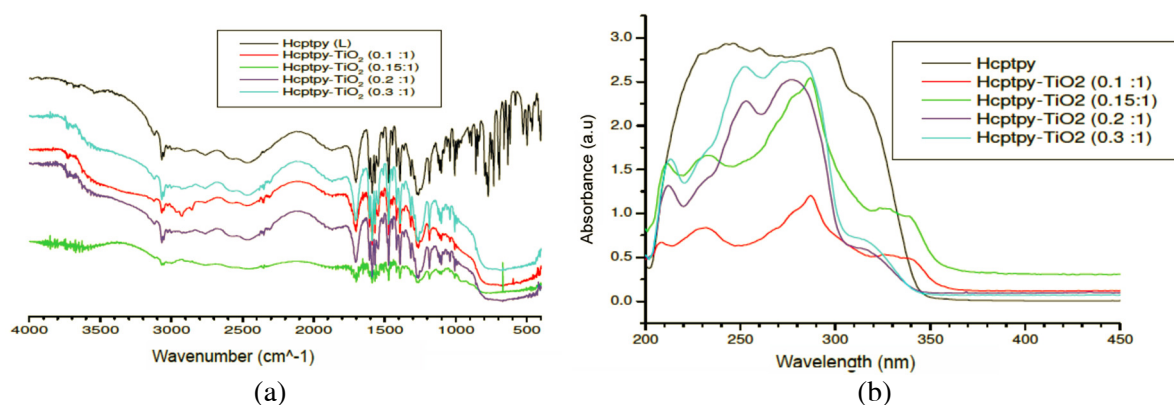
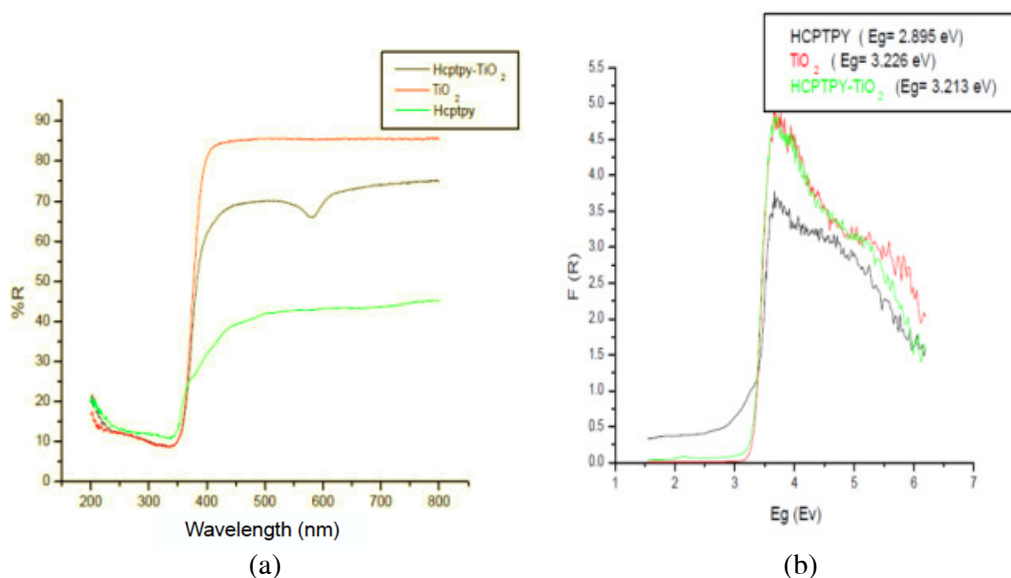


Figure 1. Scheme synthesis of Hcpty

**Figure 2.** Scheme Hcpty grafting TiO_2 **Figure 3.** (a) Spectra FTIR and (b) UV-VIS absorbance spectra of Hcpty- TiO_2 **Figure 4.** (a) UV-VIS DRS spectra and (b) energy gap of Hcpty- TiO_2 (1 : 0.15)

3.3. Synthesis M-Hcpty- TiO_2

The formation of complex between terpyridine ligand and transition metal through chelating method. The formation of complex assembly through photoinduced 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_2 . The TiO_2 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-Hcpty-TiO₂ is shown in figure 8a. The decrease of the energy gap (figure 8b) of complex assembly M-Hcpty-TiO₂ 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-Hcpty-TiO₂

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 TiO₂ will occur in interfacial electron system to conduct in TiO₂ 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

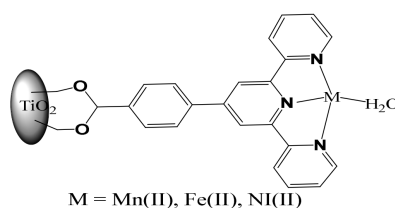


Figure 5. Functionalization M-Hcpty-TiO₂

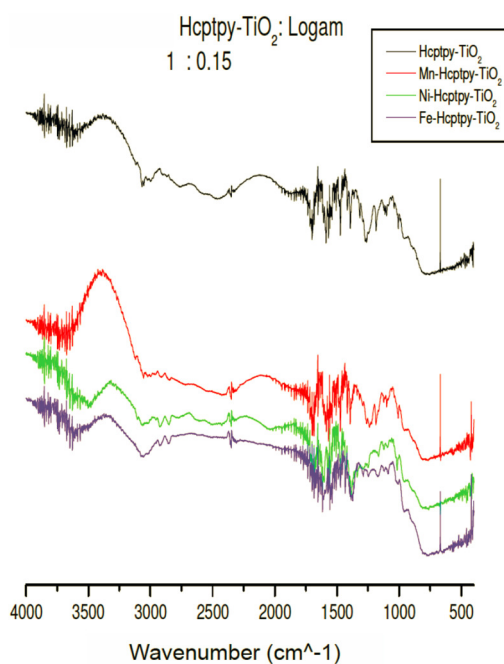


Figure 6. FTIR Spectra of M- Hcpty-TiO₂

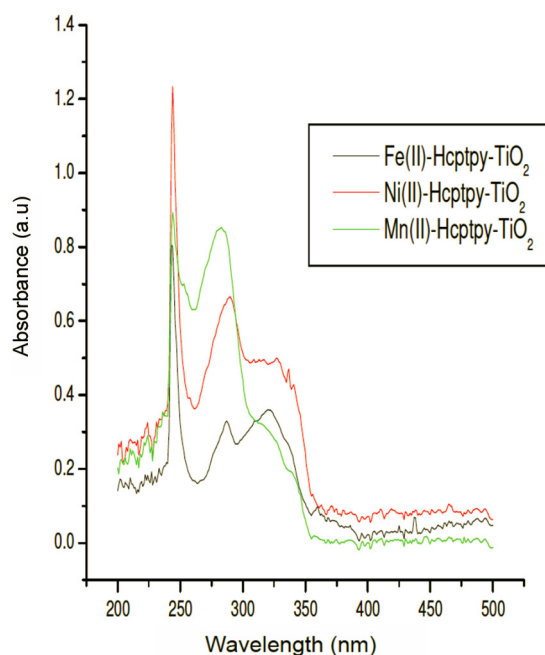


Figure 7. UV-VIS absorbance of M- Hcpty-TiO₂

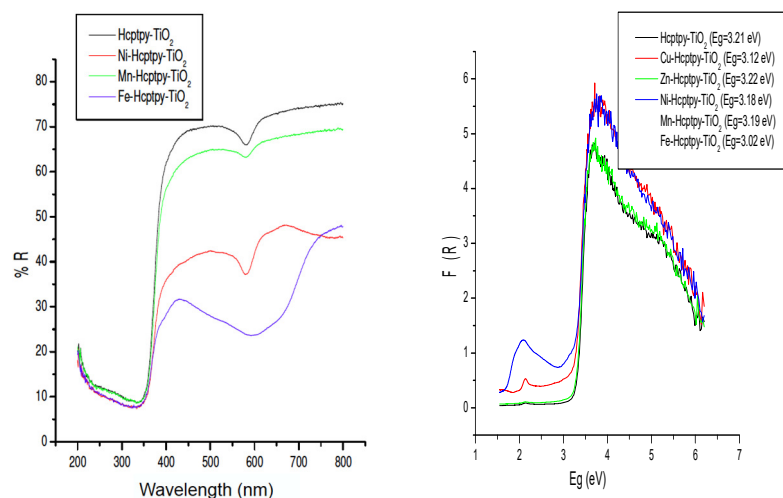


Figure 8. (a) UV-VIS DRS spectra and (b) energy gap of M- Hcpty-TiO₂ (1 : 0.3) mol.

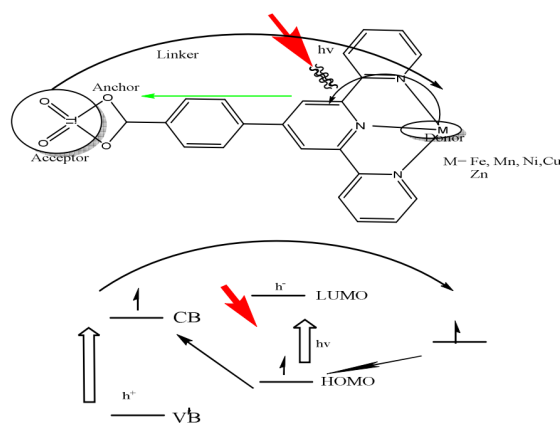


Figure 9. PET of M-Hcpty-TiO₂ [1]

state due to the energy content. The excited state of reduction-oxidation reaction is stronger than the ground state. The PET process takes place in coordinating atom which has lone pair of electrons. The presence of ion metal coordination atom causes lower energy of lone pair electron. The PET process in fluorescent process did not cause any spectroscopic shift in the emission band upon a complexation. Its process is strongly depended on the polarity of solvent which effecting the oxidation of lone pair electrons. As the consequence, the PET plays a role in quenching effect. The process of fluorescent occurs more quickly in polar solvent.

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 Hcpty-TiO₂ and Ni-Hcpty-TiO₂

Figure 10a show the increase of fluorescent emission intensity. The Hcpty-TiO₂ (3×10^{-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 possibility interaction was chelation process with off-on (turn-on) fluorescent type. While figure 10b shows the limited response of Hcpty-TiO₂ 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-Hcpty-TiO₂ (3×10^{-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-Hcpty-TiO₂ 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-Hcpty-TiO₂ and Fe-Hcpty-TiO₂ assembly

Figure 12a shows the decrease of fluorescent emission intensity of Mn-Hcpty-TiO₂ (3×10^{-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

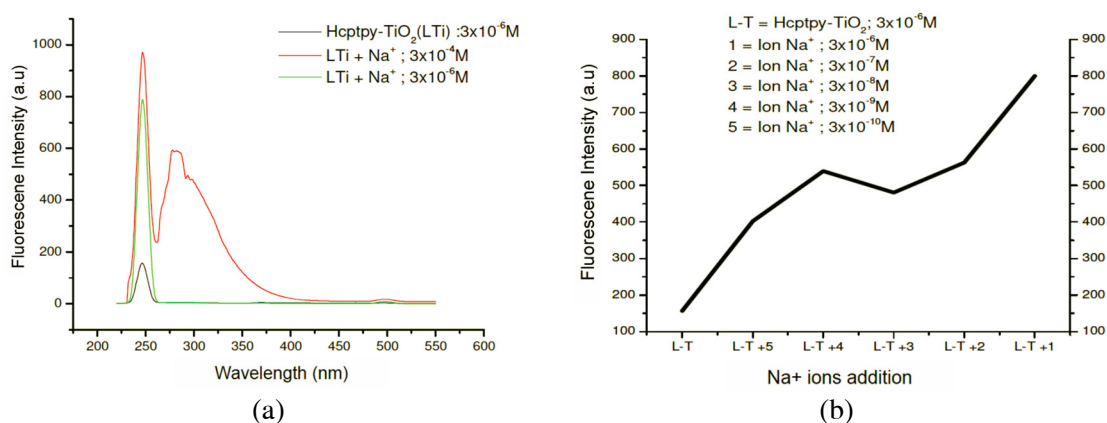


Figure 10. Fluorescent emission intensity of Hcpty-TiO₂ concentrate with the addition of Na^+ and (b) limited response of Hcpty-TiO₂ to the presence of Na^+ ions

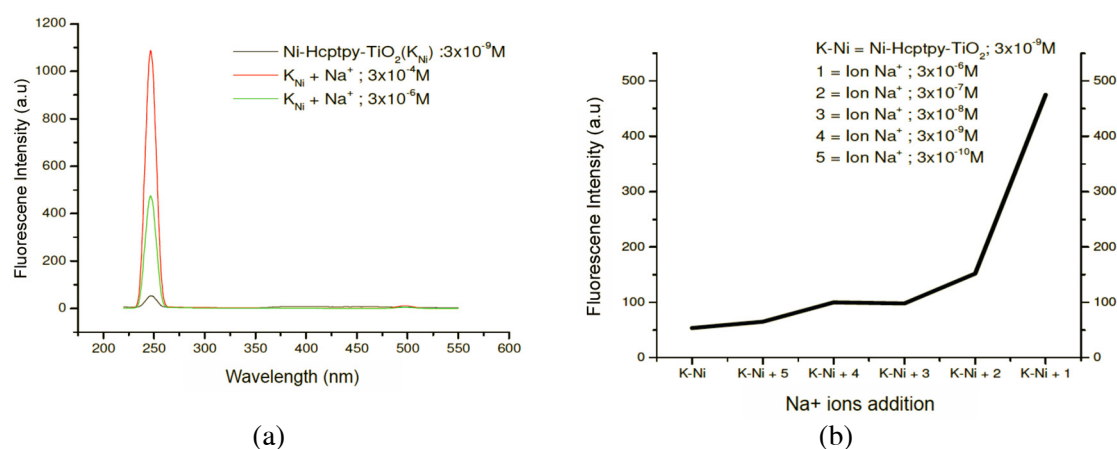


Figure 11. Fluorescent emission intensity of Ni-Hcpty-TiO₂ concentrate with the addition of Na^+ and (b) limited response of Ni-Hcpty-TiO₂ to the presence of Na^+ ions

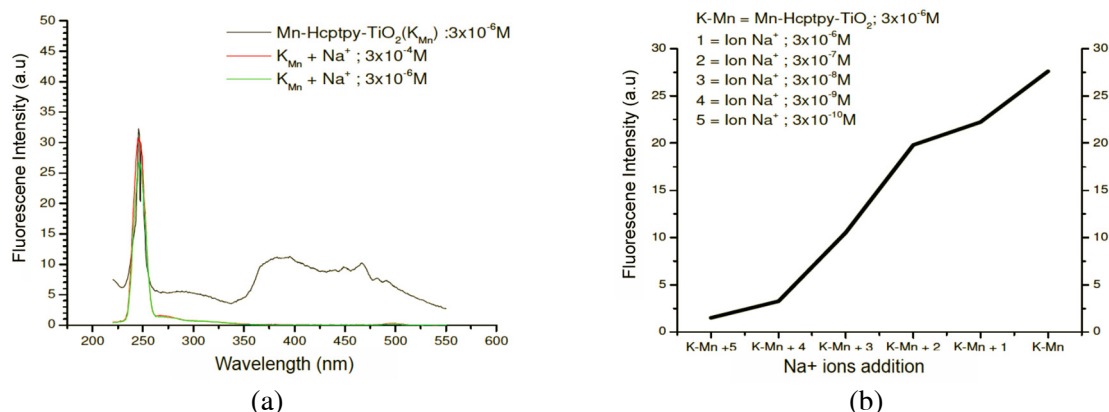


Figure 12. Fluorescent emission intensity of Mn-Hcptpy-TiO₂ concentrate with the addition of Na⁺ and (b) limited response of Mn-Hcptpy-TiO₂ to the presence of Na⁺ ions

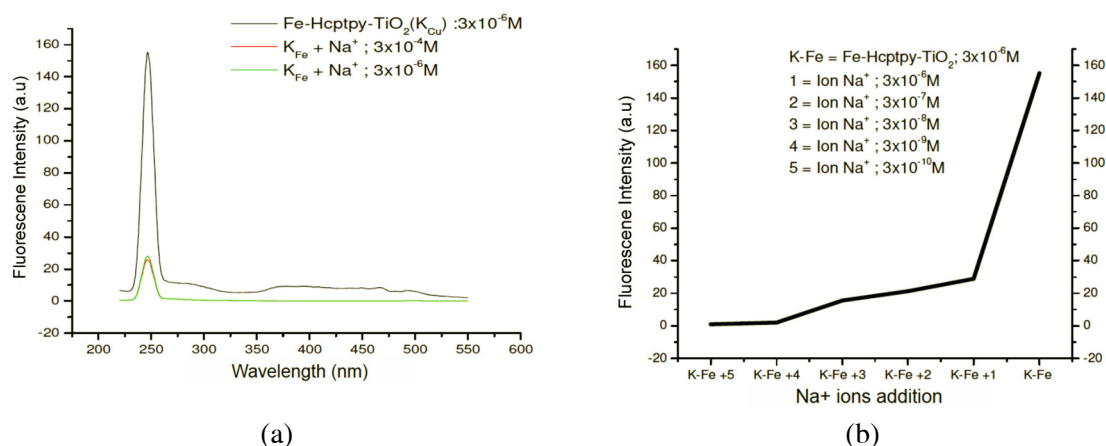


Figure 13. Fluorescent emission intensity of Fe-Hcptpy-TiO₂ concentrate with the addition of Na⁺ and (b) limited response of Fe-Hcptpy-TiO₂ to the presence of Na⁺ ions

shows the decrease in fluorescent emission intensity of Fe-Hcptpy-TiO₂ (3 × 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 Mn²⁺ and Fe²⁺ in complex with Na⁺ ions, with on-off (turn-off) fluorescent type. Figure 12b shows the limited response of Mn-Hcptpy-TiO₂ to detect the presence of Na⁺ ions up to 10⁻⁸ M, with the decrease of fluorescent intensity at 67%, while Fe-Hcptpy-TiO₂ 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 TiO₂. The TiO₂ 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-TiO₂ and Fe-Hcptpy-TiO₂ (paramagnetic metals) and the second type is *Chelation Enhanced effect (off-on signal)* showed by Hcptpy-TiO₂ and Ni-Hcptpy-TiO₂ which enhance the fluorescent intensity (diamagnetic metals). Generally all the complex assembly can detect Na⁺ ion in some concentrations.

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