SYNTHESIS AND PHOTOLUMINESCENCE PROPERTIES OF ALKYLBROMOPORPHYRIN

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ABSTRACT

The usage of porphyrin as a light-harvesting chromophore is considered as one of the keys to obtaining low-cost and high-efficiency dye-sensitized solar cell (DSSC). In this paper, a novel porphyrin, 5,10,15-tris(nitrophenyl)-20-(p-(11-bromo)dodecoxyphenyl))porphyrin, having a long alkyl chain and three nitro groups was synthesized. The nitro groups serve as anchoring groups to TiO_2 surfaces and long alkyl chain prevents unwanted dye aggregation. The porphyrin was synthesized by condensation of *p*-(12-Bromododecoxy)benzaldehyde and pyrrole in propionic acid according to an adaptation of the general Rothemund method [1]. *p*-(12-Bromododecoxy)benzaldehyde was synthesized by nucleophilic substitution reaction between 4-hydroxybenzaldehyde and 1,12-dibromododecane in acetone. The reaction products were analyzed by ^{1}H-NMR and mass spectroscopy. The absorption and fluorescence spectra of the porphyrin were also recorded. As results, the absorption spectrum of the porphyrin consists of a strong Soret and four weak Q-band. Compared to 5,10,15-tris(nitrophenyl)-20-(p-(11-bromo)dodecoxyphenyl))porphyrin spectrum, there is no wavelength shifting because of the incorporation of the alkyl chain. The fluorescence spectrum of the porphyrin shows two characteristic emission bands and the intensity ratio of those emission bands is always constant when irradiated by different excitation wavelength related to Soret and Q-band.

Keyword: DSSC, porphyrin, absorption spectrum, emission spectrum.

INTRODUCTION

Porphyrins and their derivatives are one of the important chromophores for DSSC with high efficiency because of their chemical stability, intrinsic spectroscopic properties, and their electronic levels can be rationally manipulated by chemical modification [2, 3, 4, 5]. A series of zinc *meso*-tetraphenylporphyrin (TPP) [6] and 4-methylTPP [7] containing carboxylic acid anchoring group and they showed the power conversion efficiency (η) of 5.6% and 7.1% respectively. In addition to widely used carboxylic acid anchoring group, He *et al.* found that very strong adsorption of porphyrin DPZn on TiO_2 surface was obtained when 8-hydroxyquinoline was utilized as anchoring group attaining η-value of 3.09% [8].

However, since some attempts to utilize porphyrin as potential sensitizers for

DSSCs have been made, the power conversion efficiency (η) of porphyrin based DSSCs is still low. One of vital parameters for porphyrin to be used as a sensitizer in DSSC is having good electronic coupling to TiO_2 surface and it can be achieved by utilizing a anchoring group bonded strongly to TiO_2 surface [9]. Another parameter is reducing undesirable dye aggregation [5]. Both parameters determine the efficiency of charge transfer between porphyrin and TiO_2 surface therefore they determine the cell performance.

In an attempt to further improve the efficiency of porphyrin based DSSC, we have synthesized a novel 5,10,15-tris(nitrophenyl)-20-(*p*-(11-bromo) dodecoxyphenyl))porphy-rin **2** with a long alkyl chain and nitrophenyl groups. Porphyrin **2** that has not been synthesized before has three nitrophenyl groups and one long alkylbromide group attached on the core of porphyrin via β-position. It was previously shown that the nitro groups served as electron-withdrawing groups and can be used as new types of anchoring groups to TiO_2 surfaces [10]. This type of anchoring group is responsible for strong bonding and good electronic coupling to the TiO_2 surface. In addition, the long alkyl chain on non-porphyrin dyes can prevent intermolecular interaction and charge recombination, resulting in an improvement of DSSC performance [11,12] and stability [13].

METHODS

1. Materials

4-hydroxybenzaldehyde ($C_7H_6O_2$, MW 122.12, purity >98.0%), 1,12 dibromodo-decane ($C_{12}H_{24}Br_2$, MW 328.13 purity >98.0%), benzaldehyde (C_7H_6O, MW 106.12, purity >98.0%), and *p*-nitrobenzaldehyde ($C_7H_5NO_3$, MW 151.12, purity >98.0%) and pyrrole (C_4H_5N, MW 67.09, purity >99.0%), chloranil ($C_6HCl_4O_2$, MW 245.86, purity >98.0%) was were purchased from Tokyo Chemical Industry. Propionic acid ($C_3H_6O_2$, MW 74.08, purity >99.0%), K_2CO_3 (MW 138.21, purity >99.0%), $MgSO_4$ (MW 120.37, purity >98.0%), BF_3-diethyl ether complex ($C_4H_{10}BF_3O$, MW 141.93, purity 48.0 – 54.0%) and organic solvents (purity >99%) such as acetone, hexane and CH_2Cl_2 were purchased from Merck Millipore. All materials were used without further purification.

2. Apparatus

^1H NMR spectra were recorded in deuterated chloroform on ECS400 (400 MHz) spectrometers relative to the TMS as internal standard. Mass spectra were recorded using matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometer. UV-Vis absorption spectra and fluorescence spectra were recorded in dichloromethane solution with a Shimadzu UV-3150 double-beam spectrophotometer and a JASCO FP-6600 spectrometer respectively.

3. Synthesis

a. *p*-(12-Bromododecoxy)benzaldehyde (1)

To a solution of 4-hydroxybenzal-dehyde (2.0 g, 16.40 mmol, 1 eq) and K_2CO_3 (3.97 g, 28.7 mmol) in 20 mL of acetone, 1,12-dibromododecane (16.14 g, 49.2 mmol, 4 eq) in 5 ml of acetone was added at room temperature and the resulting mixture was

refluxed for overnight. The solvent was removed via rotary evaporation. The residue was redissolved in 20 mL CH_2Cl_2 and washed several times with water. After drying over $MgSO_4$, the solvent was evaporated and the residue was purified by column chromatography using hexane/CH_2Cl_2 (1:4, v/v, Rf 0.4). The second fraction was collected and the solvent was evaporated to get yellowish residue. Recrystallization by CH_2Cl_2/hexane afforded 4-(12-bromo-dodecyloxy)benzaldehyde as a white solid (4.8 g; yield 80%).
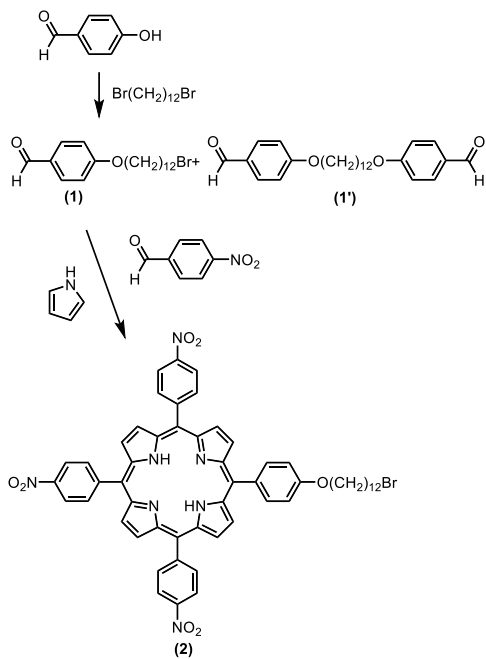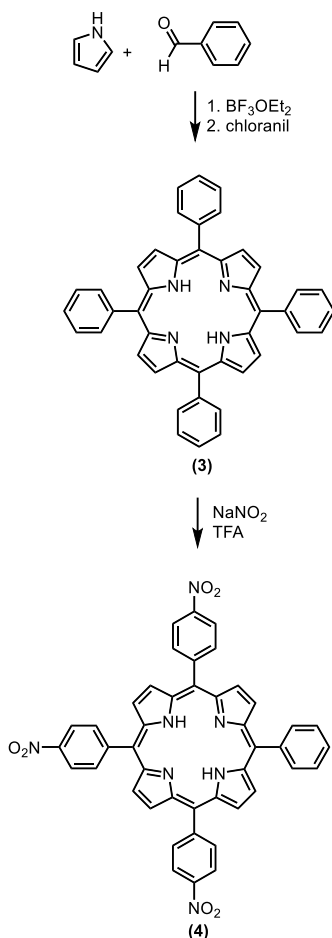

Scheme 1

b. 5,10,15-tris(nitrophenyl)-20-(*p*-(11-bromo)dodecoxyphenyl))porphyrin (2)

The porphyrin **2** was synthesized according to an adaptation of the general Rothemund method[1]. Benzaldehyde **1** (1.388 g, 3.8 mmol, 1 equiv.) and *p*-nitrobenzaldehyde (1.705 g, 11.3 mmol 3 equiv.) were added to refluxing propionic acid (85 mL). Once the aldehydes had completely

dissolved, freshly distilled pyrrole (1.7 mL, 4 equiv.) was added and refluxed for 1 h. The reaction mixture was then cooled and allowed to stand overnight. After diluting with distilled water and adjusting the pH to 6–7 with aqueous sodium hydroxide (6 mol L^{-1}), filtration and washing with hot water and methanol were performed. The crude product was separated using silica gel column chromatography with dichloromethane as eluent. The second fraction (Rf 0.3) was collected and the solvent was evaporated to afford porphyrin **2** as a crystalline dark purple solid (119 mg, yield 3%).

c. Synthesis of 5,10,15,20-Tetraphenyl-porphyrin (3)

Porphyrin **3** was synthesized using a method proposed by Lindsey [14]. Briefly, to a stirred solution of benzaldehyde (3.0 ml, 28.96 mmol, 1 eq) in dry CH_2Cl_2 (2 L) was added pyrrole (2.08 ml, 29.76 mmol, 1.03 eq) at room temperature under nitrogen atmosphere. After 15 min, BF_3etherate (0.55 µL, 0.93 mmol) was added. After 1 h, *p*-chloranil (5.560 g, 22.4 mmol) was added and the solution was stirred for 1 h at 45 °C. Then the solvent was evaporated and the solid was purified using silica chromatography with CH_2Cl_2 as eluent (Rf 0.9). Solvent evaporation gave dark purple solid (1.842 g, yield 47%). MS (MALDI) m/z 614.5 (M^+); ^1H NMR (400 MHz, CD_3Cl) δ = 8.84 (s, 4H, *β*-pyrrole), 8.21 (dd, J = 7.1, 1.6 Hz, 4H, *o*-phenyl), 7.82 – 7.68 (m, 6H, *m- and p*-phenyl), -2.77 (s, 1H, NH). Those spectral matched with published data [15]: 8.85, 8.28, 7.75, 7.77, -2.79.

Scheme 2

d. Synthesis of 5,10,15-Tris(4-nitrophenyl)-20-phenylporphyrin (4)

Modified Luguya [16] procedure was used for preparing porphyrin **4**. To a solution of **3** (500 mg, 0.814 mmol) in tetrafluoroacetic acid (25mL) and CH_2Cl_2 (20 mL) was added sodium nitrite (562 mg, 8.14 mmol). After 2 h stirring at room temperature, the reaction was neutralized with saturated $NaHCO_3$ solution. The mixture was extracted with dichloromethane (6x25 mL). The organic layers were washed once with saturated aqueous $NaHCO_3$ and once with water before being dried over anhydrous Na_2SO_4. The solution was filtrated and vacuum evaporated. To purify the product, silica

column chromatography was used with $CHCl_3$ as eluent. After solvent evaporation, the product was 435 mg (71%) dark red solid. MS (MALDI) m/z 749.1 (M+); ^{1}H NMR (400 MHz, CD_3Cl) δ = 8.94 (d, J = 4.87 Hz, 2H, *β*-pyrrole), 8.82 (s, 4H, *β*-pyrrole), 8.78 (d, J = 5.37 Hz, 2H, *β*-pyrrole), 8.67 (m, 6H, *o*-phenyl-NO_2), 8.42 (m, 6H *m*-phenyl-NO_2), 8.22 (m, 2H, *o*-phenyl), 7.80 (m, 3H, *m*-and *p*-phenyl), -2.80 (s, 1H, NH). Those spectral matched with published data [16] : -2.80 (br, 2H), 7.80 (m, 3H), 8.20 (m, 2H), 8.40 (d, J=7.50 Hz, 6H), 8.65 (d, J=7.50 Hz, 6H), 8.80 (m, 6H), 8.93 (d, J=5.0 Hz, 2H).

RESULTS AND DISCUSSION

Synthesis of tetraphenylporphyrin **3** involves the condensation reaction between four benzaldehydes and four pyrroles in the presence of an acid catalyst. Derivation of atom H on phenyl ring can be conducted by two different approaches. The first method is the selective substitution reaction after TPP synthesis [17,18], and the second is by using substituted benzaldehyde precursor before TPP synthesis [19]. Although the first method seems plausible, the proper method to selectively substitute atom H on phenyl group of TPP has not been found. Therefore, the products are a mixture of mono-, di-, tri- and multi substitution with different substitution position resulting in difficulty in purification processes.

In this research, the second method was chosen. The substituted benzaldehyde (1) was synthesized by nucleophilic substitution reaction between hydroxy-benzaldehyde and dibromododecane in a basic condition to facilitate deprotonation of

hydroxyl group as shown in Scheme 1. Considering two bromide substituents were present on dibromododecane molecule, two substitution reactions on both sides of alkyl chain were possible to happen resulting monosubstituted **1** and disubstituted **1'** products. To minimize the amount of disubstituted product **1'**, an excess amount of 1,12-dibromododecane was used.

After column chromatography, three fractions were obtained. The first fraction was unreacted dibromododecane, the second fraction was target product **1**, and the third fraction was disubstituted product **1'**. The target molecule **1** is the major product in this synthesis reaction. The ^{1}H-NMR of the three molecules is shown in Figure 1.

Figure 1**Error! Reference source not found.** shows that the difference between the three spectra is only on the triplet peak at ~3.40 ppm corresponding to the methylene groups attached by bromine (-CH$_2$Br) [20]. The triplet peak appears on dibromododecane and benzaldehyde **2** and it disappears on by-product. It means that all bromide atoms on by-product **1'** has been subtituted. The chemical shift of all peaks and their integration confirms the structure of compounds **1** and **1'**.
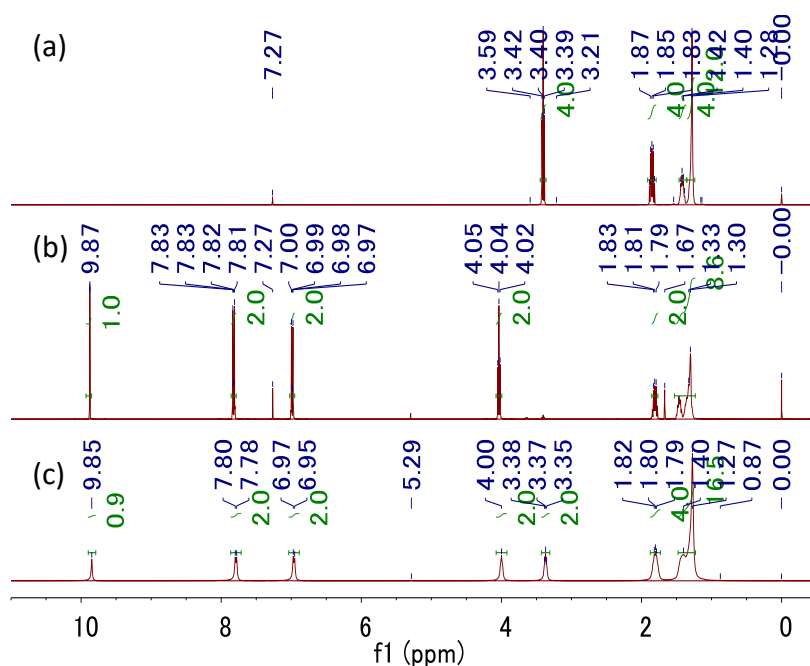

Figure 1. ^{1}H-NMR spectra of (a) dibromo-dodecane, (b) by-product **1'**, and (c) benzaldehyde **1**.

The porphyrin **2** was synthesized according to an adaptation of the general Rothemund method [1]. This method is suitable to synthesize nitroporphyrin because nitroporphyrin has low solubility in a common organic solvent such as dichloromethane.

The reaction between two different benzaldehydes affords six different products and two among them are *cis-trans* isomers. The mass spectra of the crude product is shown in.**Error! Reference source not found.**
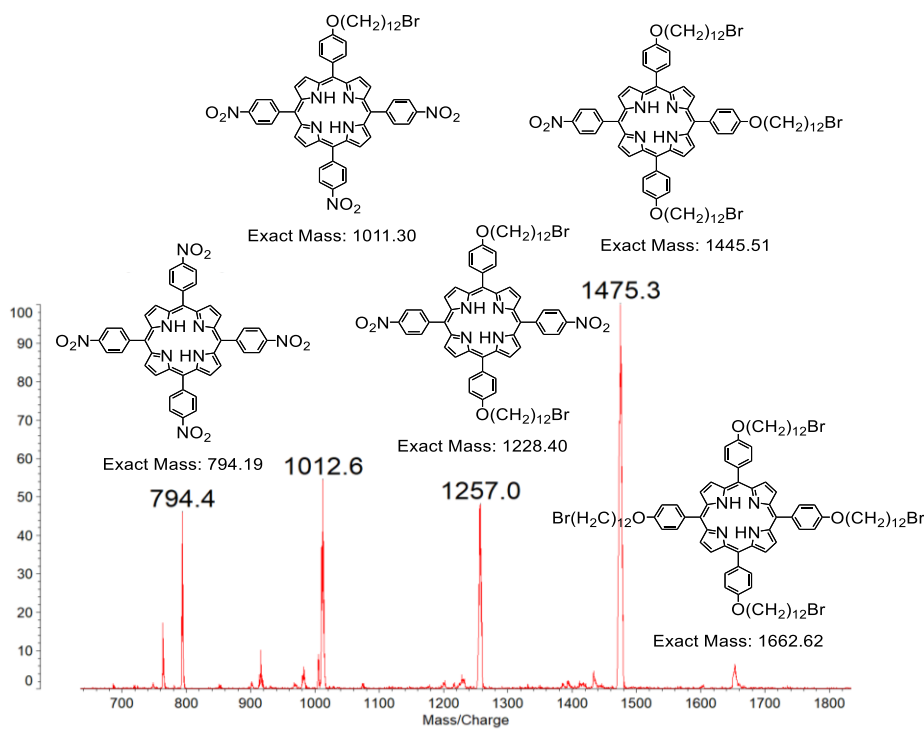
Figure 2 Mass spectrum of crude product of porphyrin **2**

Figure 2**Error! Reference source not found.** shows that five peaks are corresponding to five different porphyrin. The dinitroporphyrin has two different isomers, mainly *cis* and *trans* isomer and both isomers give the same m/z ratio on a peak of 1257. The trinitroporphyrin **2** as a target product gives peak at 1012.6. The percent yield of trinitroporphyrin **2** is only 3%, smaller compared to dinitro, mononitro and zeronitro products. A direct nitration reaction on porphyrin also produces a lower percentage yield of trinitro product than that of dinitro and mononitro products [21]. The low percent yield can be attributed to the low solubility of the nitroproduct in common organic solvents such as dichloromethane, hexane or methanol.
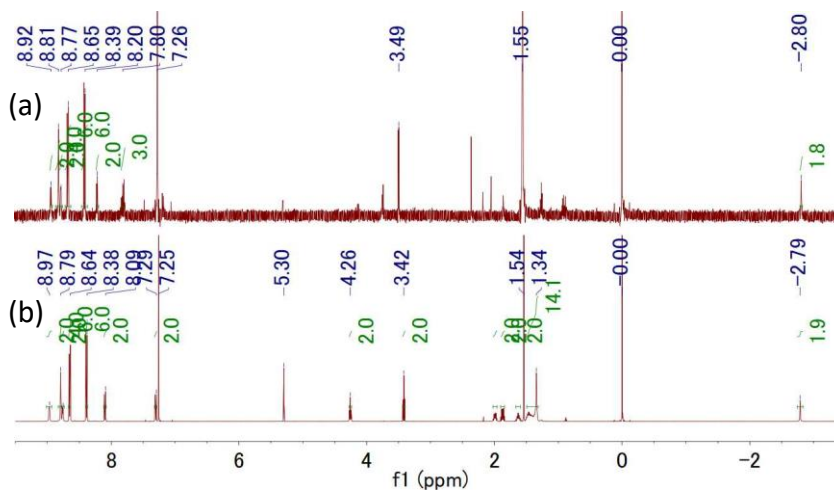
Figure 3. ^{1}H-NMR spectra of (a) porphyrin **4** and (b) porphyrin **2**.

The ^{1}H-NMR spectra of porphyrin **2** and porphyrin **4** as comparison are shown in Figure 3**Error! Reference source not found.**. Same as porphyrin **2**, porphyrin **4** has three nitro groups but it does not have an alkylbromide group. As shown in Figure 3**Error! Reference source not found.**, both porphyrin have a characteristic peak at the aromatic region (8.92; 8.81; and 8.77) belonging to H of pyrrole groups. The chemical shift different is only ~0.02 ppm. The significant peak shifting only appears at H of aromatic phenyl directly bonded by alkylbromide group. The peak of 8.20 shifted to 8.09 ppm for meso position and the peak of 7.80 shifted to 7.29 ppm for ortho position with concerning alkylbromide group. This suggests that the addition of long alkylbromide group does not affect the porphyrin core electronically. The alkylbromide position is far from porphyrin core, separated by phenyl group, therefore the inductive effects of alkylbromide to porphyrin core is not significant.
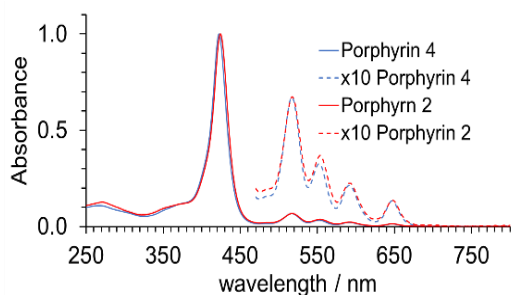

Figure 4. Normalized UV-Vis absorption spectra of porphyrin **2** and **4**. Dash lines obtain from absorbance multiplied by ten to enlarge the spectra at Q band region.

As shown in Figure 4**Error! Reference source not found.**, both porphyrins have overlapping absorption spectra. A strong Soret band absorption appears at 424 nm and four weak Q-bands absorptions appear at 517, 554, 592, and 648 nm. The Soret and Q-bands in porphyrin are caused by $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ transitions respectively [22]. The overlapping spectra between porphyrin **2** and **4** can be attributed to the fact that the bromoalkylgroup has no π-electron. As a result, the π-conjugation system of the porphyrin core is not interrupted.

The fluorescence emission spectra of porphyrin **2** are shown in Figure 5**Error! Reference source not found.**. The spectra consist of two emission bands with maximum at 656 and 721 nm. Both emission bands wavelengths are longer than that of excitation Q-band. It suggests that both emission bands are caused by $S_0 \leftarrow S_1$ transition with different on vibrational bands at S_0 state.
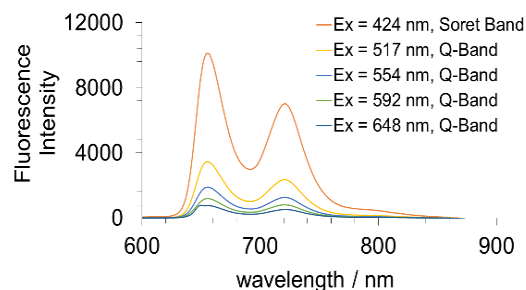

Figure 5. Fluorescence emission spectra of porphyrin 4 (5.5 μM). The spectra were recorded using different excitation wavelength related to Soret and Q-bands.

Using different excitation wavelength related to Soret and Q-band, the λ_{max} of emission band is still the same, only the intensity is different. The shorter excitation wavelength, the stronger emission intensity. The variation for fluorescence emission intensity at different wavelengths was also reported for TPP [22] and ZnTPP [23]. Although Soret band excitation promotes an

electron to S_2, the emission process is still from S_1 to S_0. The S_2 to S_1 transition involves the radiationless relaxation process [23].
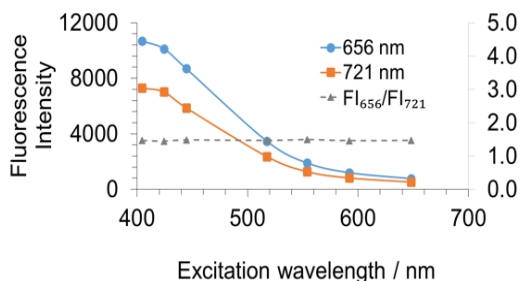

Figure 6. Fluorescence emission intensity as a function of excitation wavelength.

Then the intensity of emission on maximal wavelength (656 and 721 nm) was plotted against excitation wavelength as shown in Figure 6**Error! Reference source not found.**. Although the intensity of fluorescence is higher as the excitation wavelength is shorter, the ratio between the fluorescence intensity at 656 nm and that in 721 nm is constant, mainly ~1.47, indicating that the probability of both emission processes is still same.

CONCLUSION

Modification of nitro porphyrin with alkylgroup does not change its electronic properties significantly. The characteristic properties on absorption and emission spectrum are maintained. However, the addition of nitro and alkyl groups open the new gate to be used as new chromophore of DSSC. Nitro groups as new anchoring groups to TiO_2 surface and alkyl group to prevent unwanted chromophore aggregation.

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