



โครงการ

การเรียนการสอนเพื่อเสริมประสบการณ์

ชื่อโครงการ การพัฒนาตัวเร่งปฏิกิริยาเชิงแสงจากกราฟีนออกไซด์

Development of Photocatalyst Based on Graphene Oxide

ชื่อนิสิต นายณุกร เปลี่ยนปาน

ภาควิชา เคมี

ปีการศึกษา 2558

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

Development of Photocatalyst Based on Graphene Oxide

Nukorn Plainpan

In Partial Fulfillment for the
Degree of Bachelor of Science in Chemistry
Department of Chemistry, Faculty of Science
Chulalongkorn University
Academic Year 2015

Project Title: Development of photocatalyst based on graphene oxide
By: Mr. Nukorn Plainpan
Field of study: Chemistry
Project Advisor: Pannee Leeladee, Ph.D.

Accepted by Department of Chemistry, Faculty of Science, Chulalongkorn University
in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science program in
Chemistry.

..... Head of Department of Chemistry
(Associate Professor Vudhichai Parasuk, Ph.D)
...../...../.....

PROJECT COMMITTEE

T. Tuntulani.....Chair Committee
(Professor Tawatchai Tuntulani, Ph.D)

Pannee Leeladee.....Project Advisor
(Pannee Leeladee, Ph.D)

Sakulsuk Unarunotai.....Committee
(Sakulsuk Unarunotai, Ph.D)

Quality of the following work is rated: Excellent Good Average

Project Title: Development of photocatalyst based on graphene oxide

Student name: Nukorn Plainpan Student ID: 5533084023

Advisor name: Pannee Leeladee, Ph.D.

Department of Chemistry, Faculty of Science, Chulalongkorn University, Academic year 2015

Abstract

In recent years, graphene oxide (GO) has emerged to be a promising material for photocatalytic applications. Typically, its low photocatalytic activity can be improved by modification with visible light-absorbing molecules. In this work, we aim to develop an efficient photocatalyst based on GO by noncovalent fabrication with a hydrophobic photosensitizer, 2,7,12,17-tetrapropylporphycene (H_2Pc). First, GO was prepared by the modified Hummers' method. H_2Pc was also successfully synthesized in 7 steps with an overall yield of 3%. Then, the H_2Pc -functionalized GO composite (GO/ H_2Pc) was prepared by a simple self-assembly process. The resulting composite was found to be stable in aqueous solution for at least 7 days. Furthermore, interaction between GO and H_2Pc was investigated by UV-vis and fluorescence spectroscopy. Absorption bands of H_2Pc in GO/ H_2Pc were considerably broadened and red-shifted as compared to those of free H_2Pc . The spectral changes are likely resulted from the dye aggregation on the GO solid substrate through π - π stacking and hydrophobic interaction. Fluorescence quenching of H_2Pc by GO was also observed, presumably *via* photoinduced electron transfer (PET) process. This data suggests that H_2Pc is competent to transfer photoexcited electrons to the conduction bands of GO, which in turn could provide an efficient photocatalytic activity for the system. In addition, synthesis of GO/dye composites and spectroscopic studies were carried out with porphyrin derivatives for comparison purposes.

Keywords: graphene oxide, porphycene, noncovalent functionalization, photocatalyst

ชื่อโครงการ: การพัฒนาตัวเร่งปฏิกิริยาเชิงแสงจากกราฟีนออกไซด์

ชื่อนิติในโครงการ: นาย ญกร เปลี่ยนปาน เลขประจำตัว: 5533084023

ชื่ออาจารย์ที่ปรึกษา: ดร.พรณี ลีลาดี

ภาควิชาเคมี คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ปีการศึกษา 2558

บทคัดย่อ

กราฟีนออกไซด์เป็นวัสดุที่กำลังได้รับความสนใจและมีแนวโน้มที่จะนำไปประยุกต์ใช้เพื่อเร่งปฏิกิริยาเชิงแสงได้ การเพิ่มประสิทธิภาพของตัวเร่งปฏิกิริยาเชิงแสงโดยทั่วไปนั้น สามารถทำได้โดยการดัดแปรตัวเร่งด้วยโมเลกุลที่สามารถดูดกลืนแสงในช่วงที่ตามองเห็น งานวิจัยนี้มีวัตถุประสงค์เพื่อที่จะพัฒนาตัวเร่งปฏิกิริยาเชิงแสงจากกราฟีนออกไซด์ โดยการดัดแปรด้วยตัวรับพลังงานแสง 2,7,12,17-เทตระโพรพิลพอร์ไฟซิน (H_2Pc) โดยอาศัยอันตรกิริยานอนโควาเลนต์ ในขั้นแรกผู้วิจัยได้ทำการเตรียมกราฟีนออกไซด์ด้วยวิธี modified Hummers และสังเคราะห์ H_2Pc ได้สำเร็จจากการทำปฏิกิริยา 7 ขั้นตอน โดยได้ร้อยละของผลิตภัณฑ์โดยรวมเท่ากับ 3 จากนั้นจึงเตรียมคอมโพสิตของกราฟีนออกไซด์ที่ดัดแปรด้วย H_2Pc (GO/H_2Pc) โดยกระบวนการรวมตัวกันเอง (self-assembly process) พบว่า คอมโพสิตที่เตรียมได้มีความเสถียรในน้ำเป็นเวลาอย่างน้อย 7 วัน จากนั้นจึงศึกษาอันตรกิริยาระหว่างกราฟีนออกไซด์กับ H_2Pc ด้วยเทคนิคยูวี วิซิเบิล และฟลูออเรสเซนส์สเปกโทรสโกปี โดยพบว่า พิกการดูดกลืนแสงของ H_2Pc ที่ถูกดูดซับบน GO นั้นกว้างกว่าและมีการเลื่อนทางแดง เมื่อเทียบกับ H_2Pc ที่ไม่ถูกดูดซับ การเปลี่ยนแปลงของสัญญาณดังกล่าว คาดว่าจะเป็นผลมาจากการรวมตัวกันของ H_2Pc และ GO ผ่านอันตรกิริยา ไพ-ไพ และแรงไฮโดรโฟบิก นอกจากนี้ยังพบว่ากราฟีนออกไซด์สามารถดับสัญญาณเรืองแสงของ H_2Pc ได้ จากกระบวนการโฟโตอินดิวดส์อิเล็กตรอน – ทรานสเฟอร์ (photoinduced electron transfer, PET) การทดลองนี้แสดงให้เห็นว่า H_2Pc น่าจะสามารถถ่ายโอนโฟโตอิเล็กตรอนไปยังคอนดักชันแบนด์ของ กราฟีนออกไซด์ได้ ซึ่งจะช่วยเพิ่มประสิทธิภาพในการเร่งปฏิกิริยาเชิงแสงของกราฟีนออกไซด์ดัดแปรนี้ต่อไป นอกจากนี้ยังได้มีการสังเคราะห์คอมโพสิต GO/dye กับสารประกอบประเภทพอร์ไฟรินและทำการศึกษโดยใช้เทคนิคทางสเปกโทรสโกปี เพื่อเปรียบเทียบกับคอมโพสิต GO/H_2Pc อีกด้วย

คำสำคัญ: กราฟีนออกไซด์, พอร์ไฟซิน, การดัดแปรแบบนอนโควาเลนต์, ตัวเร่งปฏิกิริยาเชิงแสง

Acknowledgement

I would like to express my gratitude to the following people for helping me throughout this project. Without their help, I may not have succeeded this project. First, my project advisor; Dr. Pannee Leeladee, for giving me a great opportunity to work in a project that I am interested in and also providing guidances and supports throughout this project. Prof. Dr. Tawatchai Tuntulani, for being the chair committee. Dr. Sakulsuk Unarunotai, for being the committee and providing me a guidance for preparing graphene oxide. Assist. Prof. Dr. Kanet Wongravee, for helping me with thermal gravimetric analysis. SCRUI lab members, for their time and counsel for helping me throughout this project.

Additionally, I would like to thank Prof. Takashi Hayashi, Asst. Prof. Koji Oohora and all of the Hayashi lab members for their warm welcome and guidance during the synthesis of 2,7,12,17-tetrapropylporphycene. Also, the development and promotion of science and technology talents project (DPST) for providing me a funding for the short term research at Osaka University, Japan.

Nukorn Plainpan

ภาควิชาเคมี
คณะวิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

	Page
ABSTRACT	iii
ACKNOWLEDGMENT	v
CONTENTS	vi
LIST OF FIGURES	viii
LIST OF ABBREVIATIONS	ix
CHAPTER 1 INTRODUCTION	1
1.1 Introduction to the project and its significance	1
1.2 Literature review	1
1.3 Objectives	6
CHAPTER 2 EXPERIMENTAL SECTION	7
2.1 Materials	7
2.2 Instruments	7
2.3 Experimental Procedures	8
2.3.1 Synthesis of graphite oxide	8
2.3.2 Preparation of graphene oxide dispersion	8
2.3.3 Synthesis of 5,10,15,20-Tetraphenylporphyrin cobalt(II) (CoTPP)	9
2.3.4 Synthesis of 2,7,12,17-Tetrapropylporphycene (H ₂ Pc)	10
2.3.5 Study of non-covalent interaction between photosensitizers and graphene oxide	15
2.3.6 Fabrication of GO/photosensitizer composite	16
2.3.7 Photosensitizer desorption of GO/photosensitizer composite	16
CHAPTER 3 RESULTS AND DISCUSSION	17
3.1 Synthesis and characterization	17

3.1.1 Graphite Oxide	17
3.1.2 5,10,15,20-Tetraphenylporphyrin cobalt(II) (CoTPP)	19
3.1.3 2,7,12,17-Tetrapropylporphycene (H ₂ Pc)	21
3.2 Non-covalent interaction between photosensitizers and graphene oxide	23
3.3 GO/photosensitizer composite	26
CHAPTER 4 CONCLUSION	28
REFERENCES	28
VITAE	31



ภาควิชาเคมี
คณะวิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

	Page
Figure 1-1 Structure of graphene oxide	2
Figure 1-2 Photoexcitation of the electron in the valence band to the conduction band on a semiconductor surface	2
Figure 1-3 Photocatalytic reduction of carbon dioxide assisted by graphene based material.	3
Figure 1-4 CO ₂ reduction photocatalyst from photosensitizer- modified GO.....	4
Figure 1-5 Core structures of porphyrins (left) and porphycenes (right).....	5
Figure 1-6 Solar irradiance spectrum.....	6
Figure 2-1 Synthesis scheme of 2,7,12,17-Tetrapropylporphycene (H ₂ Pc).....	10
Figure 3-1 Graphite oxide (left) and graphene oxide dispersion in water (right).....	17
Figure 3-2 UV-Vis absorption spectrum of GO dispersion in water.....	18
Figure 3-3 TGA curve of GO	18
Figure 3-4 FTIR-ATR spectrum of GO.....	19
Figure 3-5 UV-Vis spectrum of CoTPP in DMSO	20
Figure 3-6 ESI-MS spectrum of CoTPP	20
Figure 3-7 ¹ H-NMR spectrum of H ₂ Pc.....	21
Figure 3-8 ESI-MS spectrum of H ₂ Pc.....	22
Figure 3-9 UV-Vis spectrum of H ₂ Pc.....	22
Figure 3-10 Structure of H ₂ TTPP,CoTPP and H ₂ Pc	23
Figure 3-11 Scheme of fluorescence emission and PET process.....	24
Figure 3-12 Fluorescence emission spectral change upon addition of GO dispersed in DI water (1.00 mg/mL, 0-500 μL) into a solution of H ₂ Pc, H ₂ TTPP and CoTPP (8.00 μM) in DMSO	25

Figure 3-13 Fluorescence emission spectral change upon addition of DMSO (0-500 μ L) into a solution of H_2Pc , H_2TPP and $CoTPP$ (8.00 μ M) in DMSO..... 25

Figure 3-14 UV-vis absorption spectra of GO, GO/ H_2TPP , GO/ $CoTPP$ and GO/ H_2Pc 26



ภาควิชาเคมี
คณะวิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF ABBREVIATIONS

General Abbreviations



UV-vis	ultraviolet visible
IR	infrared
NIR	near Infrared
ATR-FTIR	attenuated total reflection Fourier transform infrared
ESI-MS	electrospray ionization mass spectrometry
dil.	dilute
cal	calculated

International System of Units



nm	nanometers
W	watt
m	meters
mmol	millimol
mL	milliliter
L	liter
pH	hydrogen potential
g	gram
°C	degree Celcius
%	percentage
λ	wavelength

ภาควิชาเคมี
คณะวิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

Chapter 1 Introduction

1.1 Introduction to the project and its significance

Graphene oxide (GO) is a semiconductor, carbon-based material. It has been utilized for various applications including biosensors¹, drug delivery² and waste water treatment³. Recently, study on this material as a photocatalyst has gained much attention due to its low cost, facile synthesis and easy modification.⁴ Unfortunately, GO by itself exhibited low photocatalytic efficiency. Incorporation of a photosensitizer to GO via a covalent interaction has significantly improved its photocatalytic activity⁵. However, the synthesis of these functionalized GO with a photosensitizer can be problematic. Non-covalent link between GO and a photosensitizer could provide an easy and alternative approach to develop a new and efficient photocatalyst based on GO. In fact, many examples of GO-dye hybrid via non-covalent interactions have been reported, but study of these systems as a photocatalyst is relatively rare. In this study, the non-covalent interaction between a photosensitizer and GO as well as the photocatalytic activity of such system will be investigated. Insight into the nature of the interactions between these two macrocycles; porphyrins and porphycene, and GO will enable the developments of a better photocatalytic system using non-covalent interactions between these two species.

1.2 Literature review

Graphene oxide (GO) is a carbon-based material. The material comprises of a single layer of sp^2 -hybridized carbon with many oxygen functional groups e.g. hydroxyl, epoxide, aldehyde and carboxyl. The material can be easily prepared by oxidation of graphite. The most used method is the modified Hummers' method⁶. GO has been utilized for various applications including biosensors¹, drug delivery², waste water treatment³ as well as photocatalysis.⁴

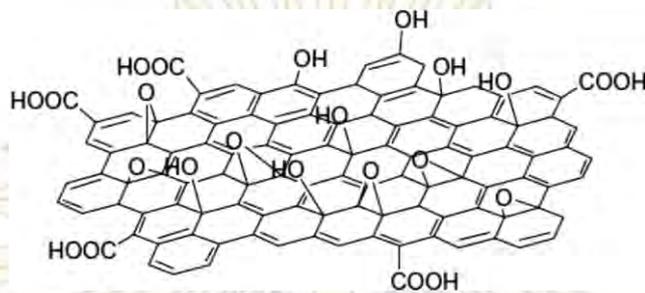


Figure 1-1 Structure of graphene oxide⁷

As a semiconductor, GO can also serve as a photocatalyst. At ground state, the electrons are populated in a valence band. When excited, the electrons will move to a conduction band. The difference between these two energy level is called a band gap. In order to excite the electron in the valence band to the conduction band, energy equal or higher than the band gap energy is required. As the electron is excited to the conduction band, it will leave behind a positive hole in the valence band and create a negative charge in the conduction band. This will result in the charge imbalance on the surface of the material. In case of GO, the positive hole is localized on the carbon adjacent to the oxygen functional group. This is because oxygen can stabilize the positive hole by sharing its lone pair electrons via resonance effect. The negative charge, on the other hand, is delocalized in the π -conjugated system of the sp^2 hybridized carbon.

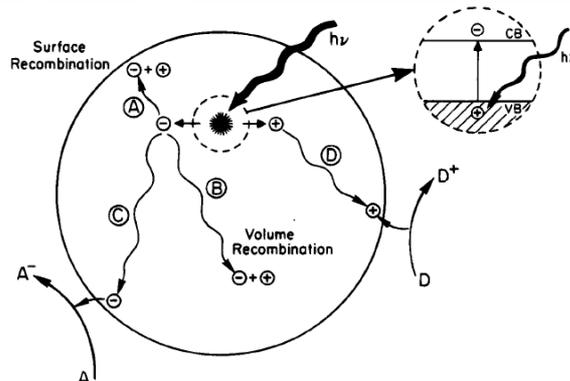


Figure 1-2 Photoexcitation of the electron in the valence band to the conduction band on a semiconductor surface⁸

The charge imbalance, the positive hole on the carbon next to oxygen functional group and the negative charge in the π -conjugated system, is a driving force for the photoredox activity of GO. The positive hole has an oxidizing power while the negative charge in the π -conjugated system possesses a reducing power.

Chen and coworkers reported that GO can catalyze a photoreduction of CO_2 to methanol^{4b}. In spite of its low efficiency and low quantum yield, this system is a proof of principle that this material can act as a photocatalyst.

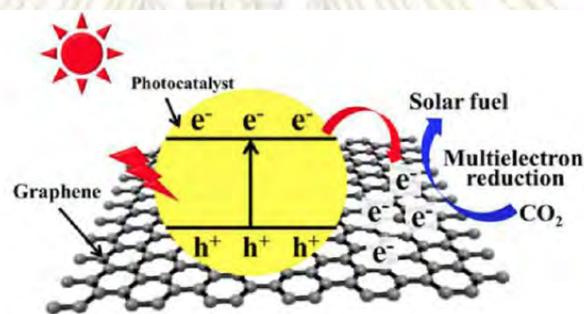


Figure 1-3 Photocatalytic reduction of carbon dioxide assisted by graphene based material⁹

The low efficiency of this system arises from the fact that the band gap of GO is large and the visible light used in this system is inefficient to excite the electron in the valence band of GO. UV light, despite having sufficient energy, is not a good option due to its potential risk to human. To cope with this problem, Jain and coworkers synthesized GO functionalized with a photosensitizer (cobalt phthalocyanin complex and Ruthenium heteroleptic bipyridine complex shown in **Figure 1-4**). They found that the photocatalytic activity and the quantum yield of the catalyst were enhanced^{5, 10}. This is because a photosensitizer can absorb light, get excited and transfer the photoelectron to the conduction band of GO. Since a photosensitizer normally can absorb light in visible region with high absorptivity, introducing a photosensitizer to GO will enhance its photocatalytic activity.

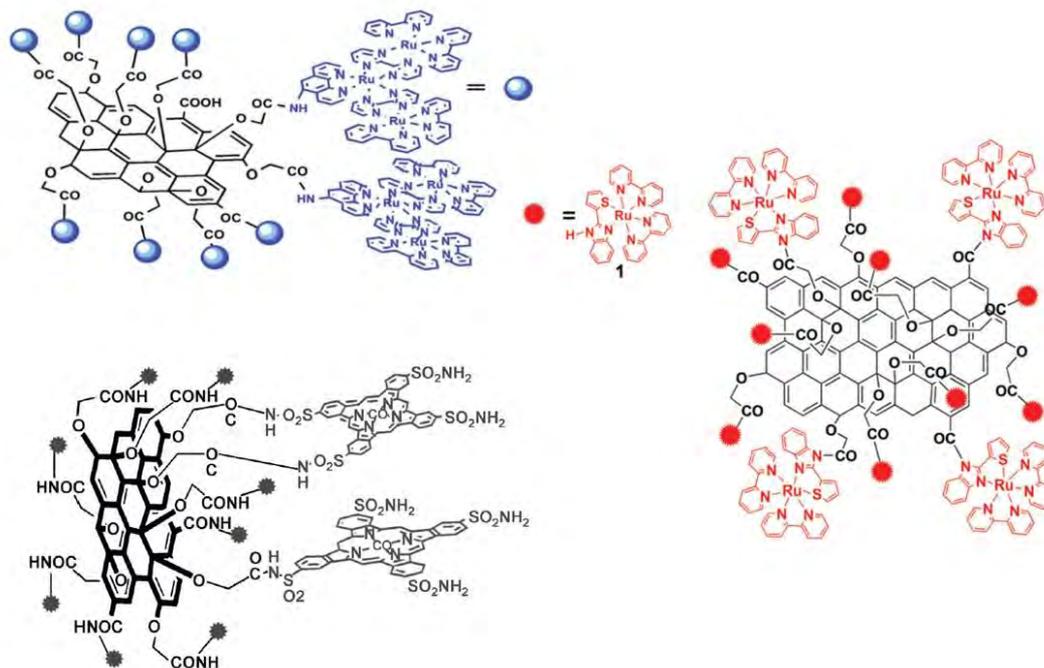


Figure 1-4 CO₂ reduction photocatalyst from photosensitizer- modified GO^{5, 10}

In addition to CO₂, there are numbers of substrate that can undergo photoredox reaction catalyzed by GO, both oxidation and reduction^{4a, 11}. Also, a large variety of photosensitizers can be used with GO, ranging from metal complexes⁵, metal oxides¹¹, to organic dyes¹². Each type of photosensitizers has its own advantages and disadvantages.

In case of metal complexes and organic dyes, their advantages include their ability to absorb light in visible region with high absorptivity. Moreover, they can be designed to absorb light in many regions from visible to NIR. This allows a certain dye to absorb light and convert it to chemical energy with higher efficiency. Nevertheless, this type of photosensitizer is typically linked to GO via covalent bond. This means that both photosensitizer and GO have to be modified to gain functional groups capable of bridging the two components via a covalent bond. This could be a complex and time-consuming process.

GO is competent to adsorb certain dye molecule through non-covalent interaction e.g., electrostatic interaction and π - π stacking. This ability makes incorporation of GO and some types of photosensitizers to be as easy as mixing them together. In fact, many examples of GO-dye hybrid via non-covalent interactions have been reported¹³, but study of these systems as a photocatalyst is rare¹⁴. For this project, porphyrin and porphycene are the photosensitizers of interest.

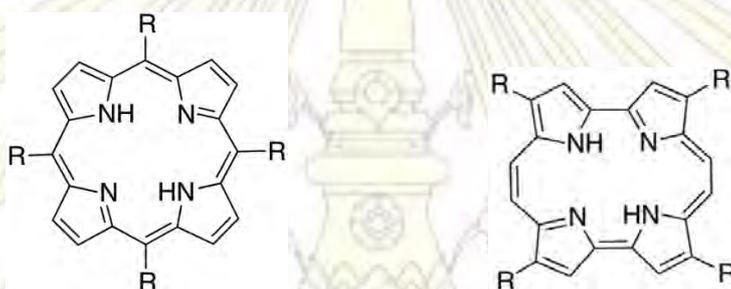


Figure 1-5 Core structures of porphyrins (left) and porphycenes (right)

Porphyrin is an aromatic macrocyclic compound found in many biological systems. Its synthetic derivatives as well as its metal complexes have been reported extensively to have many applications in various fields such as photodynamic therapy¹⁵ and photocatalysis¹⁶. Most importantly, it is known for its application in photosensitization. The compound is widely used in organic solar cell¹⁷ due to its excellence in photosensitization activity and the ease of structural modification and functionalization.

Porphycene¹⁸ is a structural isomer of porphyrins. The two share many similarities but the main difference is their UV-Vis absorption. Both of them possess two main absorption regions, Soret band (around 400 nm) and Q band (around 500-600 nm). Soret band is the more intense band than the Q band. The Q band of porphycene is more intense than those of porphyrin. According to solar irradiance spectrum, it is seen that the most intense region lies at the same region as the Q band. Therefore, porphycene has a potential to be a better dye in term of solar energy conversion than its well-known isomer, porphyrin. In addition, there are reports on porphycene's potential to be a photosensitizer¹⁹.

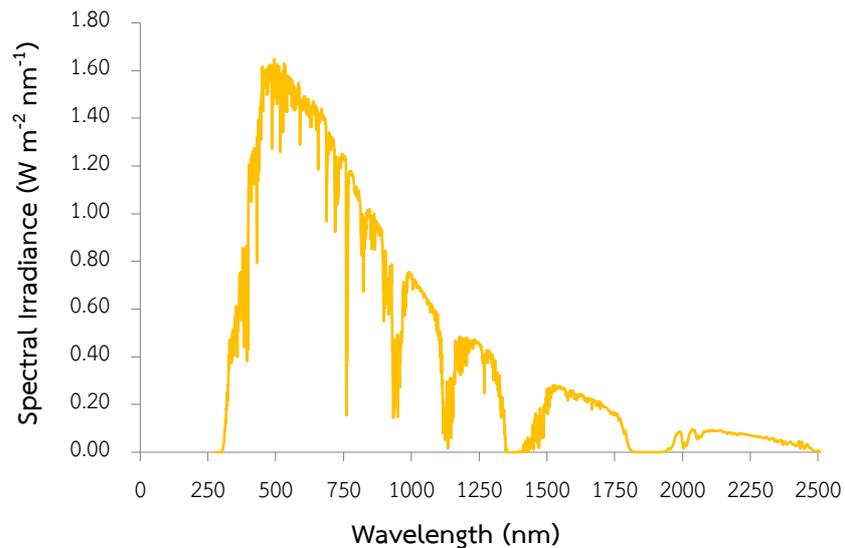


Figure 1-6 Solar irradiance spectrum²⁰

The purpose of this study is to investigate the non-covalent interaction between a photosensitizer (porphyrin and porphycene) and GO along with the photocatalytic activity of this system. Understanding in the nature of the interactions between these two species will lead to the developments of a better graphene based photocatalyst.

1.3 Objectives

1. To synthesize and characterize graphene oxide (GO), 5,10,15,20-tetraphenyl-21H,23H- porphine cobalt(II) (CoTPP) and 2,7,12,17-tetrapropylporphycene (H₂Pc).
2. To study the non-covalent interaction between H₂TPP, CoTPP, H₂Pc and GO.
3. To study the effect of the photosensitizer on the photocatalytic activity of GO

Chapter 2 Experimental Section

2.1 Materials

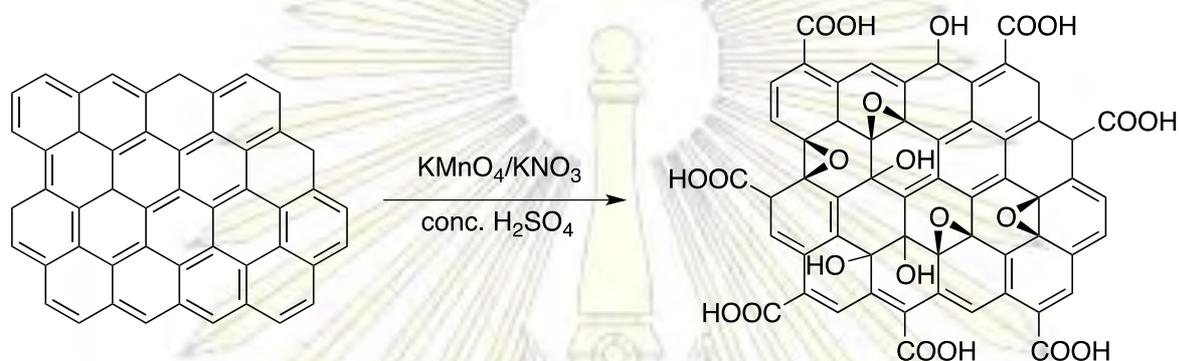
Unless otherwise noted, all solvents and chemicals used in the experiments were analytical grade and were used as received without further purification. Graphite flake was purchased from Acros Organic. Concentrated sulfuric acid (H_2SO_4 , 95-97%), hydrogen peroxide (H_2O_2 , 30%) and potassium hydroxide (KOH) were purchased from Merck. $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was purchased from BDH chemicals Ltd. All reagents used in the synthesis of H_2Pc were purchased from Wako Pure Chemical Industries Ltd. H_2TPP was kindly given from Dr. Preeyanut Duanglaor. The purity and identity of H_2TPP were confirmed by $^1\text{H-NMR}$ and UV-Vis spectroscopy.

2.2 Instruments

UV-Vis absorption spectra and fluorescence emission spectra were collected using Varian Cary 50 Probe and Varian Cary Eclipse respectively. The spectra were recorded at room temperature using a quartz cell with an optical path length of 1 cm. IR spectra were recorded on Nicolet iS10 ATR-FTIR spectrometer with ATR mode. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX 400 spectrometer operating at 400 MHz for $^1\text{H-NMR}$. The solvent used in all of the measurements was CDCl_3 . Mass spectrometry spectra were collected using Bruker Daltonics MicrOTOF-II on ESI-positive mode. Gel permeation chromatography (GPC) was performed on Nihon Bunseki Kogyo LC-908. Thermal gravimetric analysis (TGA) was performed on Perkin Elmer Pyris 1.

2.3 Experimental Procedures

2.3.1 Synthesis of graphite oxide



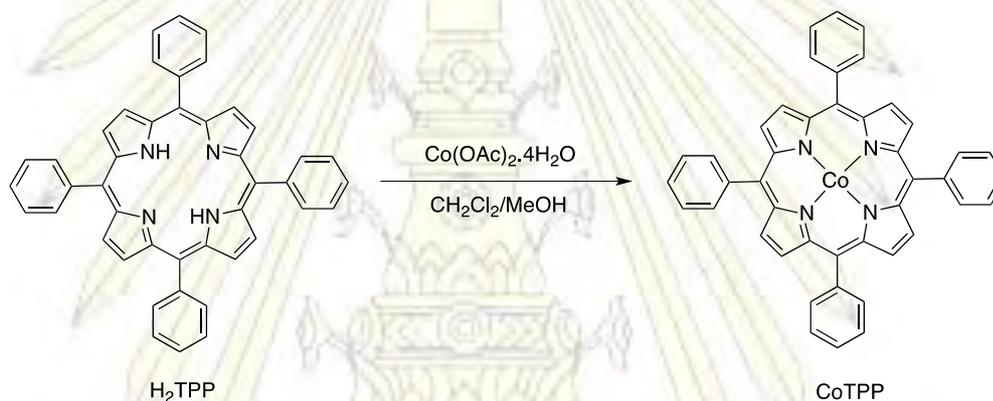
Graphite oxide was prepared according to a modified published method⁶. To a 50 mL conical flask, graphite powder (0.80 g) and NaNO_3 (0.4 g, 5 mmol) were added and dissolved into conc. H_2SO_4 (25 mL). The mixture was cooled in an ice bath for 20 minutes. Next, KMnO_4 (2.45 g, 15.5 mmol) was slowly added and the solution was stirred for 6 hours. Then, KMnO_4 (2.66 g, 16.9 mmol) was added and the reaction was stirred for 12 hours. After that, the solution was poured into a 100 mL beaker containing ice cubes and H_2O_2 (30%, 5 mL) before the washing steps. The washing step was performed by centrifugation of the mixture at 3,000 rpm for 20 minutes. Then, the supernatant was decanted away and the washing solution was transferred to the centrifuge tube, stirred with a stirring rod and repeated the centrifugation. The washing solutions were DI water, 6M HCl, DI water, Buffer solution ($\text{K}_2\text{HPO}_4 - \text{KH}_2\text{PO}_4$, pH=7), DI water and DI water respectively. After that, the precipitate was collected and dried under reduced pressure to yield graphite oxide (1.426 g). The graphite oxide was then characterized by FTIR, TGA and UV-Vis spectroscopy

2.3.2 Preparation of graphene oxide dispersion

To a beaker, an appropriate amount of graphite oxide and the desired volume of solvent (DI water or DMSO) were added. The mixture was sonicated until the graphite oxide

was fully dispersed (1 hour for DI water, 3 hours for DMSO). Then, the dispersion was transferred to a volumetric flask and the final volume was adjusted to give brown dispersion of graphene oxide.

2.3.3 Synthesis of 5,10,15,20-Tetraphenylporphyrin cobalt(II) (CoTPP)



2.3.4 Synthesis of 2,7,12,17-Tetrapropylporphycene (H₂Pc)

2,7,12,17-Tetrapropylporphycene (H₂Pc) was synthesized following reported procedure²¹.

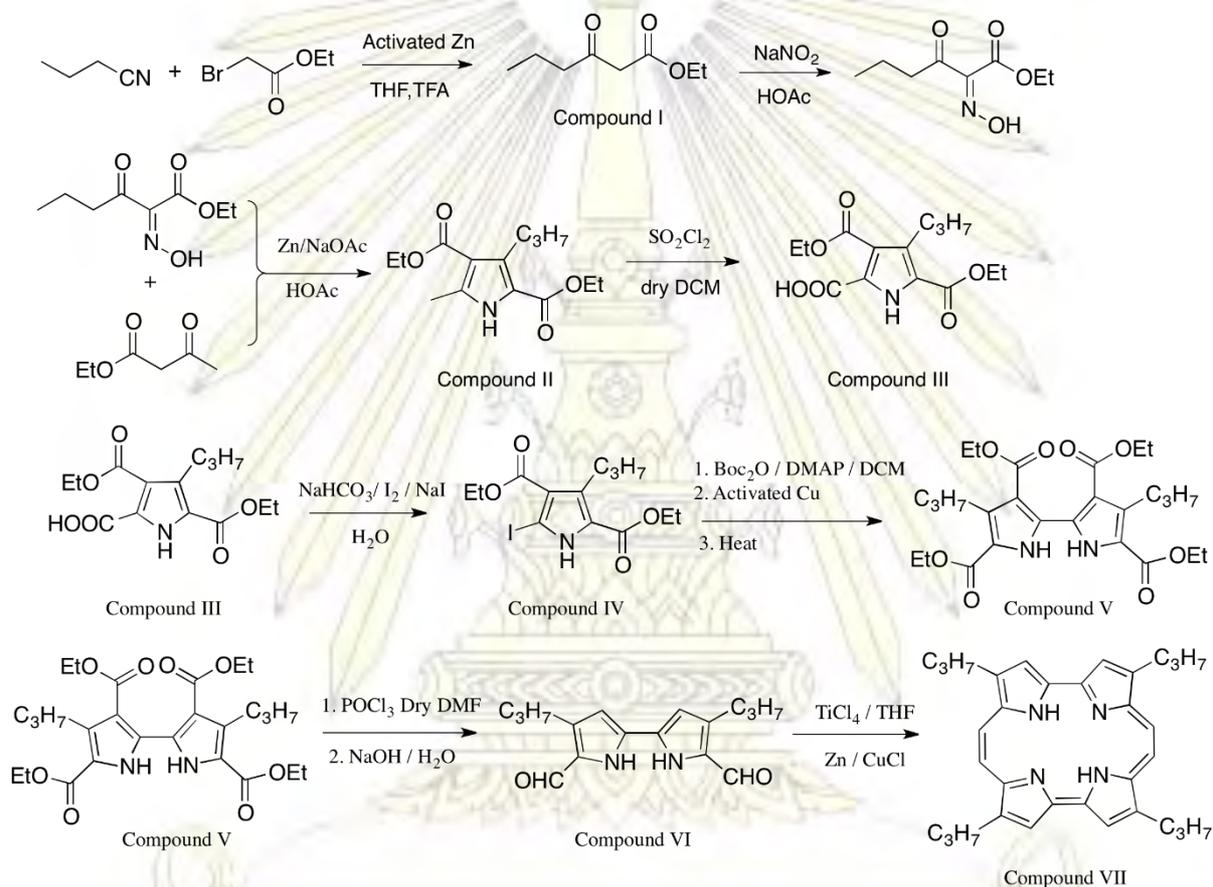


Figure 2-1 Synthesis scheme of 2,7,12,17-Tetrapropylporphycene (H₂Pc)

Ethyl-3-oxohexanoate (compound I). To a stirring 80 g of Zn suspension in 180 mL of THF in a 4-neck bottle under nitrogen atmosphere was added 0.50 mL of TFA. The mixture was heated to 85 °C for 20 minutes and 55 mL of butyronitrile was added to the reaction mixture. After that, 110 mL of ethyl-2-bromoacetate was added to the reaction mixture dropwise over 1.5 hours using a dropping funnel. The reaction mixture was kept on refluxing for 30 minutes after addition of ethyl-2-bromoacetate was finished. Then, the mixture was taken off the nitrogen atmosphere and cooled to 5 °C in an ice bath. Next, 174 mL of 3 M

HCl was added to the mixture. Two separate layers were observed. After over night stirring at room temperature, 5% citric acid_(aq) and EtOAc were added to the mixture. The mixture was stirred using glass rod and EtOAc layer was collected. The collected solution was transferred into separation funnel and washed with 3 M HCl, sat. NaHCO₃ solution and sat. NaCl solution. The organic layer was collected, water was removed by Na₂SO₄ and dried in vacuum to yield 94.5 g yellow clear liquid of ethyl-3-oxohexanoate (92% yield). ¹H-NMR (400 MHz, CDCl₃): δ4.13 (q, 2H), 3.38 (s, 2H), 2.47 (t, 2H), 1.57 (m, 2H), 1.22 (t, 3H), 0.87 (t, 3H).

Diethyl 5-methyl-3-propyl-1H-pyrrole-2,4-dicarboxylate (Compound II). To the 4-neck round bottle flask, ethyl-3-oxohexanoate (compound I, 56.2 g, 0.355 mol) and 270 mL of glacial acetic were added. The mixture was cooled to 5 °C using an ice bath and kept in nitrogen atmosphere. Next, NaNO₂ aqueous solution (25 g of NaNO₂ in 50 mL solution) was added to the reaction dropwise over 3 hours. The temperature of the reaction was maintained at 5 °C over the time of addition of NaNO₂ solution. After addition of NaNO₂ has been completed, the reaction was kept stirring at room temperature for additional 24 hours to yield an orange-red solution. To another 3-neck round bottle flask containing ethyl-3-oxobutanoate (45.0146 g, 0.3461 mol), the orange-red solution was added dropwise over 2 hours. The reaction mixture was kept stirring at 75 °C under nitrogen atmosphere. After the addition of the orange-red solution, activated zinc (11.5 g) and NaOAc (14.25 g) were added to the reaction mixture every 30 minutes for 4 times and the reaction was kept stirring for another 2.5 hours after the fourth addition. After that, the reaction mixture was poured into 2 L of water and then extracted with chloroform. The organic layer was washed with water and saturated NaHCO₃ solution, dried with MgSO₄ and the solvent was removed *in vacuo*. The residue was purified by recrystallisation with EtOH/water to yield a pale yellow powder of compound II 47 g (52 % yield). ¹H-NMR (400 MHz, CDCl₃): δ9.18 (s, 1H), 4.30 (m, 4H), 3.03 (t, 2H), 2.51 (s, 3H), 1.56 (m, 2H), 1.37 (m, 6H), 0.967 (m, 3H)

3,5-bis(ethoxycarbonyl)-4-propyl-1H-pyrrole-2-carboxylic acid (compound III). To a 2-neck round bottom flask, diethyl-5-methyl-3-propyl-1H-pyrrole-2,4-dicarboxylate (compound II, 10.1435 g, 37.97 mmol) and 200 mL of dry DCM were added under nitrogen atmosphere. After compound (II) was completely dissolved, sulfuryl chloride 9.5 mL (117 mmol) was transferred to the reaction using a glass syringe. The reaction mixture was kept stirring for 1 hour at room temperature. Then, the solvent was removed under vacuum. To the residue of the reaction mixture, 1,4-dioxane (250 mL) and NaOAc aqueous solution (5 g of NaOAc in 70 mL of solution) were added. The reaction mixture was refluxed under nitrogen atmosphere for 1.5 hours. Then, the mixture was extracted by diethyl ether. The organic layer was then extracted with sat. NaHCO_3 solution and the aqueous layer was placed under vacuum to remove the remained ether. Next, concentrated HCl was added to the solution dropwise to give a white precipitation. The acidified aqueous solution was left over night in the refrigerator to complete the precipitation. Suction filtration of the solution yielded a white powder of compound (III) 4.6118 g (15.52 mmol, 41% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 10.27 (s, 1H), 4.49 4.37 (q, 2H), 3.07 (t, 2H), 1.60 (m, 2H), 1.47 (t, 3H), 1.39 (t, 3H), 0.98 (t, 3H)

Diethyl 5-iodo-3-propyl-1H-pyrrole-2,4-dicarboxylate (compound IV). To a 2-neck round bottom flask, 3,5-bis(ethoxycarbonyl)-4-propyl-1H-pyrrole-2-carboxylic acid (compound III), 4.61 g, 15.5 mmol, water (40 mL) and NaHCO_3 (4.6900 g) were added. The solution was heated to 75 °C under air until compound (III) was completely dissolved. Then, an iodine solution (I_2 , 4.158 g, 16.38 mmol in 85 mL of 0.5 M NaI aqueous solution) was added to the reaction mixture dropwise over 2 hours. A white precipitate was observed upon dropping the iodine solution. After addition of iodine solution has been completed, the reaction mixture was kept stirring for another 30 minutes and then cooled to room temperature. Then, the reaction mixture was poured into saturated NaHCO_3 solution. A vacuum filtration yields a white cream powder of diethyl-5-iodo-3-propyl-1H-pyrrole-2,4-

dicarboxylate compound (IV) 5.570 g (14.70 mmol) 98% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 9.30 (s, 1H), 4.35 (m, 4H), 3.05 (t, 2H), 1.60 (m, 2H), 1.37 (m, 6H), 0.94 (t, 3H)

Tetraethyl-4,4'-dipropyl-1H,1'H-[2,2'-bipyrrole]-3,3',5,5'-tetracarboxylate

(compound V). Diethyl-5-iodo-3-propyl-1H-pyrrole-2,4-dicarboxylate (Compound IV, 5.5649 g, 1.467 mmol), Boc_2O (10.31 g, 47.24 mmol) and DMAP (0.2398 g, 1.962 mmol) were dissolved in 80 mL of DCM in a 2-neck round bottom flask. The solution was stirred under N_2 atmosphere for 2.5 hours at room temperature. The reaction mixture was purified by flash column chromatography (stationary phase: silica gel, mobile phase: DCM) and the solvent was removed under vacuum to give a yellow oil.

Next, the yellow oil and activated Cu (10 g) were added to the round bottom flask. Then, the air was suck out and replaced by N_2 . Then, dry DMF (45 mL) was added to the flask as a solvent. The solution was left stirring over night (19 hours) at 75 °C under N_2 atmosphere. The color of the solution changed from yellow to green over the reaction. The remained Cu dust was removed from the reaction mixture by suction filtration. The filtered Cu was sonicated with DCM several times in order to remove any organic molecule that may left in Cu dust and the DCM was combined with the filtrate. The combined filtrate solution's volume was reduced to 150 mL under vacuum. Then, it was washed with water, 0.1 M HNO_3 , saturated NaHCO_3 and water respectively. It was also found that after washed with 0.1 M HNO_3 , the solution turned from green to yellow. After washing, the solvent was removed completely from the organic layer under vacuum to give a yellow oil.

To a round bottom flask, the yellow oil was added and heated to 170 °C under N_2 atmosphere for 1 hour. A bubbling was observed from the yellow oil as the temperature reached 170 °C and it had been continuously bubbling for 30 minutes. After 1 hour, the color of the oil changed from yellow to orange and it was then cooled to room temperature. As it cooled to the room temperature, it was found that the oil turned into orange solid. The orange solid was recrystallized with hot MeOH and was left over night at room temperature to give a needle-shape white crystal of compound (V) 2.8697 g, 5.691 mmol,

77.6 % $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 14.15 (s, 1H), 4.39 (m, 4H), 3.10 (t, 2H), 1.54 (m, 4H), 1.41 (m, 6H), 0.98 (t, 3H)

4,4'-Dipropyl-1H,1'H-[2,2'-bipyrrole]-5,5'-dicarbaldehyde (compound VI). To a round bottom flask, tetraethyl 4,4'-dipropyl-1H,1'H-[2,2'-bipyrrole]-3,3',5,5'-tetracarboxylate (Compound V, 1.2074 g, 2.394 mmol), NaOH (0.6693 g, 16.73 mmol) and ethylene glycol (30 mL) were added. The reaction was refluxed at 200 °C under nitrogen atmosphere. All of the apparatus was covered by aluminium foil to protect the reaction intermediates from the light. After 65 minutes, the reaction was cooled to room temperature. It was observed that the color of the solution changed from colorless to green. Next, to the green solution, 40 mL of water was added and it was then left overnight in the refrigerator. After that, the crude was extracted with DCM. The organic layer was washed with water, dried with MgSO_4 and the solvent was removed under vacuum.

To a 2-neck round bottom flask, the residue from the organic layer was added and dissolved in 45 mL dry DMF. The solution was cooled to 0 °C in an ice bath. Next, 1.5 mL of POCl_3 (16 mmol) was added to the solution slowly. The reaction was then heated and stirred at 60 °C. All the apparatus was covered by aluminum foil. After 2 hours, the reaction was cooled to room temperature and 0.29 M NaOH solution (245 mL) was added. Then, it was heated and stirred at 80 °C for another 1 hour. After that, the reaction mixture was cooled to room temperature and then left overnight in the refrigerator. The suction filtration gave a green powder of compound (VI) 0.6057 g, 2.224 mmol, 92.8 % yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 12.28 (s, 2H), 9.70 (s, 2H), 6.54 (s, 2H), 2.76 (t, 4H), 1.72 (m, 4H), 1.01 (t, 6H)

2,7,12,17-Tetrapropylporphycene compound (VII). To a 4-neck round bottom flask (1 L), activated Zn (6.40 g, 97.9 mmol), CuCl (1.0390 g, 10.50 mmol) were introduced. Then, the air in the 4-neck flask was sucked out and replaced with N_2 . Next, dry THF (200 mL) was transferred into the flask and then the mixture was cooled to 0 °C in an ice bath. TiCl_4 (5.3 g, 28 mmol) was then transferred into the 4-neck flask and the mixture was refluxed at 100 °C

for 3 hours. Next, the temperature of the system was reduced to 80 °C. Then, the solution of compound (VI) (323.8 mg, 1.189 mmol) in 200 mL of dry THF had been added into the mixture slowly over 9 hours using a dropping funnel. After the addition of compound VI had finished, the system was kept refluxing for another 30 minutes. Then, the mixture was cooled to 0 °C in an ice bath and the solution of 10% K₂CO₃ (75 mL) was poured into the 4-neck flask. The mixture was stirred for another 30 minutes before it was suction filtrated and washed with water to remove the remained solid in the system. The filtrate was extracted with DCM and the organic layer was collected. The solvent in the collected organic layer was removed in vacuum before it was purified by flash column chromatography (stationary phase: silica gel, mobile phase: DCM) to removed black sticky side product. The purified product solution from flash column chromatography was concentrated in vacuum and was then purified further using column chromatography (stationary phase: silica gel, mobile phase: DCM). The first purple-blue band was collected and concentrated in vacuum. Finally, the collected product from column chromatography was purified further using gel permeation chromatography (GPC). The purified product solution from GPC was then concentrated in vacuum to yield a purple solid of 2,7,12,17-tetrapropylporphycene 72.6 mg (0.152 mmol) 25.5 % yield. ¹H-NMR (400 MHz, CDCl₃): δ 9.77 (s, 4H), 9.34 (s, 4H), 4.06 (t, 8H), 3.21 (s, 2H), 2.44 (m, 8H), 1.36 (t, 9H) ESI-MS: [M+H⁺] peak at m/z = 479.31 (cal. m/z = 479.31)

2.3.5 Study of non-covalent interaction between photosensitizers and graphene oxide

Fluorescence titration: In a typical experiment, to a solution of the photosensitizer dye (8 μM) in DMSO (2.00 mL) was added successive aliquots of GO (1.00 mg/mL, 25 μL, dispersed in DI water). After each addition, the solution was stirred for 1 minute and immediately monitored by Fluorescence spectroscopy. The λ_{ex} for CoTPP, H₂TPP and H₂Pc were 416, 420 and 370 nm respectively.

2.3.6 Fabrication of GO/photosensitizer composite

To separated beakers, GO (10 mg) in DI water (4.0 mL) and photosensitizer (41 mg for H₂Pc and H₂TPP, 11 mg for CoTPP) in DMF (2 mL) were sonicated for 2 hours. Then, the two mixtures were combined and sonicated for another 2 hours. After that, the combined mixture was sonicated at 11,000 rpm for 50 minutes. After decantation, the remained solid was then redispersed in 10 mL of DI water by sonication for another 1 hour. The resulting mixture was then centrifuged at 4,000 rpm for 10 minutes. The supernatant was collected and filtered through cotton wool to give a GO/photosensitizer composite aqueous dispersion.

2.3.7 Photosensitizer desorption of GO/photosensitizer composite

The as prepared GO/photosensitizer aqueous dispersion (1 mL) was diluted with DI water to the final volume of 10 mL. Then, the diluted dispersion was extracted with CH₂Cl₂ (20 mL, 3 times). The organic layer was then combined, dried over MgSO₄ and concentrated in vacuum. The aqueous was placed in vacuum to remove the dissolved CH₂Cl₂. Both aqueous layer and organic layer were then studied by UV-vis spectroscopy.

Chapter 3 Results and Discussion

3.1 Synthesis and characterization

3.1.1 Graphite Oxide

Graphite oxide was synthesized following a modified Hummers' method⁶. After the reaction is completed, typically one of the work-up steps is neutralization of GO by repeatedly washing with DI water or dialysis with dil. NH_3 solution and DI water. We have found that washing with phosphate buffer (KH_2PO_4 - K_2HPO_4 system) work as good as the reported procedure. Normally, using buffer with GO could be problematic since most buffer salts are not compatible with GO and usually cause GO to precipitate out. Our idea to use KH_2PO_4 - K_2HPO_4 system arise from the fact that in the improved Hummers' method⁶ for synthesis of GO, H_3PO_4 is used instead of H_2SO_4 . So we hypothesized that phosphate ions is compatible with GO and used it as a buffer salt in washing step. In addition, our new procedure can significantly reduce the time and workload used in reported procedure.

The synthesized graphite oxide appears as a black solid. Its dispersion (graphene oxide) in water appears as a brown solution as shown in **Figure 3-1**. GO can also be dispersed in DMSO but heating and prolong sonication is required. GO was characterized using FTIR-ATR spectroscopy, UV-Vis spectroscopy and TGA.

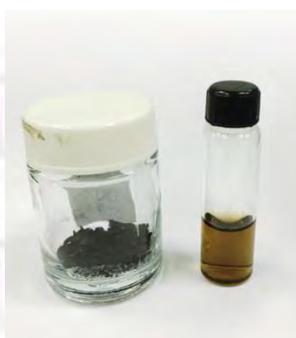


Figure 3-1 Graphite oxide (left) and graphene oxide dispersion in water (right)

The UV-Vis absorption spectrum (Figure 3-2) of the dispersion in water shows absorption at $\lambda_{\text{max}} = 231 \text{ nm}$ corresponding to $\pi \rightarrow \pi^*$ transition of C=C bond. The shoulder around 300 nm is also observed. This shoulder peak is attributed to $n \rightarrow \pi^*$ transition.

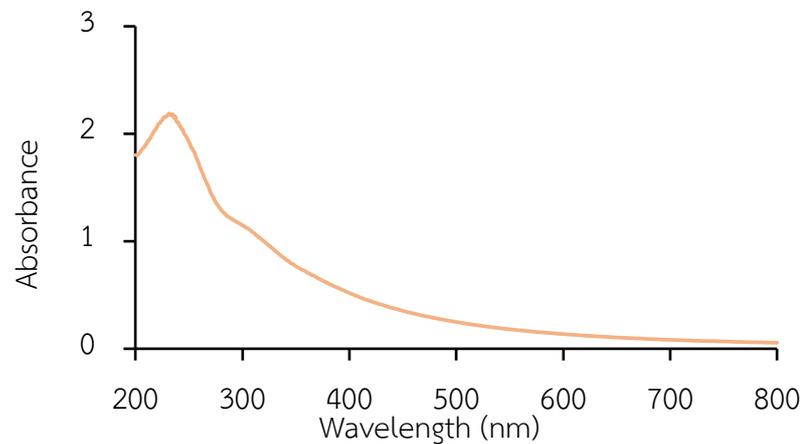


Figure 3-2 UV-Vis absorption spectrum of GO dispersion in water

Thermal gravimetric analysis (TGA), Figure 3-3, shows two main weight loss regions. The weight loss between 150-200°C corresponds to the loss of CO_2 , CO and water from labile oxygen functional groups²² *i.e.*, carboxylic group. The other main weight loss occurs between 450-550°C, this weight loss results from the loss of the more stable oxygen functional groups⁶ *i.e.*, hydroxyl and epoxide group. The TGA curve is in good agreement with the reported literature^{6, 22}.

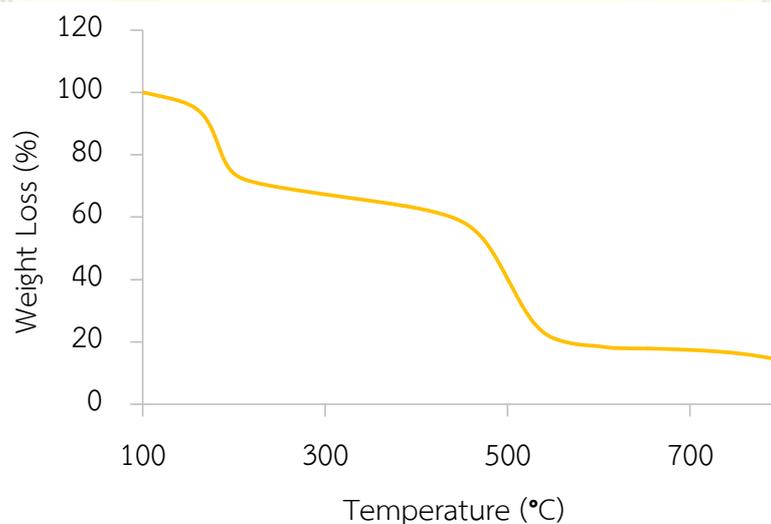


Figure 3-3 TGA curve of GO

From FTIR-ATR (**Figure 3-4**), the following functional groups can be identified: O-H stretching vibrations (3300 cm^{-1}), C=O stretching vibration (1731 cm^{-1}), C=C from unoxidized CC bonds (1622 cm^{-1}), C-OH (1360 cm^{-1}) and C-O-C (1244 cm^{-1}). The functional groups found on the material are consistent with those reported in the literature²³.

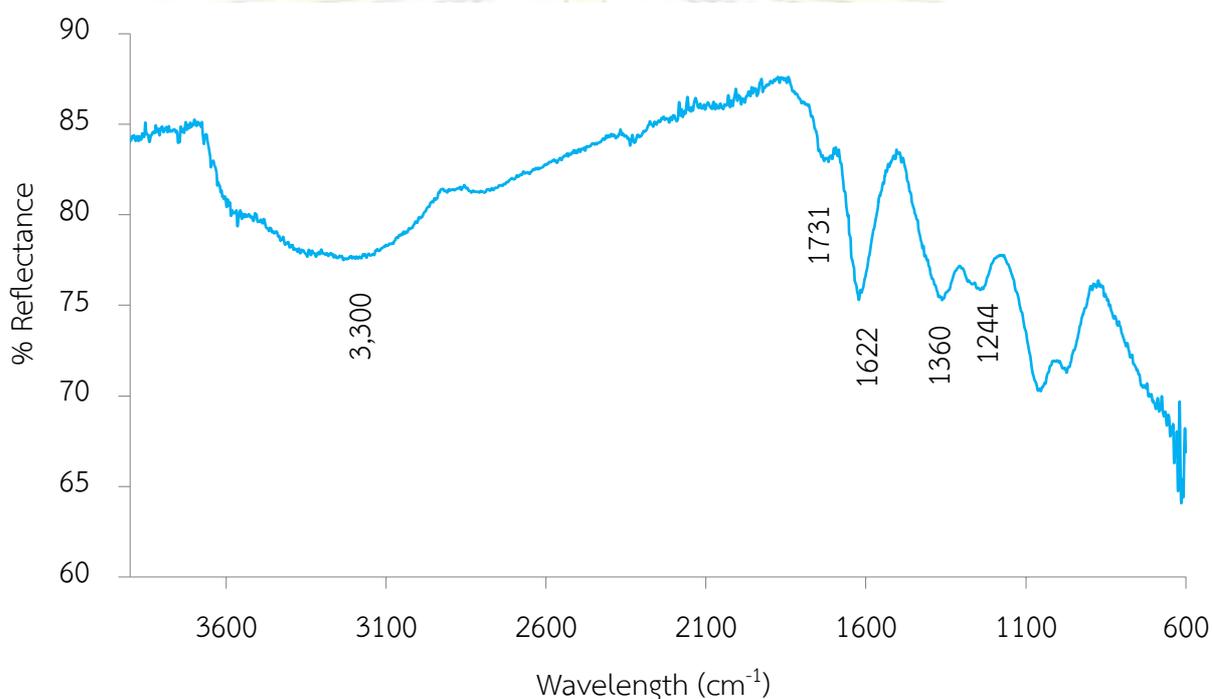


Figure 3-4 FTIR-ATR spectrum of GO

In summary, from these three characterization techniques, it can be confirmed that graphite oxide was successfully synthesized.

3.1.2 5,10,15,20-Tetraphenylporphyrin cobalt(II) (CoTPP)

CoTPP was synthesized following the reported procedure²⁴. The synthesis yielded 33 mg of CoTPP as a red-purple solid (62% yield). The product was characterized by ESI-MS and UV-Vis spectroscopy. UV-Vis spectrum (**Figure 3-5**) of CoTPP in DMSO shows two main absorption peaks. The stronger one at 416 nm is a Sorret band. The weaker one at 530 nm is

a Q band. The UV-Vis spectrum of CoTPP is resemble that of the reported literature²⁴. From ESI-MS (Figure 3-6), $[M^+]$ peak can be observed at $m/z = 671.16$ (cal. $m/z = 671.16$).

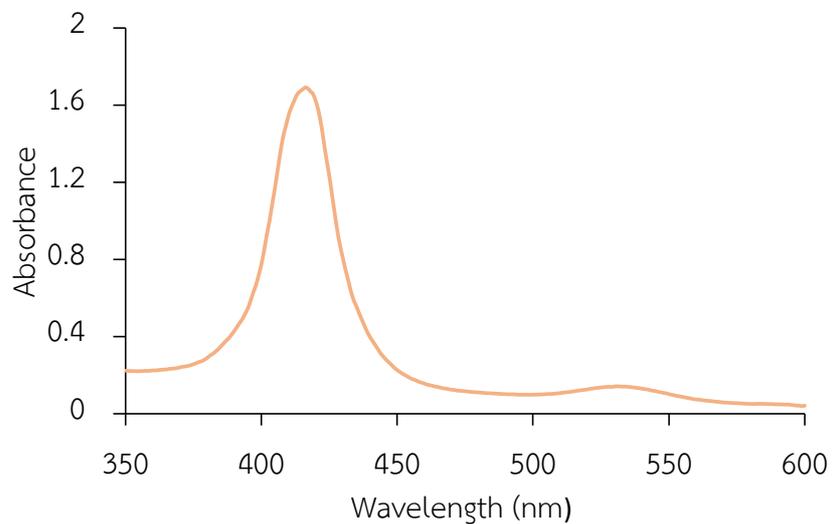


Figure 3-5 UV-Vis spectrum of CoTPP in DMSO

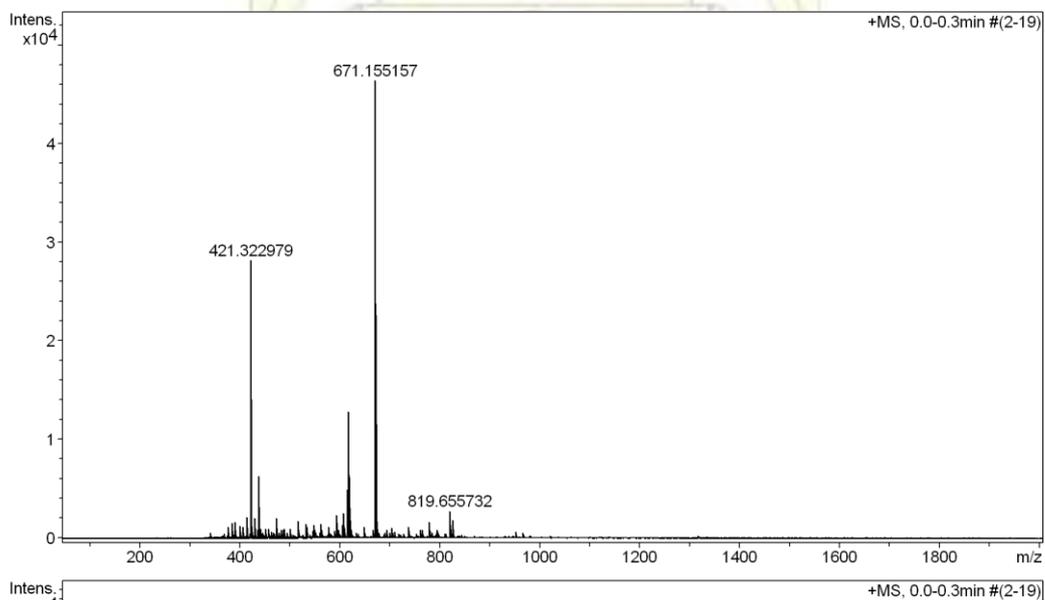


Figure 3-6 ESI-MS spectrum of CoTPP

3.1.3 2,7,12,17-Tetrapropylporphycene (H₂Pc)

H₂Pc was successfully synthesized through several steps²¹ and purified using column chromatography and gel permeation chromatography (GPC). The final purification step yielded 72.6 mg of H₂Pc as a purple solid (3 % yield). The synthesized product was characterized using ¹H-NMR spectroscopy, UV-Vis spectroscopy and ESI-MS. The ¹H-NMR spectrum of H₂Pc (**Figure 3-7**) is consistent with the reported literature^{21a}. (400 MHz, CDCl₃): δ 9.77 (s, 4H), 9.34 (s, 4H), 4.06 (t, 8H), 3.21 (s, 2H), 2.44 (m, 8H), 1.36 (t, 9H). Thus, the structure of H₂Pc can be confirmed. ESI-MS spectrum (**Figure 3-8**) shows [M+H⁺] peak at m/z = 479.31 (cal. m/z = 479.31). UV-Vis spectrum (**Figure 3-9**) shows two main absorption regions, Soret band and Q band. Soret band is observed at 372 nm with a shoulder at 380 nm. In the Q band region, there are three peaks located at 564, 602 and 635 nm respectively.

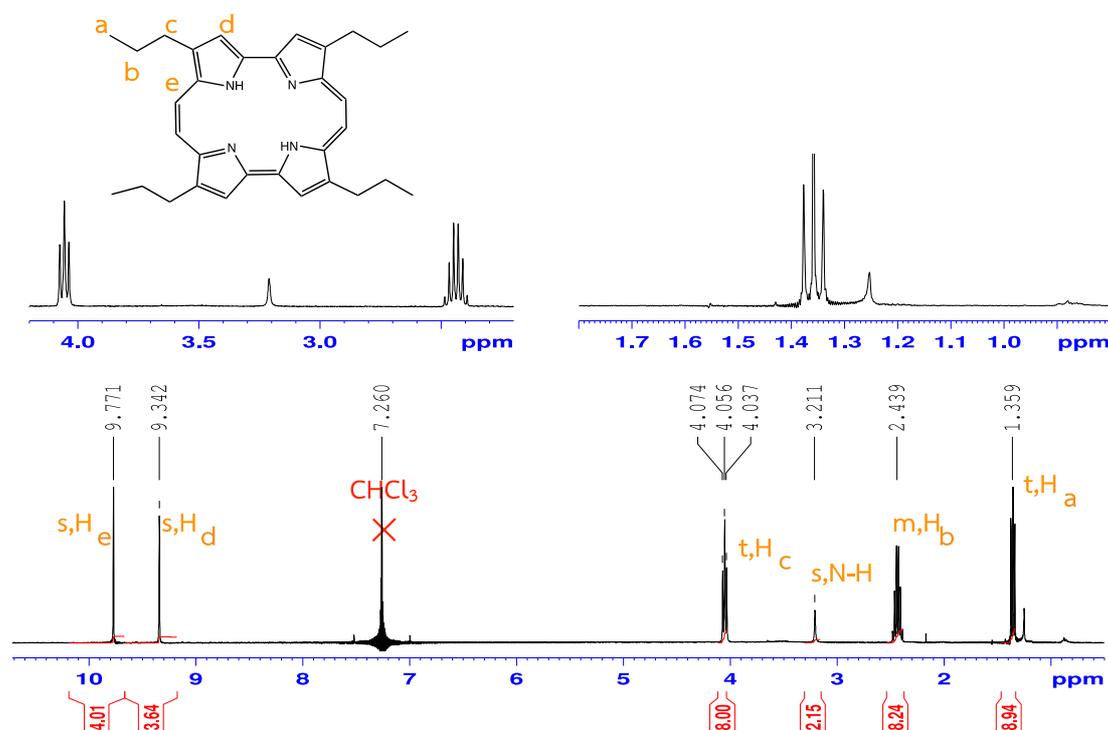
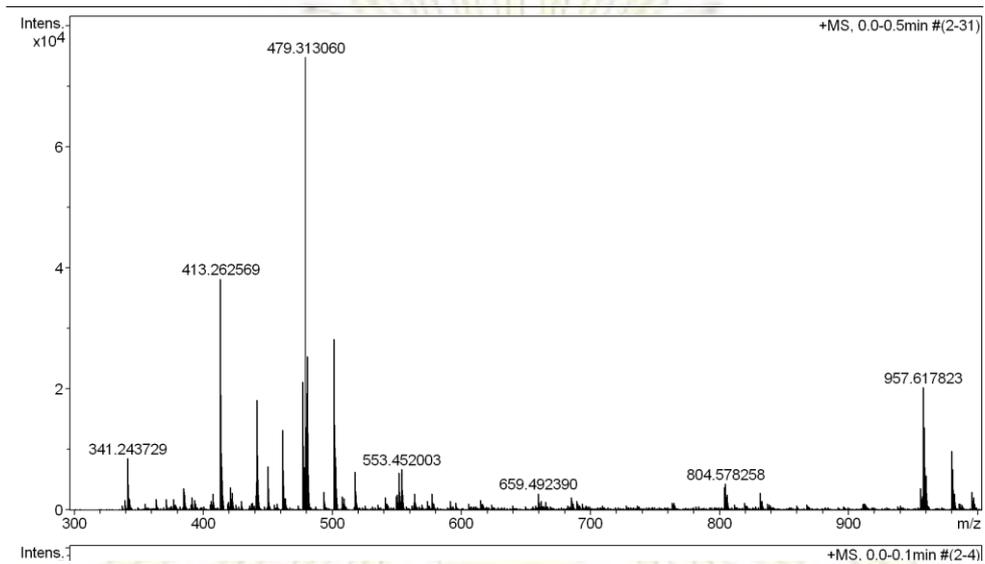
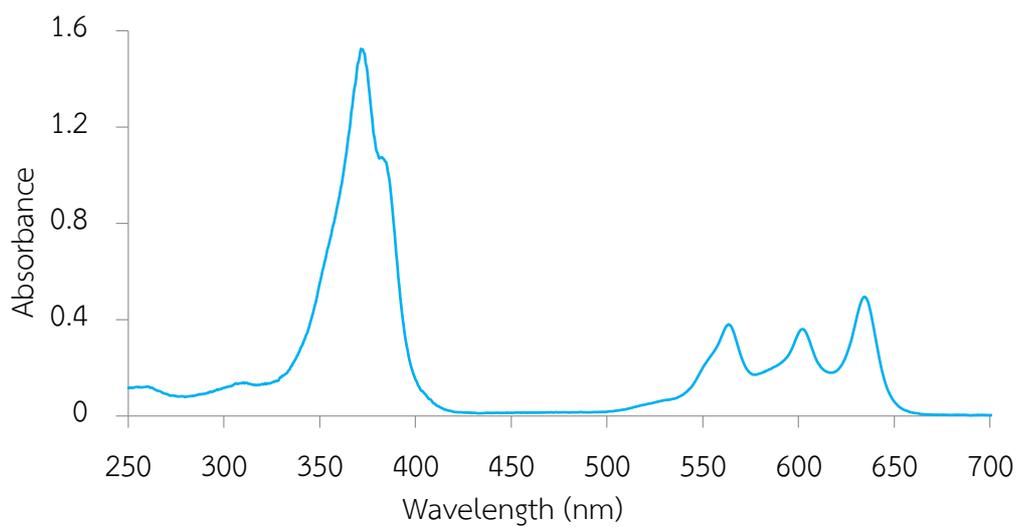


Figure 3-7 ¹H-NMR spectrum of H₂Pc

Figure 3-8 ESI-MS spectrum of H₂PcFigure 3-9 UV-Vis spectrum of H₂Pc

ภาควิชาเคมี
คณะวิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

3.2 Non-covalent interaction between photosensitizers and graphene oxide

Incorporation of a photosensitizer to GO can dramatically enhance its photocatalytic activity. In this work, particular attention is given on preparation of GO/photosensitizer composite via non-covalent interaction. Interaction between graphene oxide and photosensitizers *i.e.*, H₂TPP, CoTPP and H₂Pc are examined by fluorescence spectroscopy. Their structures are shown in **Figure 3-10**.

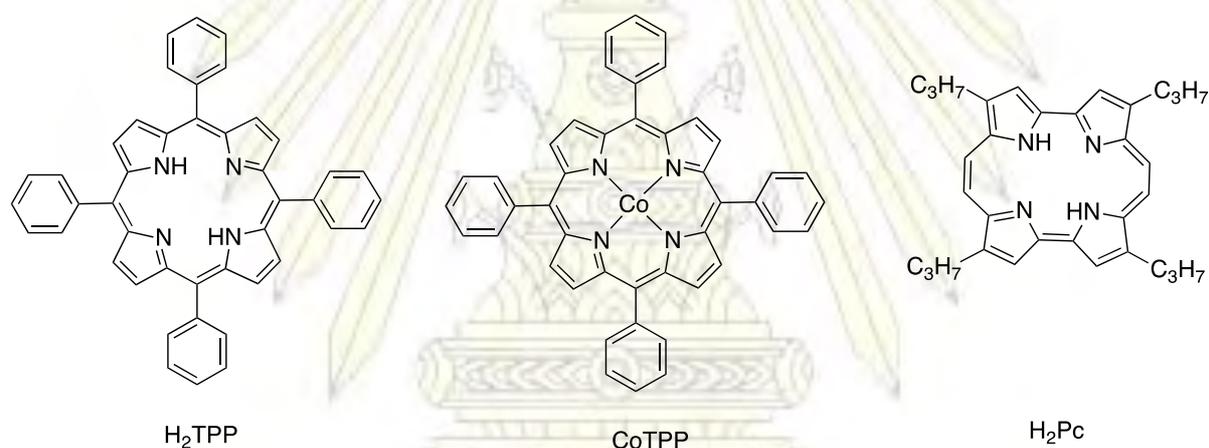


Figure 3-10 Structure of H₂TPP,CoTPP and H₂Pc

Fluorescence spectroscopy has been widely used to investigate the interaction between photosensitizer (which can give a fluorescence emission) and GO²⁵. The interaction can be studied on the basis of Photoinduced Electron Transfer (PET), which is one of the fluorescence quenching mechanism. Typically, when the dye molecule is excited by the light, its electron will go up to the excited state. To lower its energy, the excited dye molecule will undergo a non-radiative relaxation through bond vibration and rotation. Finally, the excited dye molecule can return to the ground state by gives off a fluorescence emission. Alternatively, in the presence of the GO, the excited molecule can also return to

the ground state by transferring the photoinduced electron to the conduction band of the GO. This process is called PET. As PET occurred, the fluorescence intensity of the dye molecule will decrease. As a result, if fluorescence quenching is observed upon addition of GO into the dye solution. The interaction between the two species via PET can be confirmed.

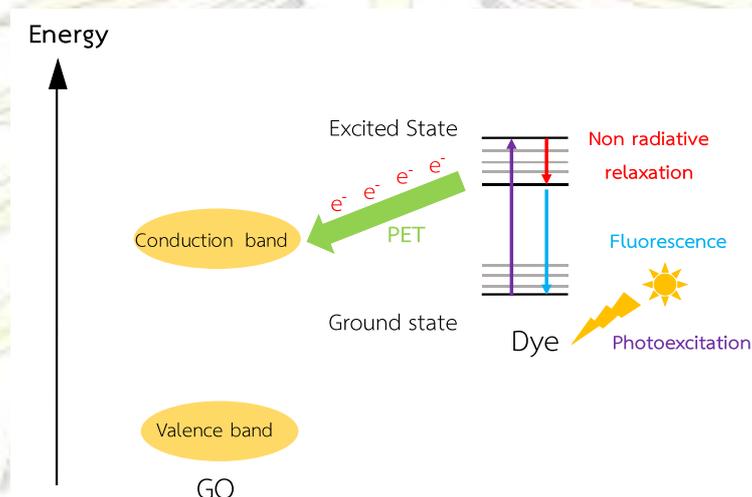
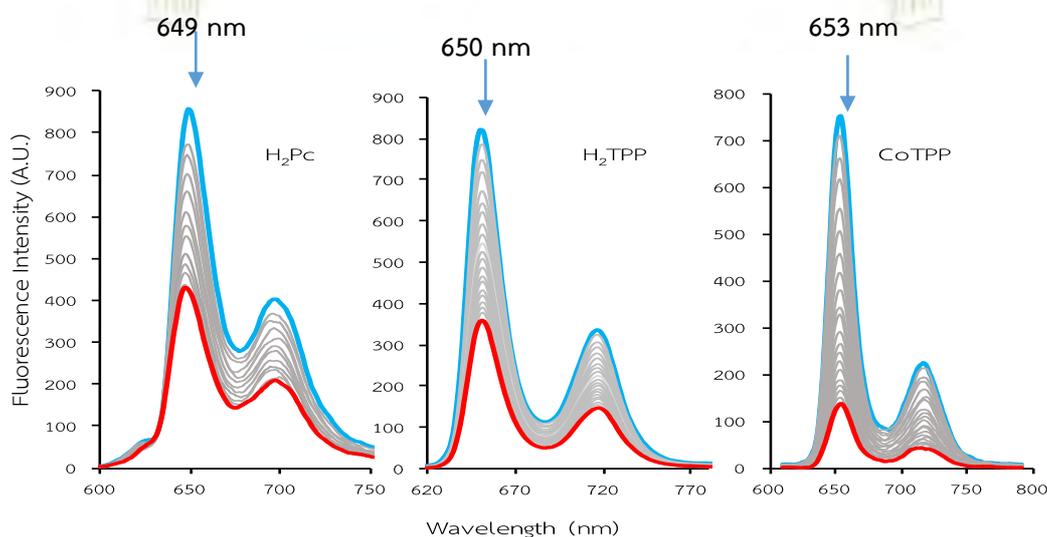


Figure 3-11 Scheme of fluorescence emission and PET process

From this principle, fluorescence titration between H_2Pc , H_2TPP , $CoTPP$ and GO were conducted. The spectral change is presented in **Figure 3-12**. Quenching was observed for all compounds. The fluorescence intensity of the photosensitizers gradually decreased as GO solution was added. The quenching was probably due to Photoinduced Electron Transfer process (PET). The electron is transferred from the photoexcited dye to the conduction



band of GO. Thus, the interaction between H₂Pc, H₂TPP, CoTPP and GO can be confirmed.

Figure 3-12 Fluorescence emission spectral change upon addition of GO dispersed in DI water (1.00 mg/mL, 0-500 μ L) into a solution of H₂Pc, H₂TPP and CoTPP (8.00 μ M) in DMSO

The control experiments were also conducted. dye solution was titrated with DI water instead of GO dispersion. The fluorescence spectra are shown in **Figure 3-13**. From the titration spectra, the added DI water enhanced the fluorescence intensity of the dye solution. This can be described by the process called aggregation-induced emission²⁶. It should be noted that all the dyes used in this experiment are hydrophobic. When water is added to the dye solution, the dye molecules tend to aggregate. As the dye molecules stack together, it is harder for the substituent groups (phenyl group for CoTPP, H₂TPP and propyl group for H₂Pc) to rotate and vibrate due to the steric hindrance. Since the rotations and vibrations of these substituent groups are the major non-radiative relaxation modes, the reduction of these modes enhanced the fluorescence of the dye.

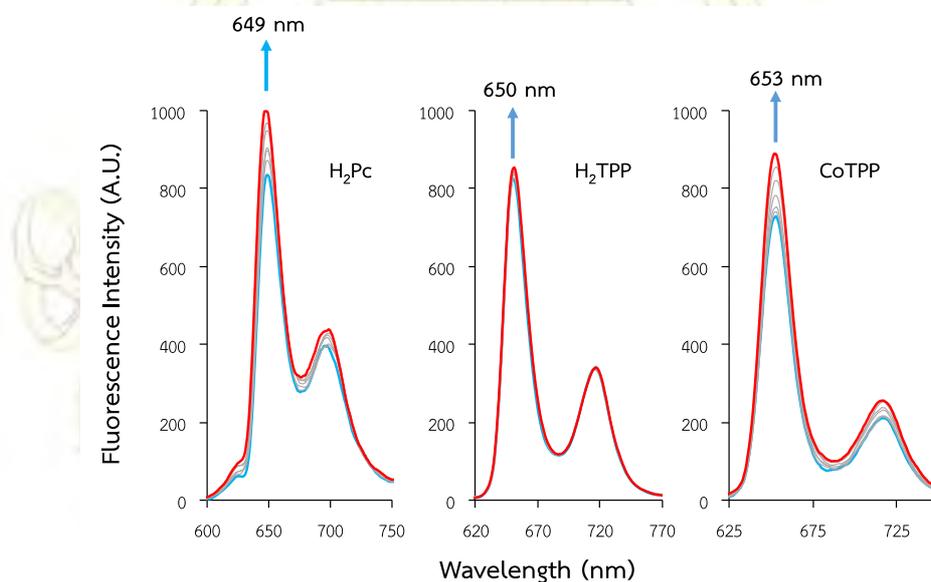


Figure 3-13 Fluorescence emission spectral change upon addition of DMSO (0-500 μ L) into a solution of H₂Pc, H₂TPP and CoTPP (8.00 μ M) in DMSO

In summary, H₂TPP, CoTPP and H₂Pc have a potent photosensitization activity toward GO. Thus, incorporation of these three dyes may enhance photocatalytic activity of GO.

3.3 GO/photosensitizer composite

The composite between photosensitizer (H_2TPP , $CoTPP$ and H_2Pc) and GO was confirmed by UV-vis spectroscopy. In GO/H_2TPP and $GO/CoTPP$ composite, the Soret band of porphyrin were observed (424 nm for GO/H_2TPP and 422 nm for $GO/CoTPP$). In GO/H_2Pc , both Soret band and Q bands of H_2Pc were observed (414 and 671 nm respectively). The UV-vis absorption is presented in **Figure 3-14**. All of photosensitizer peaks observed in $GO/photosensitizer$ composite were found to be broaden and experienced a bathochromic shifted. These observations indicate strong interaction between the three photosensitizers and GO. In addition, it was seen the photosensitizer peaks in GO/H_2Pc is much larger than that of GO/H_2TPP and $GO/CoTPP$ composite. This may due to the higher hydrophobicity of H_2Pc over the two porphyrins and the higher amount of H_2Pc that was used in the fabrication step. In addition, GO/H_2TPP , $GO/CoTPP$ and GO/H_2Pc were found to be stable in aqueous for at least 7 days.

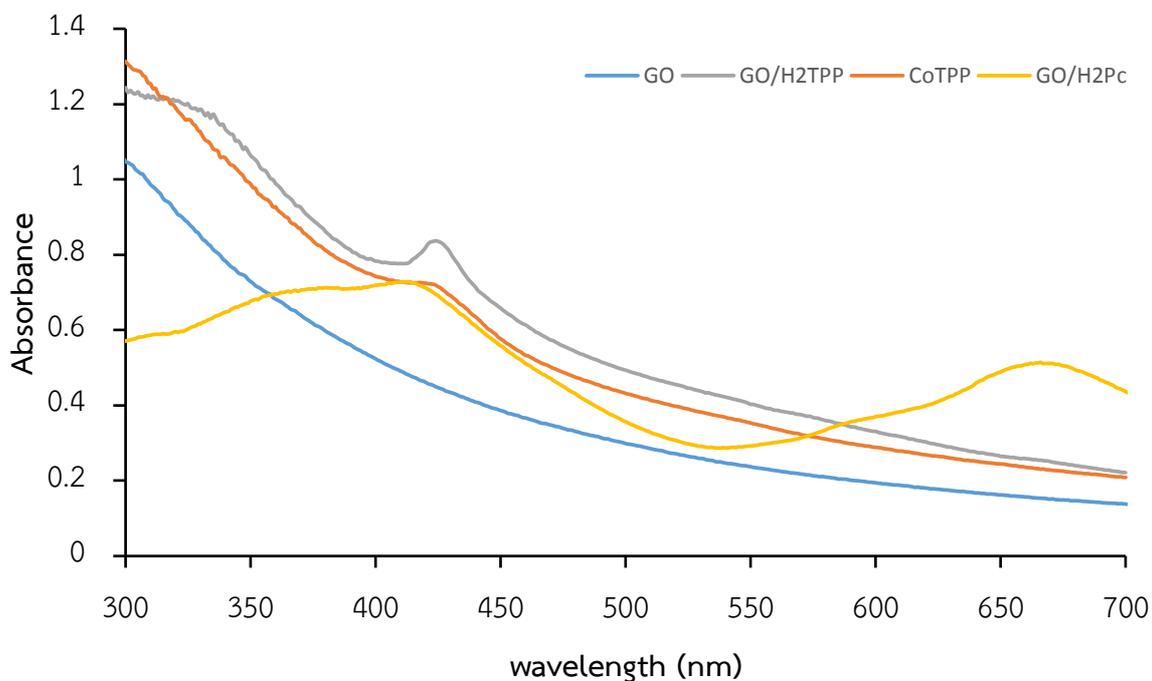
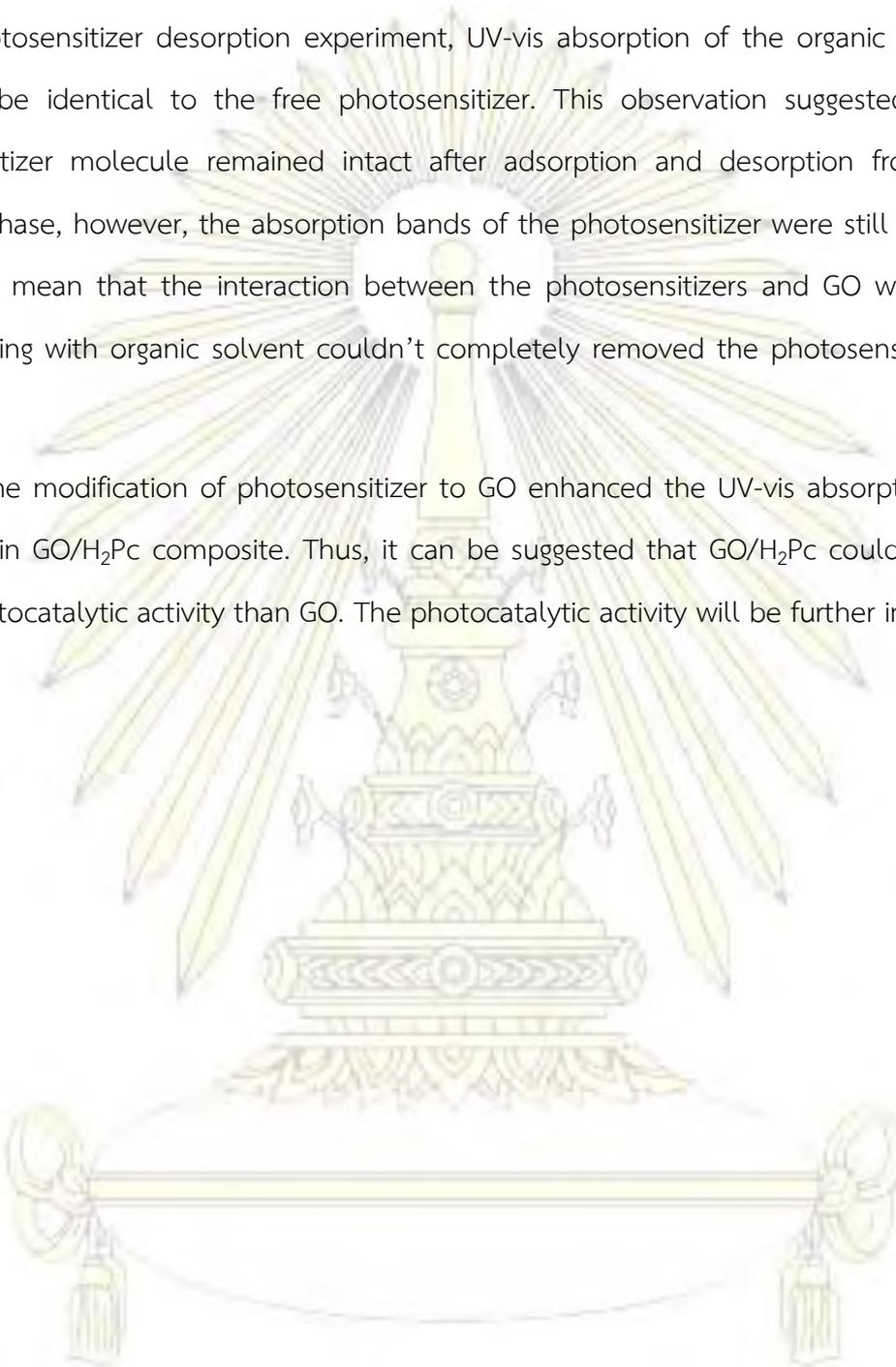


Figure 3-14 UV-vis absorption spectra of GO, GO/H_2TPP , $GO/CoTPP$ and GO/H_2Pc

In the photosensitizer desorption experiment, UV-vis absorption of the organic phase was found to be identical to the free photosensitizer. This observation suggested that the photosensitizer molecule remained intact after adsorption and desorption from GO. In aqueous phase, however, the absorption bands of the photosensitizer were still presented. This could mean that the interaction between the photosensitizers and GO were strong. Even washing with organic solvent couldn't completely removed the photosensitizer from GO.

The modification of photosensitizer to GO enhanced the UV-vis absorption of GO, especially in GO/H₂Pc composite. Thus, it can be suggested that GO/H₂Pc could process a better photocatalytic activity than GO. The photocatalytic activity will be further investigated.



ภาควิชาเคมี
คณะวิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

Chapter 4 Conclusion

In summary, GO, H₂Pc and CoTPP were successfully prepared and characterized by various spectroscopic techniques. The synthesis of H₂Pc and CoTPP gave 3 % and 62 % yield respectively. In the synthesis of GO, a fast and easy work-up procedure for GO synthesis (neutralization with phosphate buffer) was developed. The interaction between H₂TPP, CoTPP and H₂Pc and GO was first observed using fluorescence spectroscopy. The fluorescence emission of the three photosensitizers were quenched upon addition of GO. The quenching was due to photoinduced electron transfer (PET) process. The electron from the photoexcited dye molecule is transferred to the conduction band of GO causing the quenching in fluorescence emission. This observation suggested that H₂TPP, CoTPP and H₂Pc can potentially be used as a photosensitizer with GO. The GO/photosensitizer composite can be obtained by sonication of the concentrated mixture of GO and photosensitizer. The resulting composites were found to be stable in water. In GO/CoTPP and GO/H₂TPP, no color changes were observed in both composites. Only small Soret band peak were observed at around 424 nm for GO/H₂TPP and 422 nm for GO/CoTPP. In GO/H₂Pc, however, the color of GO solution changed from yellow-brown to green upon incorporation with H₂Pc. UV-Vis spectroscopy can confirm this observation. The broadened peaks of H₂Pc were found at $\lambda_{\max} = 414$ and 671 nm. These two peaks were found to be red shifted in comparison to the non adsorbed H₂Pc (Soret band $\lambda_{\max} = 372$ nm, Q band $\lambda_{\max} = 582, 600$ and 632 nm). These observations indicate the strong interaction between GO and H₂Pc. The spectroscopic data indicate that GO/H₂Pc nanocomposite has a potential to be a better photocatalyst than GO. The photocatalytic activity of the composite will be further investigated.

References

1. Lu, C. H.; Yang, H. H.; Zhu, C. L.; Chen, X.; Chen, G. N., A graphene platform for sensing biomolecules. *Angew Chem Int Ed Engl* **2009**, *48* (26), 4785-7.
2. Liu, J.; Cui, L.; Losic, D., Graphene and graphene oxide as new nanocarriers for drug delivery applications. *Acta Biomater* **2013**, *9* (12), 9243-57.
3. Lee, J.; Chae, H.-R.; Won, Y. J.; Lee, K.; Lee, C.-H.; Lee, H. H.; Kim, I.-C.; Lee, J.-m., Graphene oxide nanoplatelets composite membrane with hydrophilic and antifouling properties for wastewater treatment. *Journal of Membrane Science* **2013**, *448*, 223-230.
4. (a) Yeh, T.-F.; Cihlar, J.; Chang, C.-Y.; Cheng, C.; Teng, H., Roles of graphene oxide in photocatalytic water splitting. *Materials Today* **2013**, *16* (3), 78-84; (b) Hsu, H. C.; Shown, I.; Wei, H. Y.; Chang, Y. C.; Du, H. Y.; Lin, Y. G.; Tseng, C. A.; Wang, C. H.; Chen, L. C.; Lin, Y. C.; Chen, K. H., Graphene oxide as a promising photocatalyst for CO₂ to methanol conversion. *Nanoscale* **2013**, *5* (1), 262-8.
5. (a) Kumar, P.; Kumar, A.; Sreedhar, B.; Sain, B.; Ray, S. S.; Jain, S. L., Cobalt phthalocyanine immobilized on graphene oxide: an efficient visible-active catalyst for the photoreduction of carbon dioxide. *Chemistry* **2014**, *20* (20), 6154-61; (b) Kumar, P.; Sain, B.; Jain, S. L., Photocatalytic reduction of carbon dioxide to methanol using a ruthenium trinuclear polyazine complex immobilized on graphene oxide under visible light irradiation. *Journal of Materials Chemistry A* **2014**, *2* (29), 11246.
6. Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M., Improved synthesis of graphene oxide. *ACS. Nano* **2010**, *4*, 4806-4814.
7. Nasrollahzadeh, M.; Babaei, F.; Fakhri, P.; Jaleh, B., Synthesis, characterization, structural, optical properties and catalytic activity of reduced graphene oxide/copper nanocomposites. *RSC Adv.* **2015**, *5* (14), 10782-10789.

8. Linsebigler, A. L.; Lu, G.; John T. Yates, J., Photocatalysis on TiO₂ Surfaces- principles, mechanisms, and selected results *Chem. Rev.* **1995**, *95*, 735-758.
9. Low, J.; Yu, J.; Ho, W., Graphene-Based Photocatalysts for CO₂ Reduction to Solar Fuel. *J Phys Chem Lett* **2015**, *6* (21), 4244-51.
10. Kumar, P.; Bansawal, A.; Labhsetwar, N.; Jain, S. L., Visible light assisted photocatalytic reduction of CO₂ using a graphene oxide supported heteroleptic ruthenium complex. *Green Chem.* **2015**, *17* (3), 1605-1609.
11. Wang, Y.; Pei, Y.; Xiong, W.; Liu, T.; Li, J.; Liu, S.; Li, B., New photocatalyst based on graphene oxide/chitin for degradation of dyes under sunlight. *Int J Biol Macromol* **2015**, *81*, 477-82.
12. Zhou, L.; Jiang, H.; Wei, S.; Ge, X.; Zhou, J.; Shen, J., High-efficiency loading of hypocrellin B on graphene oxide for photodynamic therapy. *Carbon* **2012**, *50* (15), 5594-5604.
13. Georgakilas, V.; Tiwari, J. N.; Kemp, K. C.; Perman, J. A.; Bourlinos, A. B.; Kim, K. S.; Zboril, R., Noncovalent Functionalization of Graphene and Graphene Oxide for Energy Materials, Biosensing, Catalytic, and Biomedical Applications. *Chem Rev* **2016**.
14. Joseph, K. L. V.; Lim, J.; Anthonysamy, A.; Kim, H.-i.; Choi, W.; Kim, J. K., Squaraine-sensitized composite of a reduced graphene oxide/TiO₂ photocatalyst: π - π stacking as a new method of dye anchoring. *J. Mater. Chem. A* **2015**, *3* (1), 232-239.
15. Ethirajan, M.; Chen, Y.; Joshi, P.; Pandey, R. K., The role of porphyrin chemistry in tumor imaging and photodynamic therapy. *Chem. Soc. Rev.* **2011**, *40*, 340-362.
16. Grodkowski, J.; Behar, D.; Neta, P., Iron porphyrin-catalyzed reduction of CO₂. photochemical and radiation chemical studies. *J. Phys. Chem. A* **1997**, *101*, 248-254.
17. Urbani, M.; Gratzel, M.; Nazeeruddin, M. K.; Torres, T., Meso-substituted porphyrins for dye-sensitized solar cells. *Chem Rev* **2014**, *114* (24), 12330-96.
18. Sanchez-Garcia, D.; Sessler, J. L., Porphycene: synthesis and derivatives. *Chem. Soc. Rev.* **2008**, *37*, 215-232.

19. Ragas, X.; Sanchez-Garcia, D.; Ruiz-Gonzalez, R.; Dai, T.; Agut, M.; Hamblin, M. R.; Nonell, S., Cationic porphycenes as potential photosensitizers for antimicrobial photodynamic therapy. *J Med Chem* **2010**, *53* (21), 7796-803.
20. <http://www.pveducation.org/pvcdrom/appendices/standard-solar-spectra>
21. (a) Vogel, E.; Kocher, M.; Schmickler, H.; Lex, J., Porphycene-a Novel Porphin Isomer. *Angew Chem. Int. Ed. Engl.* **1986**, *25*, 257-259; (b) Sanchez-Garcia, D.; Sessler, J. L., Porphycenes: synthesis and derivatives. *Chem Soc Rev* **2008**, *37* (1), 215-32.
22. Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S., Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* **2007**, *45* (7), 1558-1565.
23. Rana, U.; Malik, S., Graphene oxide/polyaniline nanostructures: transformation of 2D sheet to 1D nanotube and in situ reduction. *Chem Commun (Camb)* **2012**, *48* (88), 10862-4.
24. Vlascici, D.; Chiriac, A.; Fayadar-Cosama, E.; Spiridon-Bizerea, O.; Tudose, R., Syntheses and spectroscopic characterization of Co(II) and Co(III) meso-tetraphenylporphyrins complexes. *Annals of West University of Timisoara: Series of Chemistry* **2004**, *13* (1), 9-20.
25. (a) Bozkurt, E.; Acar, M.; Onganer, Y.; Meral, K., Rhodamine 101-graphene oxide composites in aqueous solution: the fluorescence quenching process of rhodamine 101. *Phys Chem Chem Phys* **2014**, *16* (34), 18276-81; (b) Liu, Y.; Liu, C.-y.; Liu, Y., Investigation on fluorescence quenching of dyes by graphite oxide and graphene. *Applied Surface Science* **2011**, *257* (13), 5513-5518; (c) Shu, J.; Qiu, Z.; Wei, Q.; Zhuang, J.; Tang, D., cobalt-porphyrin-platinum-functionalized reduced graphene oxide hybrid nanostructures: a novel peroxidase mimetic system for improved electrochemical immunoassay. *Sci Rep* **2015**, *5*, 15113.
26. Hong, Y.; Lam, J. W. Y.; Tang, Z., Aggregation-induced emission. *Chem. Soc. Rev.* **2011**, *40*, 5361-5388.

Vitae

Mr. Nukorn Plainpan was born on April 27th, 1994 in Chonburi, Thailand. He graduated from Yothinburana school in 2011 and continued the study in bachelor degree at Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, Thailand. The current address is 326/3 Amnuay songkram road, Nakornchaisri, Dusit district, Bangkok 10300.

Contact information: nukorn.p27@gmail.com

ภาควิชาเคมี
คณะวิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย