

**ChPGS7**



# The 7<sup>th</sup> Chemistry Postgraduate Symposium

**May 8<sup>th</sup>, 2018**

**Department of Chemistry, Faculty of Science**



**Kasetsart University**





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ChPGS7**

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**Room 202, Department of Chemistry,  
Faculty of Science, Kasetsart University**

<i>Schedule</i>	
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13.00 - 13.10	Opening Remarks
<b>13.10 - 15.00</b>	<b>Poster Presentation</b>
15.00 – 15.15	<i>Coffee Break</i>
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## The Synthesis of Metal/PDDA/rGO Catalyst for Detection of Nitrite

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### Abstract

The metal/poly(diallyldimethylammonium chloride)/reduced graphene oxide (metal/PDDA/rGO) modified glassy carbon electrodes (GCEs) were successfully prepared by a chemical reduction. The electrodes were used to determine various concentrations of nitrite by cyclic voltammetry. The formation and composition of metal/PDDA/rGO were characterised by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS). The electrocatalytic response of nitrite oxidation measured on Ni/PDDA/rGO modified electrode is higher than that of Fe, Zn and Co, respectively. The calibration curve is linear over two concentration ranges from 0.8 to 4.0  $\mu\text{M}$  and 4.0 to 20  $\mu\text{M}$ . The linear regressions are  $i_p (\mu\text{A}) = 0.05312C (\mu\text{M}) - 0.04971$  and  $i_p (\mu\text{A}) = 0.08225C (\mu\text{M}) - 0.14747$ , respectively. The modified GCE was then employed to determine the concentration of nitrite in real sample.

**Keywords:** Nitrite, Electrochemical detection, Ni/PDDA/rGO

**Simultaneous determination of *p*-coumaric acid and naringenin  
in honey using dispersive liquid-liquid microextraction and high performance liquid  
chromatography**

Korbkarn Khukitirat<sup>1</sup>, Pongsak Lowmunkhong<sup>1</sup>, Somyote Sutthivaiyakit<sup>2</sup>,  
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### **Abstract**

*p*-Coumaric acid and naringenin have anti-inflammatory and antioxidant benefits. However, they have not been determined in honey from Thailand. A simple, rapid and sensitive dispersive liquid-liquid microextraction (DLLME) followed by HPLC with diode array detection was developed for simultaneous determination of the two compounds. Some important parameters for DLLME were optimized. A mixture of acetonitrile (disperser solvent) and dichloromethane (extraction solvent) was rapidly injected to a sample solution in 0.01 M ammonium acetate adjusted to pH 3 by a syringe, thereby forming a cloudy solution. After centrifugation at 4°C, the enriched analytes in the sedimented phase were filtered prior to injection. The separation was performed on a Pursuit<sup>®</sup> XRS Diphenyl column (150 x 3.0 mm, 3 μm) at 40°C with 0.1% formic acid – methanol gradient as the mobile phase. The detection wavelengths were 291 nm and 311 nm for naringenin and *p*-coumaric acid, respectively. The flow rate was 0.3 mL min<sup>-1</sup>. Due to the lack of matrix blank, standard addition was performed in the method development. The concentrations of *p*-coumaric acid and naringenin in lychee are 0.5 ± 0.01 μg.g<sup>-1</sup> and 0.38 ± 0.03 μg.g<sup>-1</sup>, respectively.

**Keywords:** Dispersive Liquid-Liquid Microextraction; *p*-Coumaric acid; Naringenin; Honey from Thailand

## Highly sensitive electrochemical capsaicin sensor based on polyaniline-derived N-doped mesoporous carbon

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**Abstract:** A glassy carbon electrode (GCE) modified with N-doped mesoporous carbon (N-MC) with high catalytic activity was employed for sensitive determination of capsaicin. The N-MC/GCE was characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) and its electrochemical property by Linear Sweep Voltammetry (LSV). The SEM images revealed the linear array of connected rod-like particles and confirmed the successful synthesis of the mesoporous carbon. The electrochemical performance study showed that the N-MC/GCE facilitates the adsorption of capsaicin on the electrode surface and provides fast electron transfer due to its high surface area and charge polarization. Furthermore, the presence of N-MC on GCE significantly enhances the oxidation peak current, indicating that the N-MC showed excellent electrocatalytic activity to the redox reaction of capsaicin. Under optimized conditions the proposed electrochemical sensor showed a linear response to capsaicin from 1.0 to 10.0  $\mu\text{M}$  with detection limit of 0.62  $\mu\text{M}$  (S/N=3) and the coefficient of determination ( $R^2$ ) of 0.9993. Thus, the N-MC/GCE demonstrated the promising electrochemical sensor that can be further developed as a sensitive portable electrochemical sensor for the determination of capsaicin in food and pharmaceuticals.

**Keywords:** Mesoporous carbon; Capsaicin; Linear sweep voltammetry



## Paper-based ammonia gas sensor using zinc complex of Eriochrome Black T and digital image analysis

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### Abstract

Colorimetric paper-based sensor for ammonia gas has been developed by coating an aqueous mixture (pH2) of synthesized Zn complex of Eriochrome Black T and TiO<sub>2</sub> in the presence of polyvinyl alcohol (binder) and polyethylene glycol (dispersing agent) on a filter paper. The paper changes from red to blue upon exposure to ammonia gas. Its color change increases with the ammonia concentration. The quantitation of ammonia gas was performed by digital image analysis using a commercial scanner and the Image J free software. The RGB values are converted to 2D CIE 1931 chromaticity space followed by the interpolation technique. The calibration graph is in the range of 200-2,000 ppmv with a detection limit 24 ppmv. The method was applied to analyze air samples collected from workplace environment in a small rubber pilot plant. The results obtained from the method developed are in good agreement with those obtained from the commercial detector tube method.

**Keywords:** ammonia gas; colorimetric paper based sensor ;Zn complex of Eriochrome Black T ; digital image analysis

## Extraction of phenol using poly(styrene-co-divinylbenzene) monolithic bead

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### Abstract

In this work, poly(styrene-co-divinylbenzene) or PS-DVB monolithic adsorbent was synthesized as a bead shape to extract phenol from water matrix. Quantitative level of the target analyte will be performed by gas chromatography with flame ionization detection (GC-FID). In the synthesis of this adsorbent, styrene and divinylbenzene were used as monomer and dibenzoyl peroxide was used as an initiator. In order to improve porosity, decanol and tetrahydrofuran were added into the polymerization step. The morphology of synthesized material showed an interconnected spherical shape of monolith structure of about 2  $\mu\text{m}$  diameter. Owing to internal particles of the material that are uniform and thoroughly interconnected within the macropore network, the selectivity and permeability for extraction of phenol from 50 mL of water sample was improved. In this work, several parameters which affect the extraction efficiency were evaluated. The results showed recovery in the range of 48-113% and linear relationship with  $R^2 \geq 0.99$ .

**Keywords:** monolithic adsorbent; poly(styrene-co-divinylbenzene); phenol ; gas chromatography with flame ionization detection.

## Preparation and characterization of nanodot MoS<sub>2</sub> @ 3DOM TiO<sub>2</sub> composites

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### Abstract

In this work, the strategy for preparation of nanodot MoS<sub>2</sub>@ 3-dimensional ordered macroporous (3DOM)TiO<sub>2</sub> was presented. Nanodot MoS<sub>2</sub> suspension was synthesized by intercalation and exfoliation processes. To give the high yield of nanodots, MoS<sub>2</sub> prepared by the hydrothermal method was selected instead of large-plane commercial MoS<sub>2</sub>. In case of 3DOM TiO<sub>2</sub>, polystyrene opal prepared by self-assembly method was used as the 3DOM template. Then, the hydrolysis and calcination of titanium alkoxide filled in template void were employed to get the 3DOM TiO<sub>2</sub> structure. Finally, nanodot MoS<sub>2</sub> and 3DOM TiO<sub>2</sub> was combined via the impregnation method. Interestingly, nanodot MoS<sub>2</sub>@ 3DOM TiO<sub>2</sub> exhibited the higher performance in degradation of methylene blue than non-doping 3DOM TiO<sub>2</sub>. It strongly emphasizes that MoS<sub>2</sub> still exhibits the quantum confinement effect when deposited on 3DOM TiO<sub>2</sub>. Nanodot MoS<sub>2</sub> can prohibit the electron-hole recombination on TiO<sub>2</sub> surface. Furthermore, the 3DOM structure of TiO<sub>2</sub> can also improve the scattering of incident light. Thus, nanodot MoS<sub>2</sub>@ 3DOM TiO<sub>2</sub> is underlined to be of interest in the electronic material and photocatalyst.

**Keywords:** nanodot MoS<sub>2</sub>, 3DOM TiO<sub>2</sub>, photocatalyst, degradation

## Inhibition of photocatalytic activity of basic blue-41 by ZnO modified surface with amino silane

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### Abstract

The reduction of the photo catalytic efficiency of ZnO can be achieved by modifying its surface with amino silane (ZMAS), which synthesized through condensation reaction under basic condition. The pH of solution was varied from 8 to 14 during the synthesis and was found that pH 12 was the most suitable pH for the preparation. All of ZMAS were characterized by Elemental Analysis which showed the highest percentage of nitrogen at 3.1064% and IR technique which indicated the Si-O-Zn bond at about  $1000\text{ cm}^{-1}$ . The photodegradation property of ZMAS prepared at pH 8-12 toward basic blue 41 was retarded when compared with the unmodified ZnO. Effect of mole ratio of ZnO:APTES (1:0.1, 1:0.5, 1:1, and 1:2) in the preparation of ZMAS was investigated. The photodegradation activity of ZMAS prepared at mole ratio of ZnO:APTES as 1:0.5 to 1:2 toward basic blue 41 was retarded when compared with the unmodified ZnO. The coating of amino silane on ZnO surface did not have much effect on the band gap energy of modified ZnO. The absorption edge of ZMAS was only slightly shifted from 392 to 397 nm.

**Keywords:** amino silane, photodegradation, and basic blue 41

## Total Synthesis of Melotenine A

Adisak Thanetchaiyakup, Hassayaporn Rattanarat  
and Paiboon Ngermmeesri\*

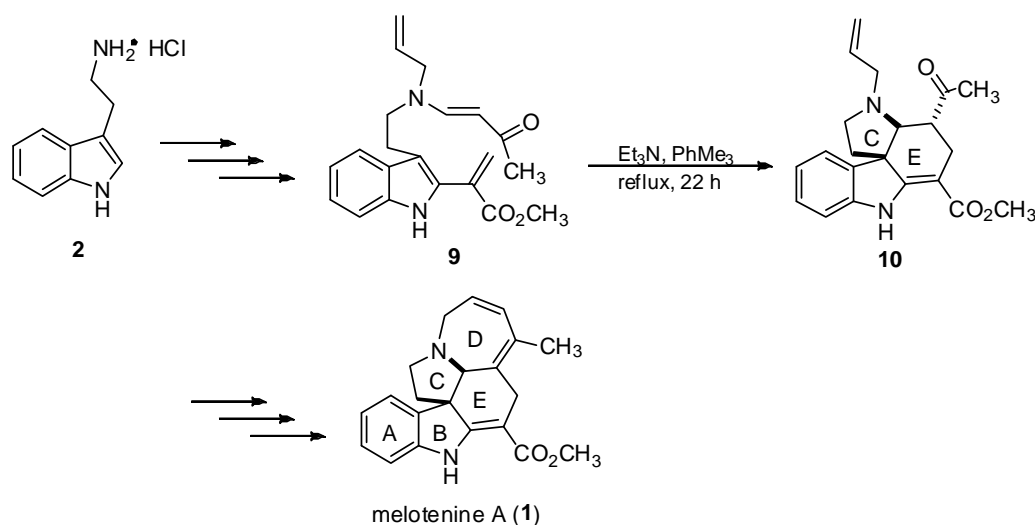
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### Abstract

Melotenine A is a monoterpene indole alkaloid, which contains an unprecedented skeleton with 6/5/5/7/5 pentacyclic rearranged ring system. This natural product shows a strong inhibitory effect against human cancer cell lines. In this research, we would like to synthesize melotenine A from tryptamine hydrochloride in 11 steps. The key step of our strategy is Diels-Alder reaction of compound **9** to construct the C and E bicyclic rings of compound **10**. This method will provide a novel and short route to synthesize melotenine A.

**Keywords:** Melotenine A, Anti-cancer, Diels-Alder reaction



## Searching for a new environmentally-friendly botanical insecticide from Thai plants

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### Abstract

The synthetic insecticides are usually used in agriculture for control the insects such as *Plutellaxylostella*, *Spodopteraexigua* and *Spodopteralitura*. These cause the residue of chemicals in the environment. The aim of this study was to find a new botanical insecticide from Thai plants for the control of *S.litura*. Rhizomes of *Alpinia galanga* (Zingiberaceae) were selected to extract with hexane, ethyl acetate, and ethanol, respectively. The bio-efficacy of *A.galanga* extracts against the second instars of *S. litura* by topical application method was investigated and the mortality data were recorded at 24 and 48 hours. The ethyl acetate extract from the rhizomes of *A. galanga* showed the highest toxicity with LD<sub>50</sub> 3619.35 ppm after 48 hours post-treatment. Moreover, the chemical constituents of the ethyl acetate extract of *A. galanga* rhizomes were described. Seven known phenylpropanoids were successfully isolated by using chromatography techniques. Among them, 1'S-1'-acetoxychavicolacetate, *trans-p*-coumaryldiacetate, and *p*-hydroxycinnamylacetate were the most numerous presented in the rhizome of *A. galanga*.

**Keywords:** *Spodopteralitura*, *Alpinia galanga*, insecticidal activity

## Chemical Constituents and Biological Activities of the Fruits of *Piper retrofractum* and Structure Modification

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### Abstract

This study aimed at assessing the potential of *Piper retrofractum* against *Spodoptera litura* larvae. The fruits of *P. retrofractum* were extracted with hexane, dichloromethane, ethyl acetate and methanol, respectively. Each crude extract was examined for toxicity against the second instars of *S. litura* according to a topical application method. The hexane extract showed the highest toxicity with LD<sub>50</sub> = 436 ppm at 24 h post-treatment. Furthermore, four isolated alkaloids from the hexane extract, methyl piperate, (2*E*,4*E*,14*E*)-*N*-isobutyleicosa-2,4,14-trienamide, retrofractamide D, piperanoline, and piperanine were identified as the inactive ingredients. In addition, piperate esters, derived from piperine as a major composition, will be synthesized and evaluated their insecticidal activity against *S. litura*.

**Keywords:** *Piper retrofractum*, *Spodoptera litura*, insecticidal activity

## The Barton ester free-radical reaction to synthesize naphthoquinone derivatives

Chaiyawat Aonsri<sup>1</sup> and Witcha Imaram<sup>1,2\*</sup>

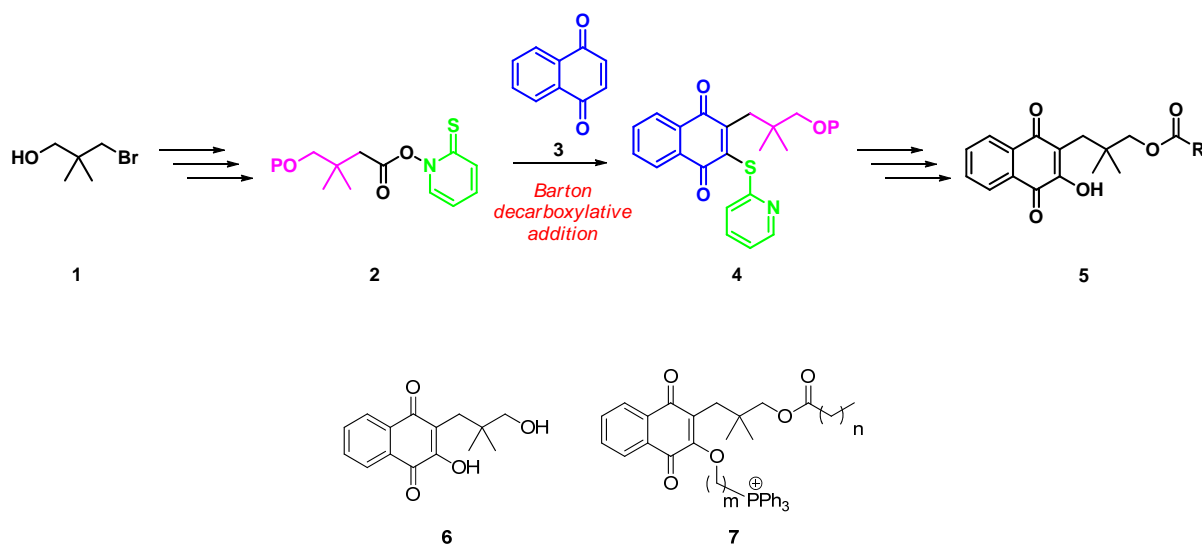
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### Abstract

The development of proficient drugs is a challenging goal for organic and medicinal chemists. One of the interesting compounds is the rhinacanthin analogues which are naphthoquinone derivatives. These compounds have shown strong anticancer activity and some synthetic compounds exhibit antimalarial activity as well. We are interested in developing an effective methodology to create a new library of cationic naphthoquinone analogues. Our synthetic strategy is to use the Barton decarboxylative addition, a free-radical reaction, to construct a C-C bond between the *gem*-dimethyl moiety and naphthoquinone. This is usually difficult to achieve with other methods because of the steric hindrance asserted by the *gem*-dimethyl group. Now, the precursor **6** has been already achieved through our synthetic route in 8 steps with 13% overall yield. Cationic naphthoquinone aliphatic esters **7** will be further prepared and evaluated their antimalarial activity against *P. falciparum*.



**Keywords:** Naphthoquinone, Barton decarboxylation, Radical reaction, Light initiation, Antimalarial activity.



## A new method for the preparation of aryl halides from phenols by nucleophilic aromatic substitution

Korakot Saowalak<sup>1</sup>, Parinthorn Temyarasilp<sup>2</sup>, Wanchai Pluempanupat<sup>1,\*</sup>

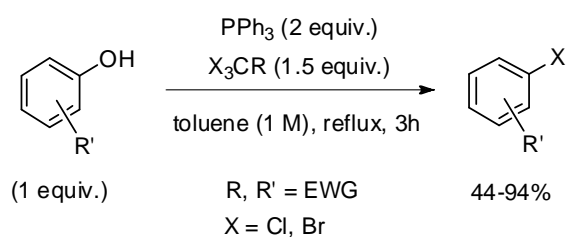
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<sup>2</sup>Chemistry Program, Faculty of Science and Technology, ValayaAlongkornRajabhat University under the Royal Patronage, PhatumThani 13180, Thailand

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### Abstract

A new and convenient method for the conversion of phenols into aryl halides through nucleophilic aromatic substitution ( $S_NAr$ ) using  $PPh_3$  and halogenating agent ( $X_3CR$ ) is described. Phenols containing electron withdrawing groups (EWG) were transformed into the corresponding aryl halides in moderate to high yields.  $PPh_3/Cl_3CCN$  and  $PPh_3/CBr_4$  were the most effective reagents for the chlorination and bromination, respectively.



**Keywords:** Phenols, Aryl halides, Halogenating agents,  $S_NAr$

## Synthesis of substituted benzoxepino[3,2-*b*]pyridines and their *N*-oxide derivatives

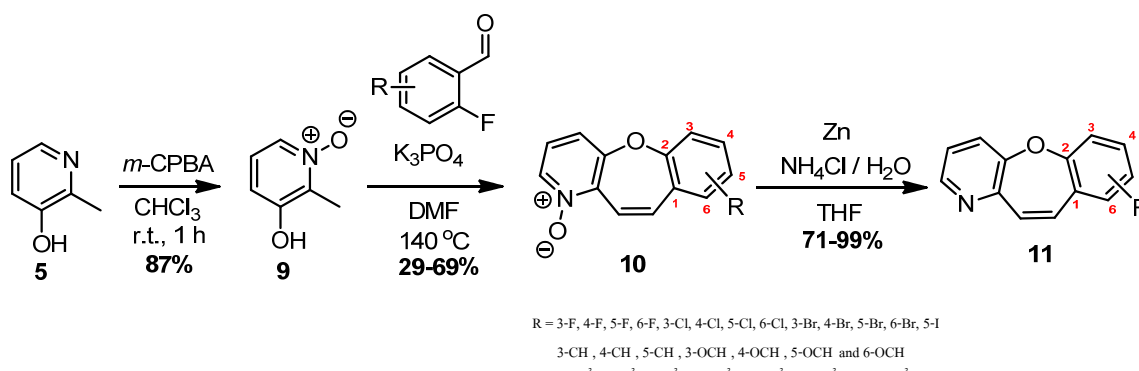
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### Abstract

Dibenzo[*b,f*]oxepine and its derivatives can be found as a core structure of many biologically active natural products. Although benzoxepino[3,2-*b*]pyridine is structurally similar to dibenzo[*b,f*]oxepine, the synthesis and biological evaluation of this compound have never been reported. In this work, we were able to synthesize substituted benzoxepino[3,2-*b*]pyridines in 3 steps from 2-methyl-3-pyridinol (**5**). The successful strategies include an oxidation reaction of to install electron-withdrawing group, a one-pot synthesis by nucleophilic aromatic substitution, S<sub>N</sub>Ar and Knoevenagel condensation to construct a benzoxepino[3,2-*b*]pyridine-*N*-oxides and a reduction reaction of these *N*-oxide derivatives to provide benzoxepino[3,2-*b*]pyridines in low to moderate yields.



**Keywords:** nucleophilic aromatic substitution, benzoxepino[3,2-*b*]pyridine, dibenzo[*b,f*]oxepine

## Toward the Total Synthesis of Anti-HIV Waltherione C

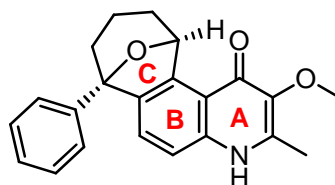
Pondpavee Taweesak, Watthanapong Khamphaya and Paiboon Ngermmeesri\*

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### Abstract

Waltherione C was isolated from *Melochiaodorata*, which is a plant found in Papua New Guinea. This compound possesses biological activity against human immunodeficiency virus, HIV. Our objective is to synthesize waltherione C, and we have 2 methods to construct the framework of this compound. In method A, we plan to synthesize this natural product employing the Michael addition and aldol reaction to form its 6-membered ring (ring B). In method B, we plan to form its 7-membered ring (ring C) by the Friedel–Crafts acylation and 6-membered ring (ring A) by aldol condensation.



waltherione C (1)

**Keywords:** Waltherione C, Friedel–Crafts acylation, Michael addition, Aldol condensation.

## Synthesis and anticancer activity evaluations of 2,3-arylpyridylindoles

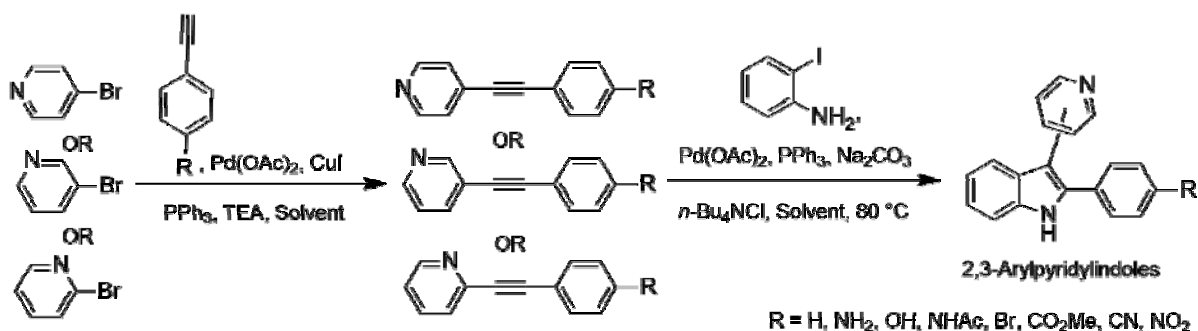
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### Abstract

Cancer is a disease involving abnormal cell growth. Some of the cancer cells can spread to other parts of the body from the origin by detaching themselves into small lymph or blood vessels. Many cancer treatments are available including surgery, radiation therapy, bone marrow and stem cell transplants, and chemotherapy. Chemotherapy is a treatment that uses anticancer drugs for primarily killing cancer cells that divide rapidly. Currently, there are many anticancer drugs available, and new anticancer drugs have been developed for a variety of combination of drugs that can improve success of treatment. Indole is one of promising heterocyclic moieties that has anticancer properties. Previously, we have demonstrated the anticancer activity of the synthetic 2,3-diarylindoles against A549 lung cancer cells. In this work, we focus on the synthesis of indole derivatives containing 2-, 3- or 4-pyridyl group at the 2 or 3 position of the indole nucleus. We proposed that the installation of a pyridyl group should increase hydrogen bonding capability on the aryl substituents at the C2 or C3 position of the parent compound and improve their solubility. We have synthesized 2,3-Arylpyridylindoles from 2,3, and 4-(Phenylethynyl)pyridine via Larockheteroannulation result in 35-98 %yield. Next step is to synthesize a series of 2,3-arylpyridylindoles with substituents on phenyl group.



**Keywords:** 2,3-arylpyridylindoles, an anticancer drug

## Anthraquinones and Gallic Acid Derivatives from the Roots of *Morinda scabrida*

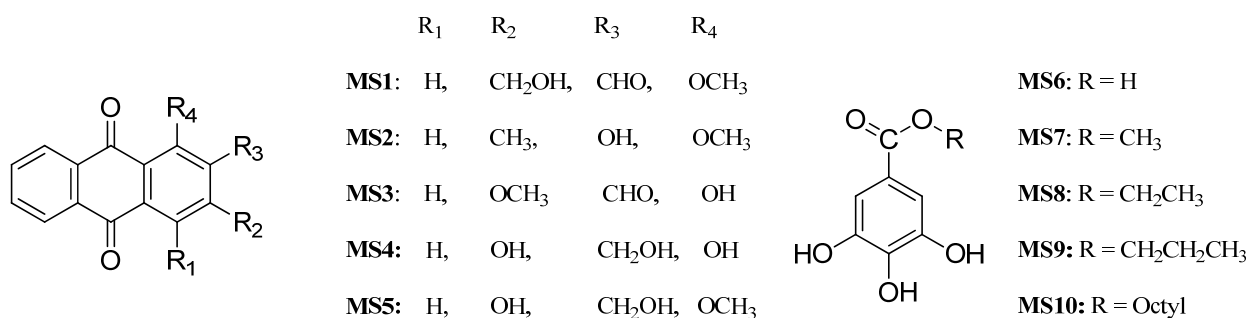
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### Abstract

*Morinda* belongs to the Rubiaceae family. The genus *Morinda* contains approximately 40 species. Nine species have been found in Thailand. *Morinda scabrida* was found for the first time in Kanchanaburi province, Thailand, and no phytochemical investigation has been carried out for this species. This prompted us to investigate the chemical components of *M. scabrida* and evaluate the biological activities of extracts and pure compounds. Air-dried powder of roots of *M. scabrida* (1.0 kg) was macerated successively with 3.0 L of methanol (2 days, 3 times). After evaporation under vacuum, the viscous methanolic extract was suspended in H<sub>2</sub>O and partitioned successively with EtOAc (200 mL, 3 times). The MeOH extract of *M. scabrida* was divided into water-insoluble and water-soluble portions, which were chromatographed repeatedly on silica gel. The selected fractions were further purified to afford ten pure compounds (**MS1- MS10**). Chemical structures of isolated compounds were elucidated using IR and 1D and 2D NMR spectroscopic techniques.



**Keywords:** *Morinda scabrida*, Anthraquinones, Gallic Acid

## Substituent Effect on Photophysical Properties of Salicylidene Schiff Base and Its Derivatives as Colorimetric Dyes: A TD-DFT Study

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### Abstract

The effects of substitution groups on the photophysical properties and excited-state intramolecular proton transfer (ESIPT) of the salicylidene Schiff base derivatives (SA1, SA2, SA3 and SA4) were considered using density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations at CAM-B3LYP/6-311G(d,p) level. Geometries and absorption spectra of all derivatives were calculated at the same level of theory. The substitution of the salicylidene Schiff base derivatives resulted in the red shift spectra, which implies that the electron donor substituted has the effect on the  $\pi$ -conjugated system. In addition, results of molecular orbital analysis show that vertical  $S_0 \rightarrow S_1$  transition of these molecules corresponds essentially excitable from HOMO ( $\pi$ ) to LUMO ( $\pi^*$ ). The potential energy curves (PECs) of selected derivatives were used to investigate the occurrence of ESIPT. The substitution of salicylidene Schiff base derivatives could easily facilitate the ESIPT process, because the electron donor substitution makes O-H bond of selected salicylidene Schiff base derivatives weaker than those of other derivatives and the hydrogen bond in N-H becomes stronger in the excited state, resulting in lower PT barrier. The obtained information of the electronic structure, the photophysical property and the chance of ESIPT of salicylidene Schiff base derivatives molecules is useful for molecular design of colorimetric molecular probes.

**Keywords:** Phototautomer, Schiff base derivatives, Time-dependent density functional theory (TD-DFT), Excited-state intramolecular proton transfer (ESIPT)

## Studies of Sildenafil and Phosphodiesterase type 5 binding properties using by computational methods

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### Abstract

Phosphodiesterases (PDEs) are significant enzymes involving hypertension and erectile dysfunction disease. The treatment of these disorders have been impacted via the use of strong PDE selective drugs. Phosphodiesterase5 (PDE5) is one of eleven isozymes in the PDE family controlling cGMP levels by cGMP hydrolysis. In this work, the crystallographic data complexed between sildenafil and PDE5 (pdb code: 2h42) was chosen to study the physical movement in the dynamic conditions using molecular dynamics (MD). The simulations were performed for 100 ns using Gromacs ver.5.0 with Amber99SB forcefield. In the binding site, there are important residues for hydrogen bond (Ala779) and hydrophobic (Leu725, Ile768, Ala783 and Val782) interactions. The equilibrated complex structure from MD and key amino acids for the binding were further investigated using quantum mechanical (QM) calculations to study binding interactions between ligand and protein in the binding pocket. The results indicate important interactions between sildenafil and PDE5 and provide insights for designing new potent PDE5 inhibitors.

**Keywords:** Hypertension, Erectile dysfunction, Phosphodiesterase(PDE), Sildenafil

**Theoretical study of twisted intramolecular charge transfer and intermolecular double proton transfer in the excited state of N,N'-bis(salicylidene)-p-phenylenediamine Schiff base**

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**Abstract**

Density functional theory (DFT) and time-dependent density functional theory method at the CAM-B3LYP/6-311G(d,p) level was applied to investigate the intramolecular and intermolecular hydrogen bonding dynamics in the first excited (S1) state of N,N'-bis(salicylidene)-p-phenylenediamine (BSP) and in ethanol solution. In the BSP single molecule, we demonstrated that the intramolecular charge transfer (ICT) takes place in the S1 state. This excited state ICT process was followed by intramolecular proton transfer. For the hydrogen-bonded BSP-H<sub>2</sub>O complex, it was demonstrated that the intermolecular hydrogen bonds can induce the formation of the twisted intramolecular charge transfer (TICT) state and the conformational twisting is along the C-C bond. Moreover, the intermolecular hydrogen bonds can also facilitate the intermolecular double proton transfer in the TICT state. This work successfully presents the stepwise excited state intramolecular double proton transfer (ESDPT) process of BSP. Therefore, the intermolecular hydrogen bonds can alter the mechanism of intramolecular charge transfer and proton transfer in the excited state for the BSP molecule.

**Keywords:** Twisted intramolecular charge transfer (TICT); Excited state intramolecular double proton transfer (ESDPT); Schiff base; time-dependent density functional theory (TD-DFT)



## Mechanistic Investigation of the Uncatalyzed Self-Esterification Reaction of L-Lactic Acid: A DFT Study

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### Abstract

Lactic acid is a bio-based organic acid derived from renewable agricultural resources. It has currently received great interest as an important reactant in many industrial synthetic processes, especially in the synthesis of environmentally friendly solvents and polymers, due to its nontoxic and biodegradable properties. However, the use of lactic acid as reactant is complicated, since the degree of intermolecular esterification of lactic acid to form linear dimer and higher oligomers increases over a concentration range of higher than 20 wt% aqueous lactic acid solutions. In this work, a comprehensive mechanistic investigation of the uncatalyzed self-esterification reaction of L-lactic acid at the molecular level was undertaken to understand the origin of such aforementioned behaviours. Two competing reaction pathways, i.e. a one-step concerted S<sub>N</sub>2-like mechanism and a two-step concerted addition-elimination mechanism in the presence of the commonly assumed tetrahedral intermediate, were studied. The effects of the water and lactic acid molecules participate as proton mediators on the free energy barriers for the proton-transfer esterification reactions were also examined. Density functional theory (DFT) calculations at the M06-2X/6-311G(d,p) level establish that the intermolecular esterification of lactic acid is a reversible reaction and favorably proceeds through the two-step concerted mechanism, with the kinetically relevant step involving the reversible elimination of water. The formation of dimer and higher oligomer acids at low and moderate concentrations of aqueous lactic acid solutions is more likely to take place via the water-mediated proton transfer esterification mechanism whereas that at high concentrations should occur more favorably via the lactic acid-mediated proton transfer mechanism. Similar conclusions are also drawn from the intramolecular esterification studies of dimer and trimer of lactic acid.

**Keywords:** Lactic acid, DFT, Esterification, Proton transfer, Mechanism

## Computational Studies of The Adsorption of Human Defensin 5 on Bacterial Membranes

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### Abstract

Human  $\alpha$ -defensin 5 (HD5) is one of the important anti-microbial peptides (AMPs) used against a broad-spectrum of pathogens in human, especially Gram-negative bacteria. HD5 kills by disrupting and making a pore in the bacterial membrane. A presence of lipopolysaccharide (LPS), located on a membrane surface, is found to have an impact on HD5's activity where the binding mechanism remains unclear. In this work, we therefore employed Molecular Dynamic (MD) simulation to investigate the binding mechanisms of HD5 on both LPS and bare lipid membranes. The activities of both stable HD5 forms (dimer and tetramer) were investigated in comparison. We observe that the chemical properties of membrane surface influence the binding affinity of HD5. Both dimeric and tetrameric HD5 can penetrate deeply into a phosphate layer in a lipid membrane, whereas HD5 only sits on a LPS membrane. Furthermore, residues in the active region (A1, T2, R6, R13, R32) appear to play a key role in membrane adsorption in all cases. Our results also show that the dimer is more desirable on a membrane. Moreover, both dimeric and tetrameric HD5 can significantly disrupt the LPS layer, whilst no serious distortion of lipid membrane is obtained. This emphasizes the importance of LPS on HD5 activity. This information is not only useful for better understanding our immune system, but also serve as a guidance for further design and development of antimicrobial drugs.

**Keywords:** Antimicrobial peptides, Human defensin 5, Lipopolysaccharide, Molecular dynamics simulations, Host-defense peptide.

## Theoretical study for absorption spectra and activity of s-tetrazine derivatives on the [4+2] Diels-Alder cycloaddition reaction with ethylene

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### Abstract

S-tetrazine is a highly reactive aromatic molecule which can interact rapidly with olefins via the inverse electron demand Diels-Alder (iEDDA) addition. The molecule itself can also absorb visible light due to its low lying  $\pi^*$  orbitals. These unique properties make tetrazine to be useful in wide range of applications. In this study, derivatives of tetrazine (R-Tz-R') were studied by using theoretical calculations to examine the effect of the substitution groups, R and R', to their absorption spectra and reactivity when interact with ethylene. Activation barrier for the addition decreased when R group was substituted by electron withdrawing groups but increased when substituted by electron donating groups. Changing substitution groups mainly affect the absorption strength of the  $\pi \rightarrow \pi^*$  transition (around 350nm) while absorption strength of the  $n \rightarrow \pi^*$  transition (around 550nm) are nearly unchanged.

**Keywords:** tetrazine, iEDDA, ethylene

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