

# An Application of the Reaction Class Transition State Theory (RC-TST): Hydrogen Abstraction of Alkanes by Nitrate Radical

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Kinetics of the hydrogen abstraction reaction of the class alkane + NO<sub>3</sub>· → alkyl + HNO<sub>3</sub> was studied using reaction class transition state theory (RC-TST) combined with linear energy relationships (LERs). The thermal rate coefficient for the reference reaction of ethane + NO<sub>3</sub>· → ethyl + HNO<sub>3</sub> was calculated by the canonical variational transition state theory (CVT) incorporating corrections from tunneling using the one dimensional Eckart tunneling approximation. All necessary parameters were derived from the reaction barriers and energies of a representative set of 16 reactions involving a range of alkanes. The outcome rate coefficients from the RC-TST/LER method are far from reproducing the result from the TST/Eckart approach with the differences as large as two orders of magnitude at the temperature range of 200-500 K, and even larger at higher temperature. However, the Arrhenius plots of the rate coefficients from the reaction class method are still in a better agreement with the available experimental results. This still gives a good outlook for the application of calculation results RC-TST/LER method in environmental modelling.

**Keywords** Reaction class transition state theory (RC-TST); Nitrate radical; Hydrogen abstraction Reaction; BH&HLYP

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## Theoretical Study on 3d Transition Metal-doped Ovalene: Structural and Electronic Properties

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The binding of single 3d transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) to ovalene has been investigated using density functional theory at the B3LYP/LanL2DZ theoretical level. The calculations indicate that Ti atom has the strongest binding ability to ovalene with binding energy of -222.76 kcal/mol. The binding abilities of all these transition metals onto ovalene are in order: Ti > V > Fe > Cr > Mn > Ni > Sc > Co > Cu > Zn. The geometrical parameters and electronic properties of transition metals-doped ovalene are also reported.

**Keywords** DFT; Doping; Ovalene; Transition metal

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# DFT and TD-DFT Investigations of [M(dcbpyH)(qsal<sup>X</sup>)CN] (M = Zn, Ru and X = H, Br, OMe) Complexes for DSSCs Applications: Effect of Metal and Ligand Substitute Group

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Metal-containing organic dyes including Ru(II) and Zn(II) complexes are the promising candidates for the research on dye sensitized solar cell (DSSCs).<sup>1-5</sup> In this work, the theoretical study of [M(dcbpyH)(qsal<sup>X</sup>)CN] (M = Zn, Ru and X = H, Br, OMe) complexes at B3LYP/6-31G\*\* level and the CAM-B3LYP/LANL2DZ level in conjunction with conductor-like polarizable continuum model method (CPCM) were performed and compared. The electronic structures of these complexes show that, with the same ligand, Zn(II) forms five coordinate complexes whereas Ru(II) forms six coordinate complexes. There are also much more electron delocalized on the metal in HOMO and LUMO of Ru(II) complexes compared with those of Zn(II) complexes. The changing of substitute group on the qsal ligand from Br to H to OMe resulted in the increase of the energy level of LUMO. However, their predicted energy level of HOMO and LUMO are still higher than those of TiO<sub>2</sub>. Moreover, the predicted UV-Vis spectra results show that Ru(II) complexes absorbed wider range of UV-Vis wavelength with lower epsilon compared with those of Zn complexes. Hence, based on theoretical results here, [Ru(dcbpyH)(qsal<sup>X</sup>)CN] (X = H, Br, OMe) are the good candidate for DSSCs applications.

**Keywords** TD-DFT; Ru(II) complexes; Zn(II) complexes; DSSCs

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# Studies of Tween 20 and Styrene-(Ethylene Butylene)-Styrene Interactions using Fluorescence Polarity Indicator and Steady-State Anisotropy

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Two different fluorescence-based techniques: pyrene polarity indicator and pyrene steady-state anisotropy have been used to study the surfactant-polymer interactions of polyoxyethylene (20) sorbitanmonolaurate (Tween 20) and styrene-(ethylene butylene)-styrene (SEBS) in toluene. Unlike in aqueous media, the fluorescence data in both methods from the system of individual component do not provide obvious information about the molecular association and organization behavior. This probably results from the expected reversed-micelle of Tween 20 which continues changing in dimension and behavior when its concentration increases. However, the fluorescence anisotropy shows increase in the system viscosity when the concentration of SEBS was increased. Fluctuation in the fluorescence data has been also seen in the system of Tween 20 and SEBS in toluene. Consequently, it is difficult to interpret the interactions between them. For comparison, the system with Xylan, instead of SEBS, in water was investigated in the identical conditions. Similar results were obtained from the fluorescence anisotropy. Furthermore, the possibility of the Tween 20-SEBS interaction-induced reversible fluorescence quenching of pyrene has been investigated with 4-nitroaniline as a quencher. The experiments were carried out with and without Tween 20 and SEBS, and the Stern-Volmer plots were created. It was found that there is no significant change in the fluorescence emission spectra and the plots of pyrene.

**Keywords** Styrene-(ethylene butylene)-styrene; Xylan; Tween 20; Fluorescence anisotropy; Fluorescence quencher

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# The Effect of Reversing the Location of Donor and Acceptor Groups on the Aromaticity and Electronic Structure of a Series of Substituted Poly-2,7-[2]calicenes

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Earlier research had reported the push-pull effect on the aromaticity and electronic structure of a series of substituted poly-2,7-[2]calicenes using density functional theory (DFT). Since poly-2,7-[2]calicene is asymmetrical, in that study we used  $-NH_2$  as an electron donor (push) on the terminal three-membered ring and  $-BH_2$ ,  $-C\equiv N$ ,  $-NO_2$ , and  $-F$  as electron acceptors (pull) on the terminal five-membered ring to enhance the natural polarity of the molecule. The dipole moments of the nine derivatives ranged from 16.0 D to 31.5 D compared to 13.0 D for unsubstituted poly-2,7-[2]calicene. In this study, we used  $-NH_2$  as an electron donor (push) on the terminal five-membered ring and  $-BH_2$ ,  $-C\equiv N$ ,  $-NO_2$ , and  $-F$  as electron acceptors (pull) on the terminal three-membered ring in order to attenuate the natural polarity of the series of substituted poly-2,7-[2]calicenes. The dipole moments of the “reversed” derivatives ranged from 0.8 D to 10.5 D. We will discuss these results along with the “reversed” push-pull effect on the structures and NMR properties of this series of substituted poly-2,7-[2]calicenes. The properties of the reference molecules calicene, benzene, cyclopentadienyl anion, and cyclopropenyl cation are also included. All geometries, vibrational frequencies, and properties (dipoles, NMR, etc.) are reported at B3LYP/6-31+g(d,p) level of theory.

**Keywords** Push-pull Effect; Calicene; Density Functional Theory; Nucleus Independent Chemical Shift; Aromaticity

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# Specific Interactions between Diarylpyrimidine Derivatives and HIV-1 RT: Molecular Docking and *ab Initio* FMO Calculations

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It has been recognized that the reverse transcriptase (RT) existing in HIV-1 is essential for increasing HIV-1. It is thus expected that inhibition of the RT activity can prevent the increase of HIV-1 [1]. As non-nucleoside inhibitors to RT, many types of diarylpyrimidines (DAPYs) have been synthesized. Among them, TMC125 was approved by the US Food and Drug Administration, while TMC278 (rilpivirine) was found to play important roles in inhibiting the HIV-1 RT [2].

In the present study, we employed some novel derivatives of TMC278 and investigated the specific interactions between HIV-1 RT and the derivatives in atomic and electronic levels, using *ab initio* molecular simulations. We first docked the derivatives into the ligand-pocket of HIV-1 RT using a protein-ligand docking program, and the docked structures were fully optimized in water by classical molecular mechanics. Finally, using *ab initio* fragment molecular orbital (FMO) calculations, we elucidated the specific interactions between each amino acid residue of HIV-1 RT and the derivatives at an electronic level. Based on the FMO results, we attempted to propose novel inhibitors to HIV-1 RT WT. The details of the results will be shown at the conference.

**Keywords** Diarylpyrimidines; TMC derivatives; Fragment molecular orbital; Binding energy; Specific interaction; Inhibitor to RT

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# Specific Interactions between Acetyl- and Butyryl-Cholinesterase and Their Inhibitors: *ab Initio* Molecular Simulations

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Acetylcholinesterase (AChE) and butyrylcholinesterase (BChE) play important roles in the hydrolyzing mechanism of neurotransmitter acetylcholine (ACh). Recently, AChE and BChE have attracted much attention because of the possibility that they may contribute to ACh hydrolysis in the brain of Alzheimer's patients, where the transmission mechanism of information between nerve cells is damaged due to a considerable shortage of ACh[1]. It is thus expected that if the hydrolysis reaction of ACh by AChE and BChE can be inhibited in the brain of Alzheimer's patients, the amount of ACh in the synapse will not be decreased so significantly and the transmission mechanism will become smoother. We here investigated the specific interactions between AChE/BChE and some types of ligands, using molecular simulations based on classical molecular mechanics (MM) and *ab initio* fragment molecular orbital (FMO) methods. Based on the results simulated for AChE and BChE, we attempted to propose novel ligands, which have strong binding affinity to both AChE and BChE.

**Keywords** Protein-ligand docking; Molecular mechanics; Molecular orbital calculation; Inhibitor; Acetylcholine

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# Epoxidation of Styrene and Cyclohexene by TBHP Oxidant: a Reaction Mechanism Investigation using Density Functional Theory

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The epoxidations of styrene and cyclohexene by using *tert*-butyl peroxide radical and *tert*-butyl oxide radical as oxidants were investigated by using the Density Functional Theory. Styrene and cyclohexene were considered as model compounds for aromatic and cyclic aliphatic systems. Both radicals were generated from TBHP (*tert*-butyl hydroperoxide). The reaction mechanism was proposed as either stepwise or concerted. The standard B3LYP/6-31G(d) level of calculation was used to determine the structure of all species along the reaction pathway. The calculations revealed that the epoxidations of both olefins occur via the concerted mechanism. The calculation results support the major product observed in the experiment. In addition, the epoxidation by *tert*-butyl peroxide radical takes place much faster than that by *tert*-butyl oxide radical.

**Keywords** Epoxidation reaction; Styrene; Cyclohexene; TBHP; DFT

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2. P. Cancino, V. Paredes-García, P. Aguirre, E. Spodine, Catal. Sci. Technol. (2014).

## Specific Interactions between *M. tuberculosis* CYP130 and Novel Inhibitors: *Ab Initio* Molecular Simulations

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Tuberculosis has been a major global health problem caused by *Mycobacterium tuberculosis* (*M. tuberculosis*). Since econazole has been known to be active against *M. tuberculosis* CYP130, many anti-tuberculosis agents such as nitroimidazole and 1H-1,2,3-triazole were developed from econazole. In the present study, using *ab initio* fragment molecular orbital (FMO) calculations, we investigated the specific interactions between CYP130 and its inhibitors, in order to propose novel potent inhibitors for CYP130. At first, using a protein-ligand docking program, we docked these inhibitors into the ligand binding pocket of CYP130, and the docked structures were fully optimized in water by classical molecular mechanics calculations. Finally, the binding properties and the specific interactions between CYP130 and the inhibitors were investigated by FMO at an electronic level. As for the CYP130+econazole complex, we obtained the structure comparable to its X-ray structure, and the FMO results highlight which residues of CYP130 and which parts of econazole are important for the binding between CYP130 and econazole. Based on the results, it will be possible to design novel CYP130 inhibitors. The detailed results will be shown in the poster.

**Keywords** Econazole derivatives; Molecular docking; Fragment molecular orbital; Molecular mechanics; Anti-tuberculosis agents

# Analysis of Cyclic Voltammogram of Hydrogen Adsorption and Oxide formation at Pt/H<sub>2</sub>SO<sub>4</sub> Interface

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The hydrogen adsorption and the oxide formation on Pt electrode surface in 0.5 M H<sub>2</sub>SO<sub>4</sub> were kinetically studied by using cyclic voltammetry (CV). The hydrogen adsorption was investigated by cycling the Pt electrode within the potential range of 0.02–0.32 V<sub>RHE</sub>. The cyclic voltammogram shows two distinct adsorption types occurring at approximately 0.10 and 0.23 V<sub>RHE</sub> which are weak and strong adsorptions, respectively. The CV profile was used to extract an equilibrium constant  $K$  of the adsorption/desorption process by conversion of CV data to the accumulated adsorption charge  $Q_{\text{ads}}$ . The potential-dependent  $Q_{\text{ads}}$  profile was fitted with kinetic equations of the weak and strong adsorptions derived based on assumptions that the adsorption of hydrogen is a monolayer and there is no interaction between the adsorbed species, so-called Langmuir adsorption isotherm. The fitting provides the values of  $K$  as 33.7 and  $6.3 \times 10^3$  for the weak and strong adsorptions, respectively. For the Pt oxide formation, Pt electrode was cycled from 0.40 V<sub>RHE</sub> to various upper potential limits (0.90–1.20 V<sub>RHE</sub>) with and without O<sub>2</sub> bubbling. Similarly to the hydrogen adsorption,  $Q_{\text{ads}}$  of the oxide formation can be obtained from the cyclic voltammogram and used to calculate the fractional surface coverage of the oxygenated adsorbed species  $\theta_{\text{O}}$ . The results indicate that  $\theta_{\text{O}}$  strongly depends on the upper potential limits and is independent on the amount of oxygen molecules in the solution. Our acquisition of  $Q_{\text{ads}}$  from the cyclic voltammogram is simple, but gives the results in good agreement with a previous work that extracted  $Q_{\text{ads}}$  from complicated impedance measurements. The methodology provided in this study is applicable for understanding the kinetics of an electrode reactions and useful for screening an electrocatalyst for the adsorption reaction on metal surfaces.

**Keywords** Pt electrode; Hydrogen adsorption; Oxide formation; Cyclic voltammetry

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# Characterization of Turbulent Waves in the 1, 4-Cyclohexanedione Belousov-Zhabotinsky by using Space-Time Plots

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The 1, 4-cyclohexanedione (CHD)Ru(bpy)<sub>3</sub><sup>2+</sup> Belousov-Zhabotinsky (BZ) reaction has become a frequently used system for studying chemical waves because of bubble-free behavior. In our research group, we found a special characteristic of wave patterns in this system which exhibits 4 states of wave patterns; ordered waves, transient state, turbulent waves, and aging, respectively. The obtained turbulent waves can be also found in the nature such as a turbulent wind, an irregular and disordered heart muscle that make them more interesting. To characterize turbulent waves, we used a Space-Time (ST) plot technique pursuing dynamics of waves. This paper presents characterization of turbulent waves in terms of front velocity, periods and wavelengths. We observed different physical properties in each state. First, chemical waves provide short periods and wavelengths. The waves arrange in regular periodic form called ordered waves. Then, the destabilization of wave front called transient state randomly emerges over the sample. The waves are split into small sections called turbulent waves. Finally, in the aging state the waves propagate with longer and longer periods and wavelengths until all waves disappear. In conclusion, ST plots can express the dynamics of waves efficiently. The analysis of physical wave behaviors such as front velocity, wavelength and period can interpret in only a single ST graph.

**Keywords** Belousov-Zhabotinsky reaction; 1, 4-cyclohexanedione; Space-time plot; Turbulent waves

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## Kinetics Adsorption of Methylene Blue using Pineapple Leaf Fiber

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The aim of this work was to study the adsorption ability of methylene blue (MB) using pineapple leaf fiber (PALF) separated by mechanical method. All the experiments were studied in batch adsorption system. The effects of amount of adsorbent, initial methylene blue concentration, pH and temperature were investigated. The results showed that increasing the amount of adsorbent increased the adsorption efficiency. Moreover, the adsorption capacity increased with the increment of the initial concentration and pH. However, increasing the temperature reduced the adsorption capacity. The equilibrium data were well fitted by Langmuir isotherm and the adsorption kinetics was fitted with a pseudo-second order kinetic model. The maximum adsorption capacity was 53.18 mg/g. The thermodynamics parameters revealed that changes in enthalpy and entropy were -9.32 kJ/mol and 50.48 J/mol·K, respectively, suggesting that the adsorption process was spontaneous and exothermic in nature.

**Keywords** Pineapple leaf fiber; Methylene blue; Kinetic adsorption; Langmuir's isotherm

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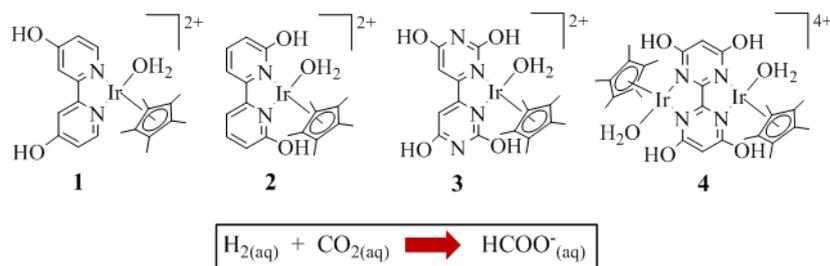
# Ligand Effects in the Proton Responsive Cp\*Ir(III) Complexes for Hydrogenation of CO<sub>2</sub>: A DFT Study

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Carbon dioxide (CO<sub>2</sub>) is one of the main reasons for global warming. The catalysts for hydrogenation of CO<sub>2</sub> have been developed in order to convert CO<sub>2</sub> into formate, a useful chemical feedstock. From the previous experimental study [1], hydrogenation of CO<sub>2</sub> can be catalyzed by a series of proton responsive Cp\*Ir(III) complexes: [Cp\*Ir(III)(OH<sub>2</sub>)(4DHBP)]<sup>2+</sup> (4DHBP = 4,4'-dihydroxy-2,2'-bipyridine) (1), [Cp\*Ir(III)(OH<sub>2</sub>)(6DHBP)]<sup>2+</sup> (2), [Cp\*Ir(III)(OH<sub>2</sub>)(TH4BPM)]<sup>2+</sup> (TH4BPM = 2,2',6,6'-tetrahydroxy-4,4'-bipyrimidine) (3), and [(Cp\*Ir(III)OH<sub>2</sub>)<sub>2</sub>(TH2BPM)]<sup>4+</sup> (4). Complex 4 catalyzed the reaction with the highest turnover frequency of 53,800 h<sup>-1</sup> at 80 °C. The catalytic activity was in the order of 4 > 3 > 2 > 1. Therefore, we are interested in how the different ligand structures affect the catalytic activity of these complexes. We performed a density functional study to investigate the reaction mechanisms for hydrogenation of carbon dioxide to formate by complexes 1-4 under basic aqueous solution. The calculations were carried out by B3LYP/6-311++G(d,p)//B3LYP/6-31G(d,p) with SMD solvation model and CPCM solvation model in conjunction with Bondi, Pauling, and UAHF radii. We first calculated proton dissociation from the hydroxyl groups on the pyridine- and pyrimidine-based ligands of complexes 1-4 to obtain the pK<sub>a</sub> of the complexes. The calculated pK<sub>a</sub> by SMD solvation model is in good agreement with the experimental pK<sub>a</sub>. According to the calculated pK<sub>a</sub>, we suggest that the active catalysts for H<sub>2</sub> activation should be in the fully deprotonated form at pH 8.3. The mechanism for hydrogenation of CO<sub>2</sub> involves two steps: (i) heterolytic cleavage of H<sub>2</sub> to form the iridium hydride complex, and (ii) hydride transfer from the Ir to CO<sub>2</sub> to generate formate. As the heterolytic cleavage of H<sub>2</sub> on Ir needs a general base to abstract a proton, complexes 2, 3, and 4, which contain a hydroxide internal base at a proper position, have the similar free energies of activation (11-13 kcal/mol) while the free energy of activation for complex 1 is relatively higher (23.6 kcal/mol) because complex 1 requires an external base to assist with the process. Therefore, the position of hydroxyl substituents on bipyridine and bipyrimidine ligands is important for the heterolytic cleavage of H<sub>2</sub>. To determine the difference in reactivity of 2-4, the hydride transfer mechanism need to be further investigated.



**Keywords** Hydrogenation of CO<sub>2</sub>; Proton responsive Cp\*Ir(III) complexes; Heterolytic cleavage of H<sub>2</sub>; Hydride transfer ; pK<sub>a</sub>

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# Synthesis and Characterization of Ruthenium Poly(vinyl pyridine) as a Metallopolymer for the Belousov-Zhabotinsky Reaction

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A self-oscillating polymer gel in the Belousov-Zhabotinsky (BZ) reaction have been developed for autonomous actuators and robots. To prepare this polymer gel, ruthenium poly(vinyl pyridine) (RuPVP) can be used as a metallopolymer that is copolymerized into a polymer chain and used as a catalyst for the BZ reaction. In this research, RuPVP was prepared under the reflux condition of *cis*-bis(2,2'-bipyridine)dichlororuthenium(II)hydrate and a 10-fold molar excess of poly(4-vinylpyridine). The obtained product was re-dissolved in absolute ethanol and precipitated in diethyl ether. The UV-Vis spectrum of the product shows the maximum absorption band of ruthenium (II) at 460 nm. And the IR spectrum confirms the existence of poly(4-vinylpyridine) on ruthenium. It presents peaks of aromatic amine at 3430 cm<sup>-1</sup>, C-H stretching vibration at 2921 cm<sup>-1</sup>, CH<sub>2</sub> stretching vibration at 2851 cm<sup>-1</sup>, C-N stretching vibration of aromatic ring at 1262 cm<sup>-1</sup>, and C=C stretching vibration of aromatic ring at 1605 and 1459 cm<sup>-1</sup>. In conclusion, the UV-Vis and IR spectra confirm that the obtained product is the ruthenium poly(vinyl pyridine). In the future studies, RuPVP will be incorporated into the polymer gel for studying the photosensitivity of the autonomous swelling-deswelling polymer gel in the BZ reaction.

**Keywords** Self-oscillating polymer gel; Metallopolymer; Ruthenium poly(vinyl pyridine); Belousov-Zhabotinsky reaction

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# Study of the “Hypercoordination” properties of hydroxide (OH<sup>-</sup>) in water by comparing of HF/MM and B3LYP/MM MD simulations

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A comparative study of HF/MM and B3LYP/MM MD simulations is used to investigate the solvation structure and dynamics of hydroxide (OH<sup>-</sup>) in water, in which the central OH<sup>-</sup> and its surrounding water molecules were treated at HF and B3LYP levels of accuracy, respectively, using a 6-311++G(d,p) basis set. On the basis of both the HF/MM and B3LYP/MM MD simulations, it is observed that the solvation shell of OH<sup>-</sup> is flexible, in which the first-shell waters can be either “loosely” or “tightly” bound to OH<sup>-</sup>, however, the quite strong hydrogen bonds (HBs) between OH<sup>-</sup> and its first-shell waters are noticed, comparing to that of bulk water. In this respect, the oxygen site in OH<sup>-</sup> prefers to be dynamically hypercoordinated by the surrounding waters, *i.e.*, by accepting four or five HBs, while the OH<sup>-</sup> hydrogen is found to donate a HB, but only transiently. This observed phenomenon strongly supports the concept that the mechanism of OH<sup>-</sup> transport in aqueous solution relies on the dynamical hypercoordination scenario. Comparing the HF/MM and B3LYP/MM results are discussed to differentiate the quality of the HF and B3LYP methods in such condensed phase system.

**Keywords** HF/MM; B3LYP/MM; Molecular dynamics; Hypercoordination

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## Temporal Oscillations of the 1,4-Cyclohexanedione Belousov-Zhabotinsky Reaction with Ru(bpy)<sub>3</sub>SO<sub>4</sub> as a Catalyst

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The 1,4-cyclohexanedione Belousov-Zhabotinsky (CHD-BZ) oscillating reaction is frequently used to study chemical waves and patterns because of its bubble-free and long-lived oscillations. In this study, the temporal oscillations of the CHD-BZ reaction with Ru(bpy)<sub>3</sub>SO<sub>4</sub> as a catalyst were observed via platinum and bromine ion selective electrodes. The initial concentrations of Ru(bpy)<sub>3</sub>SO<sub>4</sub> were varied from 0.0 to  $1.0 \times 10^{-3}$  M. For the concentrations of Ru(bpy)<sub>3</sub>SO<sub>4</sub>  $\leq 1.0 \times 10^{-5}$  M, the induction and the oscillation periods are independent on the catalyst concentration. Under this condition, there is no induction period and the average oscillation period is  $31.1 \pm 1.1$  s. At the catalyst concentrations exceed  $1.0 \times 10^{-5}$  M, the induction period increases and the oscillation period decreases with increasing of the catalyst concentration. The observed phenomena were discussed based on the kinetic mechanism of the CHD-BZ reaction. In conclusion, the oscillations of the CHD-BZ reaction depend linearly on the catalyst concentration if the concentration of Ru(bpy)<sub>3</sub>SO<sub>4</sub> exceeds  $1.0 \times 10^{-5}$  M. The photosensitivity of the CHD-BZ reaction with Ru(bpy)<sub>3</sub>SO<sub>4</sub> will be studied in the future.

**Keywords** CHD-BZ reaction; 1,4-cyclohexanedione; temporal oscillations

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## Effect of the Secondary Catalyst on the Temporal Oscillations in the Ruthenium-Catalyzed Belousov-Zhabotinsky Reaction

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The effect of the secondary catalyst on temporal oscillations occurring in the ruthenium-catalyzed Belousov-Zhabotinsky (BZ) reaction was investigated in a closed batch system. The oscillations were followed by using a potentiometric method. The oscillation dynamics, *i.e.*, oscillation period and amplitude, were characterized from the potential profile of the bromide ion selective electrode. For a single catalyst system, the oscillation period of the system with Ru(bpy)<sub>3</sub>SO<sub>4</sub> is shorter than the one with Ce(SO<sub>4</sub>)<sub>2</sub>. For the dual catalyst system, the potential sharply decreases after applying the secondary catalyst Ce(SO<sub>4</sub>)<sub>2</sub>. The decreasing of potential indicates that the concentration of Br<sup>-</sup> in the system suddenly increases. By adding the secondary catalyst, the amplitude of potential and the period of oscillations increase clearly. The change of oscillation dynamics after applying Ce(SO<sub>4</sub>)<sub>2</sub> will be discussed based on the FKN mechanism and the standard reduction potential of both Ru(bpy)<sub>3</sub>SO<sub>4</sub> and Ce(SO<sub>4</sub>)<sub>2</sub> catalysts.

**Keywords** Belousov-Zhabotinsky reaction; Dual catalysts; Oscillations

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## Characterization of Meandering Spiral Waves in the Belousov-Zhabotinsky Reaction

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Meandering spiral wave in a thin layer of the Belousov-Zhabotinsky reaction was investigated. Its tip trajectory can be described by a cycloidal motion, which is the motion of a point on the circumference of a circle that its center orbits along the circumference of another one, resulting in a two-frequency trajectory. The frequencies of the spiral tip are extracted from the Fourier transform of the oscillations of coordinate positions of the tip as a function of time. Based on a theoretical description, the ratio of these frequencies is used to define a precise number of lobes of the trajectory. Although, most properties of the meandering motion are characterized near the spiral tip, but the basic characteristics of spiral waves such as period and wavelength are measured at a point far away from the spiral center. Kinematic consideration is applied to understand the movement of the meandering spiral tip. The oscillation of tip velocity is observed as a function of the rotation phase, corresponding to the periodic change in the curvature of the wave near the tip. This local velocity-curvature relation agrees well with the eikonal equation.

**Keywords** Belousov-Zhabotinsky reaction; Meandering spiral wave; Hypocycloid; Curvature; Eikonal equation.

# The prediction of interaction between HIV-1 Integrase and Dolutegravir revealed by Molecular modeling technique

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AIDS (Acquired Immune Deficiency Syndromes) is a devastating incurable disease. It is caused by two virus species, Human immunodeficiency virus type 1 (HIV-1) and HIV-2. The patients are often infected by HIV-1. In the process of increasing the number of HIV-1, there is an important enzyme, HIV-1 integrase (IN), which enables integration between host DNA and viral DNA. The drug, currently used was found to be resisted by IN mutation. Dolutegravir, is potent inhibitor and recently approved by The United States Food and Drug Administration (FDA) for HIV infection treatment. However, there is still reported on the decreasing of activity upon HIV-1 IN mutation. The objective of this science project is to study the binding mode and interactions between Dolutegravir and HIV-1 integrase by using molecular modeling technique. The wild type (WT) HIV-1 IN (pdb code: 1WKN) was used for corresponding mutations. Subsequently, the minimizations were performed in order to geometric relaxation. The protein was, then employed for molecular docking calculations. The Autodock 4.0.2 program was used to study the binding mode and interaction involved for the molecular binding. The docking results reveal that the amino acids at position 64, 116 and 152 are important for molecular binding. A comparison of binding mode of Dolutegravir on WT IN and G140S variants revealed that the ring-A, B and C of Dolutegravir are overlapped and fluorinated ring slightly twisted. On the other hand, the mutation of E92Q/N155H, G140S/Q148K, G140S/Q148R, E138K/Q148K, this moiety is largely twisted and resulting in loss of binding interaction.

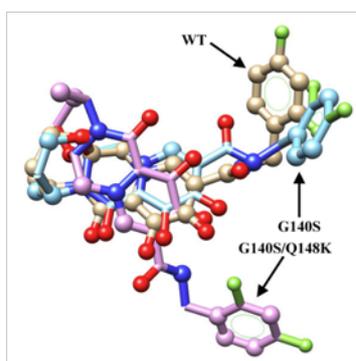


Figure 1. Comparison of Dolutegravir binding mode with WT IN (brown), and G140S (blue), and G140S/Q148K (pink)

**Keywords** HIV-1-integrase; Dolutegravir; Molecular modeling

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## Study of Mercury Adsorption on Boron Doped Graphene Surface Decorated by Transition Metals Using Computer Simulation

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In this work, the adsorption of mercury atom on boron (B) doped graphene surface decorated by transition metals (TM) was examined using density functional theory (DFT) methods. Adsorption energy calculation was performed using PW91 exchange-correlation functionals. In order to adsorb mercury atom at ambient conditions, various transition metal (TM) atoms have been decorated on B-doped graphene surface providing different binding energies. We found that among the considered TM atoms, the Cu, Ru, Pd, Pt and W atoms are suitable for decorating B-doped graphene surface, which can be adsorbed stably on the surface. Our results show that the mercury can be adsorbed stably on TM decorated B-doped graphene surface. These calculations gave insights into the adsorption of mercury on the B-doped graphene surface. Our results may serve as a basis for the development of mercury adsorption before releasing into the atmosphere in coal power plants.

**Keywords** Boron doped graphene; Mercury; Transition metals; Density functional theory

# Crystallographic, Spectroscopic and DFT/TD-DFT Investigations of Halo Substituted *N*-(2'-pyridylmethylene)aniline Ligands

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The combined experimental and theoretical study on the electronic structure and optic properties of a series of 4-halo-*N*-(2'-pyridylmethylene)aniline ligands (PM-XA; X = F, Cl, Br, I) are presented. The PM-XA ligands have been synthesized and experimentally characterized by single crystal X-ray diffraction, <sup>1</sup>H-NMR, FT-IR, UV-Vis spectroscopy and elemental analysis. To complement the experimental data, the molecular, infrared and electronic spectra of these four ligands were successfully investigated by density functional theory (DFT). The DFT calculations were performed to optimize the ground state geometries of eight possible *cis*- and *trans*-conformational structures of the four ligands. It was found that the *trans*-conformer is more stable than the *cis*-conformer. The vibrational frequency calculations were performed at PBE0/6-311G(d) and B3LYP/6-311G(d) and time-dependent DFT at TD-PBE0/6-311G (d) and TD-B3LYP/6-311G (d) levels.

**Keywords** Crystallography; Spectroscopy; Schiff's base; DFT; TD-DFT

# A DFT Mechanistic Investigation on Ethylene Oxidation by Permanganate

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The presence of ethylene gas during the fresh horticultural product storage is one of the major issues contributing to loss of postharvest quality. The ethylene removal from the storage via its oxidation is the easiest way to prevent the impact of ethylene on fresh harvests. Herein, we investigate the ethylene oxidation mechanism to ethylene glycol on the permanganate by using the density functional M06-L method. The reaction commences with ethylene being adsorbed on the  $\text{MnO}_4^-$  oxygen via hydrogen bond interaction. The calculated adsorption energy is -5.4 kcal/mol, which is comparable with the energy obtained from MP2 level of theory with the optimistic advantage that it required only a part of the CPU time. The next step, the five-membered intermediate is produced via the [3 + 2] addition transition state. This step is found to be the rate-determining step with the activation energy of 17.8 kcal/mol. Consequently, the reaction occurs via two steps of the intermediate hydrolysis to form the ethylene glycol product. The activation energies are 15.0 and 16.5 kcal/mol for the first and second hydrolysis. The results show a highly active of the  $\text{MnO}_4^-$  for the ethylene oxidation reaction. Moreover, we also investigate the effect of moisture on this reaction by adding explicit six water molecules to the reaction coordinates. We found that the water molecules prefer to solvate around the  $\text{MnO}_4^-$  cluster via hydrogen bond interaction between oxygen of  $\text{MnO}_4^-$  and hydrogen of water. The binding energy of water per molecule is -11.8 kcal/mol, which is two time higher than that of the ethylene adsorption. This result indicates that the available active sites of  $\text{MnO}_4^-$  can be prevented by water molecules leading to the decreasing of the  $\text{MnO}_4^-$  catalytic activity for the ethylene oxidation reaction.

**Keywords** Ethylene Oxidation; Postharvest; Permanganate; DFT

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# The Effect of N-Substituted Donors on the Number Density of the Adsorbed Dye on TiO<sub>2</sub> Surface as Potential Sensitizers: A Theoretical study

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A series of organic dyes containing N-Substituted carbazole, diarylamine-naphthalene and diarylamine-fluorene donor for Dye1, Dye2 and Dye3, respectively and cyanoacrylic acid acceptors bridged by thiophene fragment for DSCs applications were successfully investigated by DFT and TDDFT. Among these dyes, Dye3 with strongest electron donating ability shows the most red shifted in UV absorption spectra. Moreover, the calculated adsorption energy of -19.54 kcal/mol for Dye3@(TiO<sub>2</sub>)<sub>38</sub> complex indicates the strongest interactions between the dyes and the TiO<sub>2</sub> surface, nevertheless, Dye2 has shown the best photovoltaic performance. We performed the molecular volume and molecular width based on the geometries from the PBE functional together with the Double-Numerical with polarization performed in the DMol<sup>3</sup> program to investigate the effect of N-substituted donors on the number density of the adsorbed dye on TiO<sub>2</sub> surface. We found that bulky of the donor moiety reduces the number density of the adsorbed Dye3 on the surface dramatically (the dye uptake of 1.38 x 10<sup>17</sup> for Dye3 compared to 4.55 x 10<sup>17</sup> molecule cm<sup>-2</sup> for Dye2), corresponding to poorer energy conversion efficiency of 3.91% in Dye3 compared to the significantly better performance of 5.45% in Dye2 under simulated AM 1.5 irradiation (100 mW cm<sup>-2</sup>).

**Keywords** Dye-sensitized solar cells (DSCs); *Density functional theory (DFT)*; N-substituted donors; Molecular volume; Molecular width; Dye uptake

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## Conformers, Energies and Stability Orders of Cysteine and Serine in the Gas Phase

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Conformers, energies, and stabilities of cysteine and serine have been studied in the gas phase using the MP2 calculations. The conformational exploration of cysteine and serine was performed systematically, and full optimization was carried out at the MP2/6-311++G(2d,2p) calculations. The 15 and 12 most stable conformers of cysteine and serine were obtained, respectively. As a result, the lowest energy conformer of cysteine was found while two distinct lowest energy conformers of serine were observed. The hydrogen bond interactions formed between a thiol functional group of the side-chain and backbone part of cysteine are weaker than those formed between a hydroxyl group of serine side-chain and its backbone part. The results revealed that the intramolecular hydrogen bonds and orientations of the side-chain play significant effects on conformational diversities, energies and stability orders of cysteine as well as of serine.

**Keywords** Cysteine; Serine; Conformer; Amino acid

## Influence of Different Linker on Photovoltaic Performance of Porphyrin Sensitizers for Dye-Sensitized Solar Cells

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Density functional theory (DFT) and time-dependent DFT (TDDFT) approach have been performed to study porphyrin sensitizers with different *meso*-substituted linkages used for dye-sensitized solar cells. Two different  $\pi$ -conjugated spacers, benzene and thiophene rings, were linked to the porphyrin ring at the *meso*-pyrrolic position. The optimized structures were calculated by B3LYP functional with 6-31G(d,p) basis set. The vertical excitation energies were evaluated by single point energy calculation using time-dependent DFT method. Moreover the electron injection mechanism from porphyrin dyes to the semiconductor was obtained by TiO<sub>2</sub> cluster model employing PBE functional with DNP basis set. Our calculations showed that the electronic and optical properties of porphyrin sensitizer could be improved by means of substituting the suitable  $\pi$ -spacer. The increasing of  $\pi$ -conjugated length has significant influence on stabilizing the energy level of LUMO which is beneficial to electron injection from porphyrin sensitizer to the conduction band of TiO<sub>2</sub>. Furthermore the possibility of favorable electron transfer from excited sensitizer to semiconductor conduction band was suggested in this work.

**Keywords** Porphyrin sensitizers;  $\pi$ -conjugated spacers; Electron transfer

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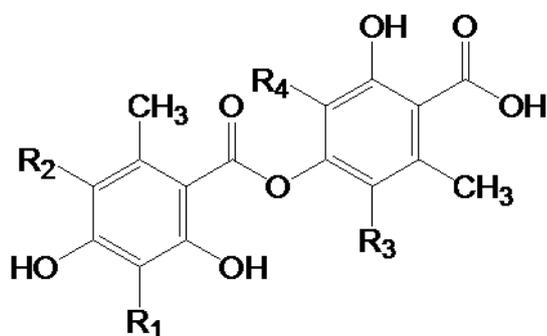
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## Theoretical Studies on the Electronic Structure and the UV Absorption Spectrum of Lecanoric Acid and Its Derivatives: Sunscreen Applications

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Nowadays sunscreen compounds play the important role in cosmetics to prevent ultraviolet (UV) radiation from the sun which causing variety of skin diseases. Although ozone in the atmosphere acts as UV filters but it can filter only UVC radiation. In these studies we performed theoretical investigations on the electronic structure and UV absorption spectrum of lecanoric acid and its derivatives which adding substitution groups (R=F, OH, CH<sub>3</sub>, NH<sub>2</sub>) in the possible positions (1-4) to design novel sunscreen compounds which can absorb broad spectrum in UVA and UVB regions.



DFT calculations were performed to the geometry optimizations and the vibrational frequency calculations of lecanoric acid and its derivatives at B3LYP/6-311++G(d,p) levels of theory. The 10 vertical excitation calculations were performed to all of the optimized structures by Time-Dependent Density Functional Theory (TD-DFT) at B3LYP/6-311++G(d,p) level of theory and compared the UV absorption spectrum of lecanoric acid to the experimental data. The calculational results reveal that the calculated UV absorption spectrum of lecanoric acid and its derivatives are broad spectrum in the range of UVA and UVB regions with high oscillator strength.

**Keywords** Sunscreen compounds; Lecanoric acid; DFT; TD-DFT; UV absorption spectrum

# Preparation of Mangosteen Peel Activated Carbon and Application for Removal of Lead (II) Ions from Aqueous Solutions

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Activated carbon was prepared from the Mangosteen peel by chemical activation with zinc chloride. The mangosteen peel was carbonized at 600 °C on conventional thermal process and used reflux technique to become activated carbon. The optimal condition for preparing mangosteen peel activated carbon was obtained under the conditions of 3 hour activation time and the ratio of charcoal : zinc chloride as 1:1. The prepared mangosteen peel activated carbon has the highest iodine number value of 820 mg g<sup>-1</sup> which can be mentioned that it has a large of adsorption capacity. The adsorption experiments were performed according to the batch method. The concentration of lead (II) ions in each material was analyzed using the atomic absorption spectroscopy (AAS). The maximum lead (II) ions removal was obtained with following conditions: an amount of adsorbent of 0.5 g, a contact time of 30 min, a particle size of ~80 mesh sieve and initial lead (II) ions of 5 ppm. The equilibrium data were found to fit well to Freundlich model. Maximum adsorption capacity (K<sub>F</sub>) of lead (II) ions onto adsorbent was 22.4 mg g<sup>-1</sup>. Therefore, from the results can be concluded that it is possible to prepare the adsorbent from Mangosteen peel.

**Keywords** Mangosteen peel; Activated carbon; Zinc chloride; Lead (II) Ions

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## DFT/TDDFT Investigation of Electron Injection in Triphenylamine-Dye Sensitized TiO<sub>2</sub> used in Dye Sensitized Solar Cells

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In this work, we performed the DFT/TDDFT calculation to provide effect of number of auxiliary donor groups on electron donating ability of dye molecules which have been constructed base on triphenylamine as electron donating group, phenothiazine as auxiliary electron donating groups, thiophene as linker group, and cyanoacrylic acid as anchoring group. The ground state geometry were optimized by DFT at the B3LYP/6-31G(d,p) level, these optimized structures were calculated for the excitation energy ( $E_g$ ), maximal absorption wavelength ( $\lambda_{max}$ ) and oscillator strengths ( $f$ ) for the 10 lowest states by using Time-Dependent Density Functional Theory (TD-DFT) with CAM-B3LYP at 6-31G(d,p) level in dichloromethane as implemented in Gaussian 09 program. In order to study the effect of different auxiliary electron donating groups on the adsorption property of triphenylamine-based dyes onto the titanium dioxide (TiO<sub>2</sub>) surface, the adsorption complexes of dye/TiO<sub>2</sub> were performed. We found that bond distances between Ti and O atom of dyes were calculated to be in the range of 2.02–2.15 Å. The adsorption energies ( $E_{ads}$ ) of NS1 (without phenothiazine auxiliary donor) and NS9 (with phenothiazine auxiliary donor) on TiO<sub>2</sub> surface were predicted to be -16.09 and -17.62 kcal/mol respectively, indicating that phenothiazine donor increased donating ability of dyes providing significantly stronger interactions between the dyes and the TiO<sub>2</sub> surface, therefore better performance in DSCs has been expected. Our calculated results can provide valuable information and promising outlook of computation-aided sensitizer design with anticipated good properties in further experimental synthesis.

**Keywords** Density functional theory; Dye-sensitized solar cells; Different auxiliary donor groups

## Study of Arsine Adsorption on Palladium-Doped Graphene Surface using Computer Simulation

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The adsorption of arsine (AsH<sub>3</sub>) molecule on palladium (Pd) doped graphene surface was studied employing periodic slab models based on density functional theory (DFT). Adsorption energy calculation was performed using PW91 exchange-correlation functional. Various adsorption sites of AsH<sub>3</sub> molecule on Pd-doped graphene surface have been performed at ambient conditions, providing different adsorption energies. The results showed that AsH<sub>3</sub> molecule can be adsorbed stably on all positions of Pd-doped graphene surface. Our results may serve as a basis for the development of arsine adsorption in coal power plants and industrial factories before releasing into the surrounding.

**Keywords** Palladium-doped graphene; Arsine; Density functional theory

# A Theoretical Study of Conformations and UV-Visible Spectra of Indigo Monomer, Dimer, and Trimer in the Implicit Water

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Indigo (IG) and its derivatives have been used as organic compound models for benchmark of the TD-DFT method due to their small sizes and simple chromophores. Theoretical prediction of an IG spectrum in the gas phase showed that the longest wavelength of maximum absorption ( $\lambda_{\max}$ ) of IG monomer appeared at about 540 nm. Theoretical spectra of IG in chloroform and ethanol showed two absorption peaks; an intense peak ( $\lambda_{\max}$ ) at 600 nm and a shoulder peak at 650 nm. The experimental spectra of IG in chloroform, ethanol, and aqueous solution also showed two absorption peaks at about 600 nm and 700 nm, but the intensity of each peak depends on IG concentrations. The spectrum of IG at the concentration of 7  $\mu\text{M}$  provided a  $\lambda_{\max}$  at 600 nm and a shoulder peak at 700 nm. The  $\lambda_{\max}$  at 700 nm and a shoulder peak at 600 nm were observed for the spectrum of IG at a concentration of 23.7  $\mu\text{M}$ . The shift to high  $\lambda_{\max}$  value at a high concentration of IG may be caused by the aggregation of IG in the medium. Until now, computational methods cannot produce results consistent with the experiments. Moreover, theoretical spectrum of IG in aqueous solution has not been reported. Therefore, it is of interest to determine  $\lambda_{\max}$  values of IG in a polar solvent. In this study, the spectra of IG in the implicit water solvent were predicted using the TD-DFT(B3LYP) method since the B3LYP functional has been previously proven to provide a good TD-DFT result. Due to the fact that IG molecules may aggregate in polar solvents possibly via intermolecular hydrogen bond or pi-pi interaction, three types of IG forms including IG monomer, IG dimer (IG<sub>2</sub>) and IG trimer (IG<sub>3</sub>) were employed in the calculations. According to our previous MD simulations of IG in aqueous solution, the IG molecules can exist in various forms and conformations. In this study, the predicted UV-Visible spectra of different conformations of IG, IG<sub>2</sub>, and IG<sub>3</sub> revealed that aggregation of the IG molecules can cause the shift of the  $\lambda_{\max}$  value and the conformations of IG have a significant effect on this  $\lambda_{\max}$  value. In addition, only the spectra of IG<sub>3</sub>, aggregated via pi-pi interaction, showed a broad peak in a range of 600-750 nm.

**Keywords** Indigo; Conformation; UV-Visible; B3LYP

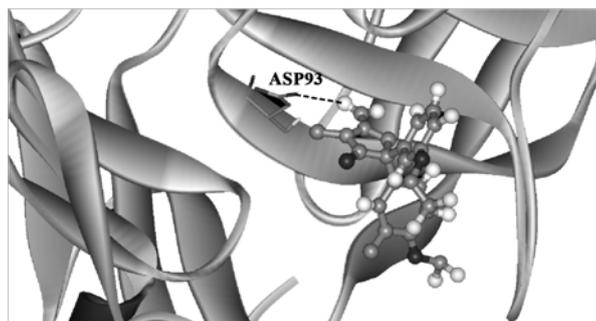
## Molecular Interactions of Bioactive Compounds with $\beta$ -secretase protein using Combined Docking and MD Simulations: Target for Alzheimer's Disease Drug Candidates

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Alzheimer's disease is a disease caused by a malfunction of the nervous system as a result of brain damage due to several reasons such as the accumulation of the protein beta amyloid ( $A\beta$ ) which caused the degradation of protein by the enzyme  $\beta$ -secretase. In the current work, the molecular docking calculations are first performed based on the crystal structure of 4HZZ to discover the potential lead compound. The obtained docking structures were refined by molecular dynamics (MD) simulations for 20 ns using GROMACS program. The models show that all ligands were located deep inside the binding pocket of the enzyme  $\beta$ -secretase. Moreover, Catechin, compounds that belong to the flavonoid class, formed the hydrogen bond with ASP93 which is the active site. These results are expected to be beneficial to predict the activities of bioactive compounds and helpful for the design of the effective therapeutic drugs for Alzheimer's disease.



**Keywords** Alzheimer's disease;  $\beta$ -secretase; Protein beta amyloid ( $A\beta$ ); Docking; MD simulations

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## Molecular Structures, Binding Affinities and Interactions of Nine DNA-DNA/Cyanine Dye Complexes

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The molecular structures and properties of cyanine dyes bound to nucleic acids have been studied theoretically to describe the intermolecular interactions of cyanine dyes and nucleic acids and the efficiency of cyanine dyes as a fluorescent dye in nucleic acids labelling. The complex formations of three different types of double-stranded DNA and three different types of cyanine dyes were predicted using the AutoDockVina v.1.1.2 program. Three double-stranded DNA which are polyATdecamer, polyCGdecamer, and polyACdecamer were generated using tLEaP module of the AMBER v.12 program. The B3LYP optimized conformers of three cyanine dyes; 3,3'-diethylthiacarbo cyanine iodide (cy3), 3,3'-diethylthiadicyanocyanine iodide (cy5), and 3,3'-diethylthiatricbocyanine iodide (cy7), were used in this study. The docking structures of the DNA-DNA/cyanine dye complexes and corresponding binding energies in kcal/mol were obtained. It should be noted that the binding energy is negative value. The predicted structures with a high binding affinity were selected. All cyanine dyes can be located in the major and minor grooves of double-stranded DNA, but the minor grooves indicate more preferable binding. The conformations of all cyanine dyes are twisted and their aromatic rings are parallel to the DNA skeleton. All cyanine dyes can interact with the double-stranded DNA via the van der Waals interaction and some binding structures also have the C-H...p interaction with the double-stranded DNA. These results reveal the conformations and arrangements of each cyanine dye that will benefit to the design of fluorescent dye for labelling nucleic acids.

**Keywords** Cyanine dye; Double-stranded DNA; Docking; Autodock vina

## Structure and Ligand Based Drug Design of Econazole Derivatives as Highly *M. tuberculosis* CYP130 Inhibitors

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Azole drug compound, econazole has been known to be active against *M. tuberculosis* CYP130 inhibitors. Nitroimidazoles and 1*H*-1,2,3-triazoles derived from econazole as anti-tuberculosis agents have been developed. In this study, molecular docking calculations using Autodock 4.2 have been performed to determine the potential binding mode and crucial interactions. The effects of atomic charges, RESP charges calculated by ab initio quantum chemical calculation (HF/6-31G\*) and Gasteiger charges on molecular docking calculations. Ligand based drug design based on 3D-QSAR approach was selected to elucidate the structural requirements of azole derivatives. Based on the statistical results and predictive ability of 3D-QSAR models are satisfying. The contour maps implemented in 3D-QSAR model indicate the structural requirement to improve the biological activity against *M. Tuberculosis*. Accordingly, the integrated results in the present work aid to better understand the structure and ligand based of econazole derivatives, which are beneficial basis to design CYP130 inhibitors with better selectivity and activities against *M. tuberculosis* CYP130 inhibitors.

**Keywords** Econazole derivatives; Molecular docking; QSAR model; Anti-tuberculosis; CYP130 inhibitors

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## Key Structural and Binding Free Energies of Heterocyclic B-ring Diphenyl Ether Derivatives as Newly Potent InhA Inhibitors

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A series of heterocyclic B-ring of diphenyl ether derivatives have been developed as direct InhA inhibitors. These inhibitors show high potency in anti-mycobacterial assay, but they fail in InhA enzyme assay. To investigate the structural basis to improve the inhibitory activity of heterocyclic B-ring of diphenyl ether derivatives, the dynamic behaviour, structural and binding free energies of three derivatives with difference substituent on heterocyclic on B-ring, hydrogen, cyano and fluoro were carried out by MD simulations and MM-PBSA calculation. The obtained results showed that the calculated binding free energies of hydrogen, cyano and fluoro substituents were  $-10.72 \pm 2.95$ ,  $-9.51 \pm 4.49$  and  $-14.71 \pm 3.07$  kcal/mol, respectively. The binding energies between heterocyclic B-ring of diphenyl ether derivatives and InhA evaluated by the MM-PBSA calculation have a correlation ( $R^2=0.99$ ) with the experimental binding free energies. Moreover, the interaction energies based on *ab initio* fragment molecular orbital (FMO) calculations indicated that Phe149, Tyr158, Ala198 and NAD<sup>+</sup> contribute significantly to the binding between InhA and heterocyclic B-ring of diphenyl ether derivatives. Based on the finding results, newly potent InhA inhibitors in a series of heterocyclic B-ring of diphenyl ether derivatives are proposed.

**Keywords** Diphenyl ether; MD simulations; InhA inhibitors; MM-PBSA

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# Electrochemical Synthesis of Poly (1-(pyren-1-yl)-1H-pyrrole) on Indium Tin Oxide Electrode and Investigation of Its Electrochromic Properties and the Eoretical Calculations

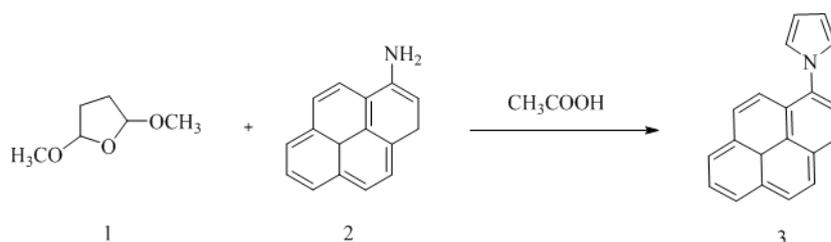
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In this work, 1-(pyren-1-yl)-1H-pyrrole (3) was synthesized in the presence of acetic acid with using 2,5-dimethoxytetrahydrofuran (1) and 1-amino pyren (2) by the condensation reaction (Fig.1). The UV absorbance, IR and NMR spectra of 3 were recorded experimentally. The redox potential of 3 were also examined. In order to compare the experimental and the theoretical results the frequency and the excited states calculation were calculated theoretically. The conformation analysis of 3 were carried out to find the most stable conformer by using a suitable software ( Marvin Beans from ChemAxon).[1] The theoretical calculations were carried out in vacuum and dichloromethane by DFT-B3LYP method 6-31++g (d,p) basis set in Gaussian 09 [2]. The electrochemical polymerization of the 3 was carried out by means of cyclic voltammetric method on the surface of the ITO. The optimum electropolymerization cycle number was found after a series of experiments. The electrochromism studies on ITO surface were also investigated.



**Fig. 1.** Chemical synthesis of 1-(pyren-1-yl)-1H-pyrrole (PP) .

**Keywords** Electrochromism; Theoretical calculation; HOMO-LUMO band gap energy

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## Adsorption of Brilliant Green on Natural White Clay: Equilibrium, Kinetic and Thermodynamic Studies

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Adsorption of brilliant green onto Narathiwat and Lampang white clays (natural white clay) from aqueous solutions was investigated. Batch adsorption experiments were carried out to evaluate the influences of experimental parameters such as adsorbent dosages (4–40 g/L), contact times (15–360 min.), initial dye concentrations (300–500 mg/L) and temperatures (298–348 K) on the adsorption process. The optimum conditions for adsorption of brilliant green were 40 g/L of adsorbent dosage and equilibrium time of 60 min. At initial dye concentration of 500 mg/L, the adsorption efficiencies of Narathiwat and Lampang white clays toward brilliant green were found to be 97.96% and 99.20%, respectively. The kinetic studies show that brilliant green onto Narathiwat and Lampang white clays were best described by the pseudo-second-order kinetic model. The Langmuir isotherm shows the best correlation for brilliant green dye onto Narathiwat and Lampang white clays. Thermodynamic studies show that the adsorption process is exothermic and spontaneous and physical reaction. Consequently, the obtained results are beneficial to recommend natural white clay, Narathiwat and Lampang, as highly effective adsorbents to remove industrial dyes contaminated in wastewater because of its low cost and environmentally friendly chemical process.

**Keywords** Adsorption; Brilliant green; Narathiwat white clay; Lampang white clay; Optimum conditions

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## **Increasing in Stability of Active Silicon in Grey Rice Husk Ash to be Utilized as Silicon Fertilizer for Rice, Sugar Cane, Cassava and Corn**

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Grey rice husk ash (GRHA), a waste of burning rice husk from rice milling, is rich in silicon. Therefore, it could be a cheap silicon source for various applications. Silicon is also an essential micronutrient with several advantages in the growth of farm plants such as rice, sugar cane, cassava and corn. To fully utilize such silicon nutrient, silicon in the GRHA has to be processed to achieve an active form of silica, a so called "ortho-silicic acid". In this research, the stability of ortho-silicic acid in GRHA has been improved by acid hydrolysis of GRHA concerned with acid conditions such as sulfuric acid and a mixture system of perchloric acid and hydrochloric acid. Characterization of the active form of silicon compared with a commercial ortho-silicic acid was carried out by means of FTIR spectroscopy. Depending on feature of the samples, either transmission or reflection modes were performed. Silicon in the active form was investigated by performing inductively coupled plasma-optical emission spectrometry (ICP-OES) and X-ray fluorescence spectrometry (XRF) analysis. The XRF result shows that the GRHA contains over 60% silicon. The obtained FTIR spectra revealed a prominent absorption band of Si-O at around 1100 cm<sup>-1</sup>, which is a characteristic of abundant silica. Changes of silica in GRHA was observed in the range of 1000-1150 cm<sup>-1</sup> when the GRHA was treated with acid. This, however, needs further optimizing acid hydrolysis conditions as well as controlling of gel time of polymerization to increase the stability of ortho-silicic acid.

**Keywords** Active silicon; Ortho-silicic acid; Silicic acid; Silicon fertilizer; Rice husk ash

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## Theoretical Investigation on Excitation Energies of Thienylene-Phenylene Copolymer (1:2 ratio)

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Thienylene-Phenylene copolymer is the interesting conducting polymer on both industry and research education because it makes many colors of circularly polarized fluorescence. In this study, the ground state geometry of thienylene-phenylene(1:2 ratio) monomer, dimer, trimer and tetramer were performed using AM1, HF/3-21G, HF/6-31G and B3LYP/6-31G methods of calculation. The results showed that the ground state geometry are non-planar. On the basis of ground state structures, the HOMO-LUMO energy gaps of thienylene-phenylene(1:2 ratio) copolymer calculated using B3LYP/6-31G//AM1, B3LYP/6-31G//HF/3-21G, B3LYP/6-31G//HF/6-31G and B3LYP/6-31G are 6.89, 7.83, 7.79 and 3.07 eV, respectively. The results implied that HOMO-LUMO energy gaps calculated by B3LYP/6-31G method is close to the experimental data. Next, the excitation energies ( $E_g$ ) and maximum absorption wavelengths ( $\lambda_{max}$ ) of thienylene-phenylene(1:2 ratio) copolymer were also predicted. It can be seen that  $E_g$  calculated by ZINDO//AM1, ZINDO//HF/3-21G, ZINDO//HF/6-31G and ZINDO//B3LYP/6-31G method of calculation are 2.93, 3.35, 3.31 and 2.72 eV, respectively.  $E_g$  calculated by ZINDO//HF/6-31G is corresponding to experimental data. Maximum absorption wavelengths performed by ZINDO//AM1, ZINDO//HF/3-21G, ZINDO//HF/6-31G and ZINDO//B3LYP/6-31G are 420.98, 374.27, 369.36 and 445.19 nm, respectively. It was found that  $\lambda_{max}$  calculated by ZINDO//HF/6-31G is close to experimental data. These information are basic knowledge to design novel conducting polymers.

**Keywords** Thienylene-Phenylene copolymer; Conducting polymer

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## Removal of Methylene Blue from Aqueous using Natural White Clay

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The adsorptions of methylene blue from aqueous solution onto Prachinburi and Narathiwat white clays were performed. We have studied various parameters such as adsorbent dosage, contact time and temperature. Batch adsorption studies showed that the optimum dosage of adsorbents per aqueous solution of 20 g/L and 60 minute adsorption time of two clays were obtained. At initial of 500 mg/L, the highest adsorption efficiency of methylene blue onto Prachin buri and Narathiwat white clays were found to be 92.71% and 89.35%, respectively, at optimal conditions. Equilibrium data of Prachin buri and Narathiwat white clays are consistent with Langmuir isotherm ( $R^2=0.99$  and  $R^2=1.00$ , respectively). The kinetic adsorption model of Methylene blue was corresponded well to the second-order kinetic model ( $R^2=1.00$  and  $R^2=1.00$ , respectively). Thermodynamic data of the adsorption process were also obtained. Based on the results, it was found that the adsorption processes of the dye on Prachinburi and Narathiwat white clays are spontaneous. Accordingly, these results indicate that Prachin buri white clay and Narathiwat white clays can be recommended as effective adsorbents to remove methylene blue from aqueous solution because of its high adsorption efficiency and environmentally friendly chemical process.

**Keywords** Natural white clay; Methylene blue; Adsorption

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