台灣理論計算分子科學學會會員大會
General Meeting of Taiwan Theoretical and Computational Molecular Sciences Association
(T^{2}CoMSA)

暨

2016年理論計算化學小組九月研討會
Theoretical and Computational Chemistry September Conference 2016

Program

September 7, 2016

Ta-Shue Chou Memorial Hall, Institute of Chemistry, Academia Sinica

09:00-09:30 registration opens

09:30-09:40 General Meeting of Taiwan Theoretical and Computational Molecular Sciences Association (T2CoMSA)

Section I

NO.01 09:40-09:55 **Jake Tan** 洪于玉 (Academia Sinica)
“Why is the ‘donor-acceptor’ coordinate a sine qua non in understanding the vibrational signatures of ionic hydrogen bonds?”

NO.02 09:55-10:10 **Hung-Hsuan Lin** 林紘玄 (Academia Sinica)
“Electronic Couplings for Intramolecular Singlet Fission”

NO.03 10:10-10:25 **Yao-Wen Chang** 張耀文 (National Taiwan University)
“Theory of charge transport in molecular junctions: Electron correlations”

NO.04 10:25-10:40 **Chi-Sheng Tseng** 曾麒升 (National Chiao Tung University)
“Solvent effects on the biochemistry and spectroscopy of anthocyanidins”

Section II

NO.05 10:40-10:55 **Wan-Ru Shie** 謝宛儒 (National Taiwan University of Science and Technology)
“First Principles Approaches for Understanding Dye Regeneration Processes in DSSCs”

NO.06 10:55-11:10 **En-Wei Chou** 周恩韋 (National Taiwan University of Science and Technology)
“A Density Functional Theory Study of CO Adsorption on Undoped and Cr, Ni, Ti, Al doped ZnO (1010) Surface”

NO.07 11:10-11:25 **Kuan-Yu Lin** 林冠宇 (National Taiwan University of Science and Technology)
“Computational Insights into Triiodide Reduction Reaction on Boron-Nitrogen-Codoped Graphene in Dye-Sensitized Solar Cells”

NO.08 11:25-11:40 **Ranganathan Krishnan** 任剛 (Chung-Yuan Christian University)
“Reaction Mechanism of CO Oxidation on Pentagraphene Surface - A Density Functional Study”

11:40-13:10 Lunch_A108 (學會第一屆第六次理監事會議_A507)

13:10-14:10 Poster

P01	Amol Deshmukh	Boron doped benzene and diphenylacetylene functionalized adamantine networks for hydrogen storage
P02	Pinit Ariyageadsakul	Dimerization of Salen-Co$^{II\bullet}$: DFT Calculations
P03	Sin-Mu Jhan 詹欣穆	Quantum TransportThroughDeformable Conjugated Systems with Lattice Relaxation Theory
P04	You-Ru Cai 蔡侑儒	Computatuinal Study for the Release of Hydrogen Sulfide by Polysulfides, and the pKa Values of Thiol Species
P05	Hung-lung Chou 周宏隆	Influence of electron storing, transferring and shuttling assets of reduced grapheme oxide at the interfacial copper doped TiO_2 p-n heterojunction
P06	Lin-Ya Su 蘇琳雅	Improvement of Adsorption Energy and Electronic Properties for Dye-sensitized Solar Cell on Fluorine doped TiO2: A DFT Study
P07	Tzu-Ting Huang 黃資庭	Enhanced spin-orbit coupling driven by state mixing in organic molecules for OLED applications
P08	Ciao-Yi Li 李巧怡	Unraveling How Water-Microsolvation Channels Drive the Allosteric Interactions of Enzyme Phosphofructokinase-1
P09	Shi-En Fu 傅識恩	The catalyst of gold clusters for CO oxidation

Section III

NO.09 14:10-14:25 **Chun-I Wang** 王俊壹 (National Chung Cheng University)
"Establishing Structure-Performance Relationship for Conjugated Polymer and Fullerene in Solution State and Condensed Phase: A Multiscale Simulation Study"

NO.10 14:25-14:40 **Ming-Hsiu Hsieh** 謝明修 (National Chiao Tung University)
"Mechanistic Study of Radical Pathway in N-Hetrocyclic Carbene(NHC) catalyzed Benzoin Condensation"

14:40-15:00 Coffee Break

Section IV

NO.11 15:00-15:15 **Ignasius Joanito** (Academia Sinica)
“The Underlying Mechanism of Arabidopsis Circadian Clock System”

NO.12 15:15-15:30 **Chen-Hao Yeh** 葉丞豪 (National Taiwan University of Science and Technology)
“Theoretical Studies of Particulate Methane Monooxygenase (pMMO) on Tricopper Complex and Tricopper Complex/Al-MCM-41 Catalysts”

NO.13 15:30-15:45 **I-Shou Huang** 黃怡碩 (National Taiwan Normal University)
“A Lesson Learned from Reparametrizing TIP3P Water Model Using a Non-Linear Force Match Method”

Section V

NO.14 15:45-16:00 **Yi-Tsao Chen** 陳奕造 (National Chiao Tung University)
“On the structural and fluctuational variation in a DNA:RNA duplex”

NO.15 16:00-16:15 **Yung-Chi Ge** 葛詠綺 (Fu Jen Catholic University)
“QM/MD Simulations on the Proton Coupled Electron Transfer of Prostaglandin H_2 *Isomerization by Prostacyclin Synthase”*

NO.16 16:15-16:30 **Ming-Yi Huang** 黃明怡 (Fu Jen Catholic University)
“Investigation of the Water Coupled Conformational Dynamics of Thromboxane and Prostacyclin Syntheses by Molecular Dynamics Simulation and Small-Angle X-ray Scattering”

16:30-16:50 Closing (Awards) Ceremony （Chair：Hsiao-Ching Yang）

Oral

Why is the “donor-acceptor” coordinate a *sine qua non* in understanding the vibrational signatures of ionic hydrogen bonds?

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The intermode coupling between O-O stretch ($Q_{O\text{-}O}$) and ionic hydrogen bond stretch (Q_{IHB}) was investigated in a series of symmetric *Zundel* dimers: $H_5O_2^+$, $(MeOH)_2H^+$, and $(Me_2O)_2H^+$. Equilibrium structures, as well as normal modes for these dimers, were obtained at MP2/aug-cc-pVDZ. The corresponding two-dimensional (2D) potential energy surface (PES) and dipole moment function (DMF) were constructed by scanning along $Q_{O\text{-}O}$ and Q_{IHB} displacement vectors. From here, the corresponding 2D vibrational Schrödinger equation was solved using the method of discrete variable representation (DVR). To understand the coupling, the vibrational Hamiltonian was casted in “pure state” (PS) representation.[2] It was found that between the first O-O stretch overtone ($2\nu_{O\text{-}O}$) and combination tone ($\nu_{O\text{-}O}+\nu_{IHB}$), only the latter couples strongly with the bright proton fundamental stretch (ν_{IHB}). Meanwhile, Fermi resonance between $2\nu_{O\text{-}O}$ and ν_{IHB} is forbidden. Such interaction results in an observable combination band and red-shifted ν_{IHB}.[1] Since experimentally, the vibrational spectra of these dimers were measured by Ar-tagged action spectroscopy, the behavior of Ar-tagged dimers was also investigated. The presence of the Ar atom descends the point group from C_2 to C_1, which relaxes the selection rule against Fermi resonance between $2\nu_{O\text{-}O}$ and ν_{IHB}. These results show the vital role of the “donor-acceptor” coordinate in modulating the ν_{IHB} peak position and intensity distribution.

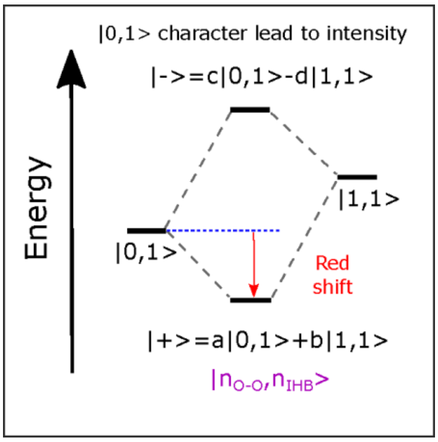

Figure 1: A two-level system explaining the $\nu_{O\text{-}O}+\nu_{IHB}$ band’s intensity.

References

[1] Tan, J. A., and Kuo, J.-L. in Progress in Theoretical Chemistry and Physics: Quantum Systems in Physics, Chemistry, and Biology: Selected Proceedings of QSCP-XX,ed. A. Tadjer, R.Pavlov, J. Maruani, E. J. Brändas, and G. Delgado-Barrio, Springer, 2016, accepted.
[2] Tan, J. A., and Kuo, J.-L. *Phys. Chem. Chem. Phys.*, 2016, *18*, 14531-14542

Electronic Couplings for Intramolecular Singlet Fission

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Singlet fission (SF) is a photochemical process which starts from a singlet excitation and ends with two triplet excited molecules. With SF efficiencies for solar energy conversion can be boosted beyond Shockley-Queisser limit. This process has been observed in single-crystal, polycrystalline and amorphous solids for many years. However, recent studies have shown that SF also occurs in a single molecule. A recent experiment revealed intramolecular singlet fission (iSF) within covalently-linked pentacenes with triplet quantum yields of 156 %. [1]

With Fragment spin difference scheme, electronic couplings for intermolecular SF has been calculated and SF rate was successfully predicted. [2] However the Hamiltonian employed, Spin-Flip Configuration Interaction Singles is prone to spin contamination and over estimation of the S1 state energy. For an improvement on the quality of Hamiltonian, the Fragment excitation difference (FED) scheme was developed with restricted active space spin-flip configuration interaction (SF-RAS). We studied iSF with this new approach for the covalently-linked pentacene. [3] Our preliminary results are in line with experimental results. Our approach allows an analysis of through-bond versus through-space in iSF.

References

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Theory of charge transport in molecular junctions: Electron correlations

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Abstract

The effects of electron correlation on charge transport processes in molecular junctions are studied by a quasi-particle formalism that combines nonequilibrium Green's function techniques and renormalized perturbation theory. In this formalism, single-impurity Anderson's model is used as the zeroth-order Hamiltonian of each channel orbital, and the interchannel interactions are treated by perturbation corrections. While the on-channel Coulomb repulsion and the single-particle spectral line-broadening are embedded in the zeroth-order scheme, Coulomb blockade and coherent tunneling on the channels can be described well. Beyond the zeroth-order description, electron correlations can be included in the present formalism by solving the perturbation expansions of electron-electron interaction in the forms of second-Born approximation and GW approximation. The effects of electron correlation on molecular junctions are shown as orbital energy correction, correlated transport process, and inelastic scattering electric current. Practical calculations are performed to study the current-voltage characteristics of phenyl-based molecular junctions with the Pariser-Parr-Pople (PPP) model as the molecular electronic Hamiltonian. The signatures of electron correlation in the simulated current-voltage curves are identified and discussed.

References

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Solvent effects on the biochemistry and spectroscopy of anthocyanidins

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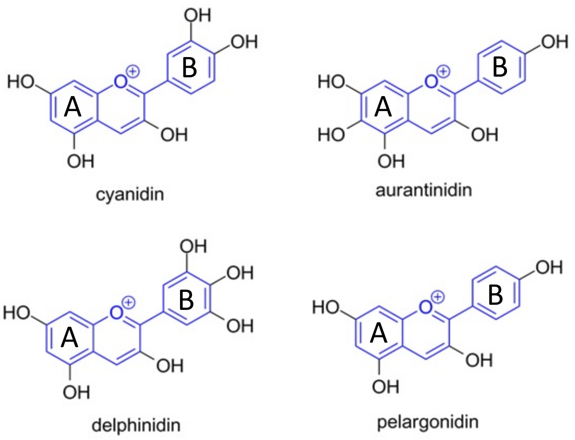
Anthocyanidins are polyoxygenated derivatives of 2-phenylbenzopyrylium cation (Figure 1) [1]. Solvent effects display considerable influences on their electron transitions, due to significant shifts in the computed spectra [1,2] compared with experimental UV-visible data. To understand the chemistry of chromophore in anthocyanidins, explicit water molecules are included in the simulation incorporated with molecular dynamics to study interactions between water molecules and pigments, followed by time-dependent density functional theory (TD-DFT) calculations using snapshot structures. Calculations show that hydrogen bonds formed between anthocyanidins and water molecules alter absorption peaks compared to those computed in the absence of hydrogen bonds. Charge transfer from water to cyanidin is also observed according to electron density analyses (Figure 2). Excitation energies obtained by our TD-DFT calculations agree excellently with experimental values [2]. Analogous phenomena are also observed in dephinidin, aurantinidin and pelargonidin. Influences of hydroxyl groups in the A and B rings are also analyzed.



cyanidin aurantinidin delphinidin pelargonidin

Figure 1. Structures of anthocyanidins.

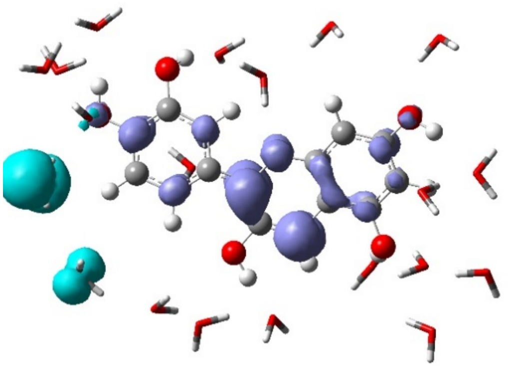


Figure 2. Charge transfer between cyanidin and waters.

References

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[2] Lu, L.; Qiang, M.; Li, F.; Zhang, H.; Zhang, S. *Dyes and Pigments* **2013**, 103,

First Principles Approaches for Understanding Dye Regeneration Processes in DSSCs

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Dye sensitized solar cells (DSSCs) have attracted considerable interest and been treated as promising alternative energy due to the high photon-to-current conversion efficiency, easy of production, and cost-effective properties. It is known that the primary function of the electrolyte is to regenerate the dye after it injects electrons into the conduction band of the semiconductor. Furthermore, it also serves as a charge transport medium to transfer positive charges toward the counter electrodes. Because of this, it is believed that, dye regeneration one of the key process which influence lifetime and open-circuit voltage of dye-sensitized solar cells. In this work, we designed a model D-pi-A type of sensitizer was selected as an example to explore the dye regeneration process by employing density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. Herein, we have proposed a highly efficient dye regeneration mechanism involving the (I^- / I_3^-) redox couple and the dye in the DSSC. We have also shown the detailed analyses such as molecular geometries, absorption spectral properties, and the corresponding energy levels for identified intermediate states during the regeneration process.

In line with some experimental findings, our results also confirm the existence of multiple dye regeneration mechanisms which involve various intermediate species that could affect the photoelectric conversion of the DSSC. This observation could also help to explain the experimentally observed deference between the photoelectric conversion efficiency and the optical absorption spectra. We believe that, our effort to add to a comprehensive understanding of the dye regeneration mechanism will help to shed light in the designing of electrolytes as well as dye-electrolyte interfacial systems for DSSCs

A Density Functional Theory Study of CO Adsorption on Undoped and Cr, Ni, Ti, Al doped ZnO $(10\bar{1}0)$ Surface

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To sense the toxic gases from atmosphere, especially CO is harmful to human beings, helps us obtain more response time to react. Therefore, we have performed density functional theory calculations with the generalized gradient approximation to investigate the CO adsorption and sensing on undoped and Cr (Chromium), Ni (Nickel), Ti (Titanium), and Al (Aluminum) doped ZnO$(10\bar{1}0)$ surfaces, respectively. In this study, Ti-doped were found to have the largest absorption energy due to strong dative bond and π-back donation. In order to analyze the effect of varying d orbital distribution of metals overlapping with the frontier orbitals (5σ and 2π*) of CO, the calculated projected density of states (PDOS) and electron density difference (EDD) analysis are used to investigate the interaction between CO and surfaces such as dative bond and π-back donation. Consequentially, the goal of this work is to provide the methodology to choose a suitable dopant for improving the sensing of Zinc-Oxide.

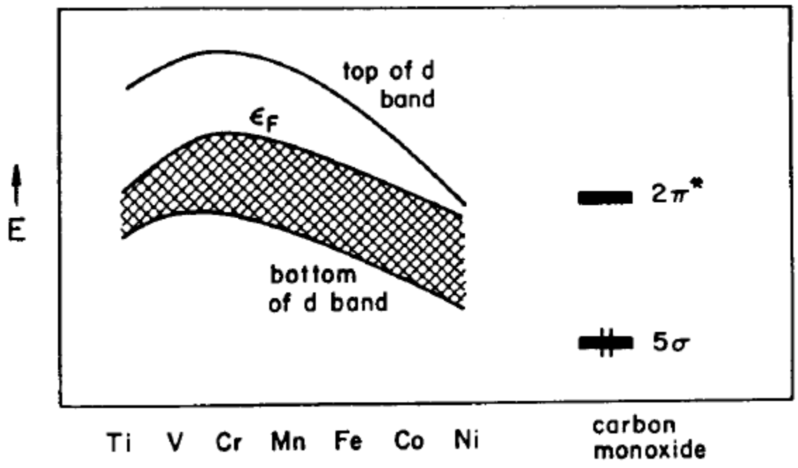

Figure 1: Picture took from Solids and Surfaces A Chemist’ s View of Bonding in Extended Structures

References

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Computational Insights into Triiodide Reduction Reaction on Boron-Nitrogen-Codoped Graphene in Dye-Sensitized Solar Cells

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Efficient catalyst as a counter electrode (EC) has a pivotal role in dye-sensitized solar cells (DSSCs) [1]. In recent years, there has been an increasing interest in graphene and its derivatives because of their high conductivity, electronic properties, hardness, and stability in corrosive electrolyte [2] [3]. By means of density functional theory (DFT) calculation, our results demonstrate that I_2 adsorbing parallelly on the boron-nitrogen-codoped graphene (BNG) surface is favorable than adsorbing on the boron-doped graphene (BDG) surface, indicating the enhancement of I_2 molecule polarization.

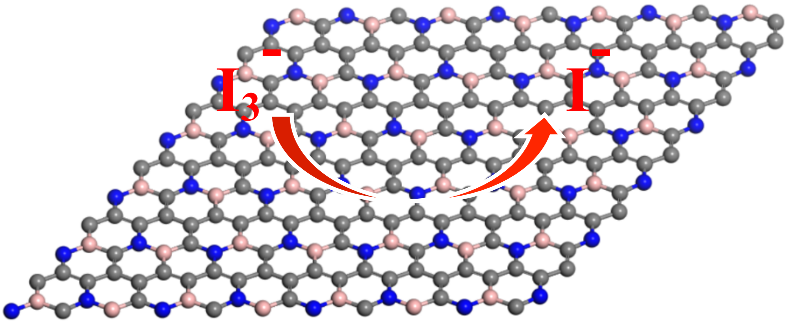

Figure 1: Schematic of Boron-Nitrogen-Codoped Graphene (BNG)

According to the calculations about the I_2 dissociative mechanism, the activation energy of iodine anion dissociating on BNG and BDG surfaces are respectively 0.41 and 0.84 eV, indicating the I_2 dissociation on BNG surface is easier than BDG surface. Further investigations of mechanism on BNG surface is helpful for improving DSSCs efficiency, and BNG surface may be a good candidate to be used for counter electrode in DSSCs.

References

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Reaction Mechanism of CO Oxidation on Pentagraphene Surface - A Density Functional Study

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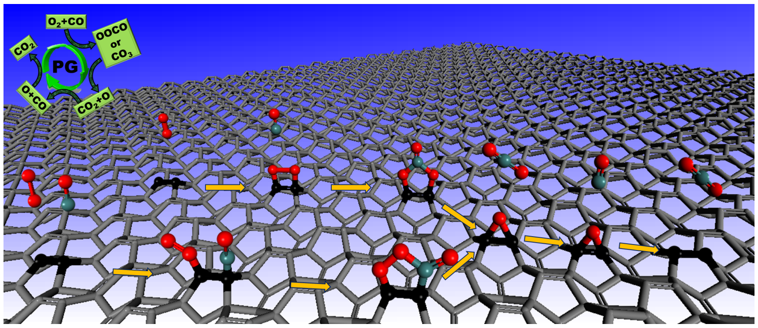
Abstract

We have presented a new type of two-dimensional (2D) catalyst, penta-graphene (PG) for CO oxidation through theoretical study. Using first-principle density functional theory (DFT) approach, the calculations were carried out for two-types of CO oxidation (CO + O_2 □ CO_2 + O and CO + O □ CO_2) reactions on PG surfaces and these reactions were considered to proceed through the Eley–Rideal (ER) and Langmuir–Hinshelwood (LH) reaction mechanism. We have first obtained the stable adsorption sites of O_2 and O as well as their adsorption energies in the PG surface under low-temperature CO oxidation conditions. Further, we found that the reaction of CO oxidation by co-adsorbed CO and O_2 on PG proceeds via the LH mechanism with a decrease in the energy of the system and the energy barrier as low as 0.31 eV, and slightly increase the energy of the system via the energy barrier of 0.65 eV as ER mechanism in the rate-limiting step, which feature an asymmetrical four-center intermediate state peroxo-type (OCOO)*. The nudged elastic band method was applied to locate transition states and minimum energy pathways of CO oxidation process on the PG sheet. Moreover, the results presented here demonstrate that PG is a good, low-cost, and metal-free catalyst for low-temperature CO oxidation, which can be used to solve problems caused by environmental CO emission and has a high ability of CO tolerance by its removal through oxidation in fuel cells.



References;

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Establishing Structure-Performance Relationship for Conjugated Polymer and Fullerene in Solution State and Condensed Phase: A Multiscale Simulation Study

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Success of contemporary applications of conjugated polymer and fullerene depends critically on a deeper understanding of their intrinsic hierarchical features, which involve structural and dynamic features on multiple length and time scales. Among the imperative issues that await to be addressed is to establish the general correlation between the geometrical features at a molecular level and the corresponding electronic properties at a quantum chemical level. By combining molecular dynamics (MD) simulations and quantum chemical (QC) calculations, we described a new strategy of characterizing polymer conformation and chain distortion that are pertinent to QC relevant chromophoric properties. We showed that for the work-horse models of MEH-PPV and MEH-PPV/C_{60} hybrid investigated herein, the features of chromophore correlate intinately with two major types of chain conformation classified as "quasi-straight" and "distorted" segment. The correlation relationship allows for a much efficient assessment of chain conformation dependent electonic properties, including the location of exciton (chromophore), trasion energy, and oscillator strength at the low-lying singlet excited states. Another essential challege one is facing in current organic electronics is to percieve the solvation/aggregation behavior of fullerene species in various types of organic solvent media for the final preperation of desirable microphase and morphorlogy in condensed thin film. Along this line, we have recently explored the essential atomic features and the known solubility of two standard fullerene species, C_{60} and PCBM (C_{60} with a side-chain substitute), in a representative series of organic solvent media. The results revealed, for the first time, that the dynamic stability of a tiny (nanoscale) solvation shell adjacent to a fullerene particle dictates its solvation behavior in a given organic solvent, having, however, distinct physics for the two fullerene species investigated. Overall, the utiliity of multiscale computational schemes has opened up a revenue for establishing structure-performance relationship from slotion to condensed phase in the upcoming development and applications in organic electronics.

Mechanistic Study of Radical Pathway in N-Hetrocyclic Carbene(NHC) catalyzed Benzoin Condensation

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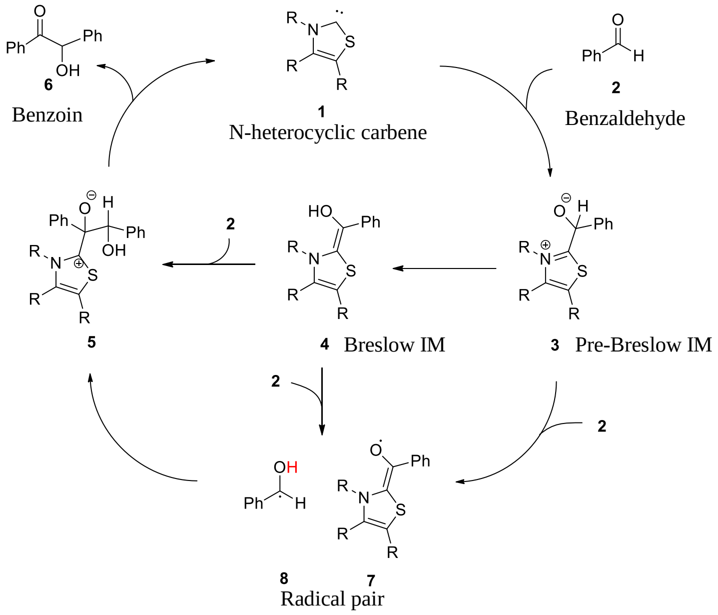
N-heterocyclic carbenes (NHCs) are reactive species in organic catalysis and organometallic chemistry. NHCs can be used as catalysts in benzoin condensation, where an enaminol-like structure **4** (Breslow intermediate) is postulated as an intermediate[1], shown in scheme 1. This benzoin reaction is thought to proceed through an ionic pathway *via* the Breslow intermediate; however, a single electron transfer (SET) process that features a radical mechanism, was observed in a recent EPR study. [2]



Scheme 1: Mechanism of NHC-catalyzed benzoin condensation[2]

In the present work the radical pathway is explored by density functional and multireference theories. The radical pair **7·8** observed in experiments can be formed from either **3** and the Breslow intermediate **4**. Calculations show that the barrier for the radical pair formation *via* **4** is much higher than that for the direct hydrogen abstraction of **3**, which indicates that the Breslow intermediate is not involved in the radical pathway. The low barrier of 3.0 kcal/mol for the hydrogen abstraction from **3** also implies that the radical-involved process can be competitive with the ionic reaction *via* the Breslow intermediate. The radical pair further undergoes the key C—C bond formation (**7·8** → **5**), yielding benzoin products. The study about the intermolecular C—C bond formation through the radical and ionic mechanisms is ongoing in our lab.

References

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The Underlying Mechanism of Arabidopsis Circadian Clock System

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Circadian clock is an endogenous timekeeper in many organisms, which allows proper response to the daily, regular changes in the environment such as light and temperature. In Arabidopsis plant, this circadian clock plays important roles such as flowering time regulation and hypocotyl elongation. Although previous studies have identified many clock-related genes in Arabidopsis plant, the complexity of the clock system makes it difficult to understand the role of each genes or molecular interaction inside. Over the last decade, mathematical modeling has been used to understand the dynamics of Arabidopsis clock system [1, 2]. Albeit the models are able to reproduce most of the observed experimental result, its complexity still makes it hard to understand the role of each gene or molecular interaction within the clock system. Therefore, with a series of simplified models at different level of complexity, we aimed to study the underlying mechanism of Arabidopsis circadian clock. Here we found that Arabidopsis clock system works in a "switch-like" manner, where *CCA1/LHY* and *TOC1* genes form a bi-stability while *PRR9/7* and evening complex (EC) help to break this bi-stability at different time (Figure 1). Similar bi-stability has been reported to play important roles in the cell cycle oscillations. As seen in *Xenopus laevis*'s cell cycle system [3], bi-stability allows the system to tune its frequency while keeping nearly constant amplitude. Our result demonstrated a theory about how the Arabidopsis clock system works. However, the advantage of having a bi-stability inside the Arabidopsis clock is still need to be elucidated.

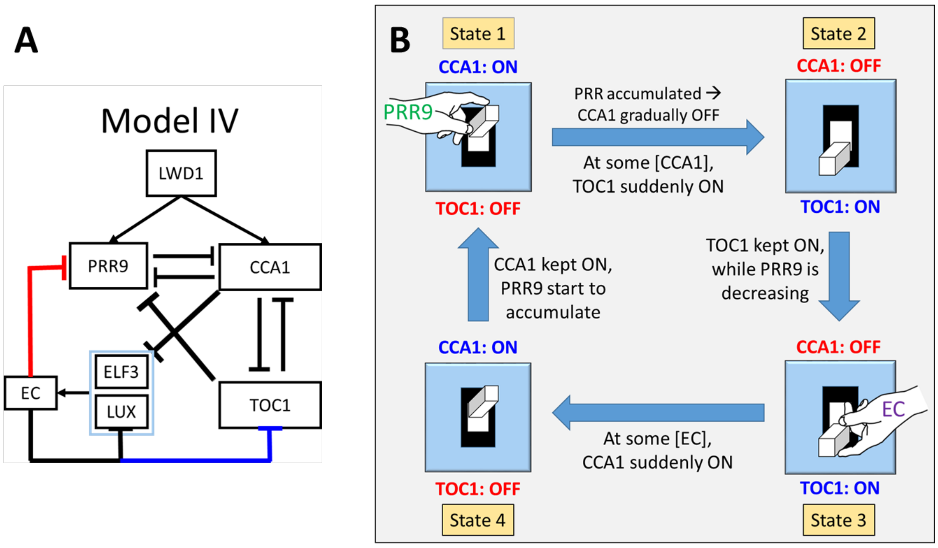

Figure 1: (A) Final Model representation used in this study. (B) An illustration showing how the Arabidopsis clock system might work.

References

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Theoretical Studies of Particulate Methane Monooxygenase (pMMO) on Tricopper Complex and Tricopper Complex/Al-MCM-41 Catalysts

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Particulate methane monooxygenase (pMMO) had been investigated as the most efficient methane oxidizer for the conversion of methane to methanol. Recently, Chan and co-worker [1] has developed the efficient tricopper complex ($[Cu^{I}Cu^{I}Cu^{I}(7\text{-N-Etppz})]^{1+}$, 7-N-Etppz = 3,3'-(1,4-diazepane-1,4-diyl)bis[1-(4-ethylpiperazine-1-yl)propan-2-ol]) for catalytic oxidation of hydrocarbons. In addition, their recent study [2] has shown that the selectivity and efficiency of methane to methanol via heterogeneous catalysis on the mesoporous silica nanoparticles immobilized by $[Cu_3(7\text{-N-Etppz})]$ complex is higher than the counterpart via homogeneous catalysis.

Using first principle calculations, we have investigated the adsorption and conversion of methane to methanol on two different systems: $[Cu_3(7\text{-N-Etppz})]^{1+}$ in acetonitrile and $[Cu_3(7\text{-N-Etppz})]$ on Al-MCM-41 zeolite, respectively. The dissociation barrier of O_2 on $[Cu_3(7\text{-N-Etppz})]^{1+}$ complex is 1.41 eV by 0.60 eV endothermicity and the dehydrogenation barrier of methane to O atom would be only 0.52 eV so that the rate-determining step could be the decomposition of O_2 molecule. In addition, in the zeolite system, we consider a large pore sized MCM-41 zeolite ($Si_{142}O_{335}H_{102}$) and replace four Al atoms in the framework to create the Al_4-MCM-41 zeolite ($Al_4Si_{138}O_{335}H_{102}$, Si/Al = 34.5). Furthermore, the binding energy of $[Cu_3(7\text{-N-Etppz})]$ complex on Al_4-MCM-41 zeolite is as large as -5.68 eV and the reaction energy of O_2 decomposition at $[Cu_3(7\text{-N-Etppz})]/Al_4$-MCM-41 could become exothermicity. These results demonstrate that the substrate effect could reduce the reaction energy of O_2 bond cleavage at $[Cu_3(7\text{-N-Etppz})]/Al_4$-MCM-41 system, which might be one of the reasons to explain the difference between tricopper homogenous and heterogeneous catalysts.

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A Lesson Learned from Reparametrizing TIP3P Water Model Using a Non-Linear Force Match Method

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Empirical potential molecular dynamic(MD) simulation is the most economic tool we have for large scale sampling—as the scope of our interested system increases, using ab initio potential energy surface rapidly becomes cost prohibitive. However, the accuracy of empirical MD depends greatly upon its force field, and the making thereof has traditionally been more of an arcane art rather than a modern science. As a response to this, a recent methodology of force field generation has started to gain grounds, known as Force Matching. The method uses forces calculated from ab initio methods to fabricate a force field, thereby reproducing the high level theory results of quantum mechanics. Further developments in this methodology has greatly increased its robustness and cost efficiency. One notable improvement is Adaptive Force Matching (AFM)[1], which cut cost in referential ab initio calculations by reducing its size and theory level, but introduces sampling, weighing and iterative processes to make up for the loss of efficacy. Ultimately AFM drastically reduces cost by moving towards linear scaling. Despite that, recent AFM experiments have been limited to parametrically linear force fields, which have heavily restricted applications. Therefore, the present work attempts to extend the subject to non-linear potentials by re-parameterizing a simple point charge water model, which is nonlinear, via an in house-developed AFM algorithm.

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On the structural and fluctuational variation in a DNA:RNA duplex

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The structural forms of double-helix nucleic acids are involved in a lot of biological processes. Generally, the DNA-DNA prefers to be B-form in the aqueous environment, and the DNA-RNA and RNA-RNA tends to be A-form. In the present study, the 1 μs molecular dynamic simulations were performed for DNA-DNA, RNA-RNA and DNA-RNA. The structural analysis confirms the B-form convergent property of DNA-DNA and the strong preference for A-form of RNA-RNA. Interestingly, the DNA strand in the hybrid system seems to mimic its RNA partner. In order to investigate factors affecting the structural form of nucleic acids, the fluctuation-matching was used to explore the mechanical coupling between residues of nucleic acids. The result demonstrates there is an oscillation corresponding to the coupling between the phosphate of residue i+1 and the sugar of residue i in the DNA strand of DNA-RNA systems, but this interaction did not appear in the DNA-DNA systems. Furthermore, we observed the base-flipping phenomenon and some secondary structures in the simulations of DNA-RNA and RNA-RNA starting from B-form. That also implies RNA which has 2'-OH increases the configurational space of nucleic acids double-helix systems.

QM/MD Simulations on the Proton Coupled Electron Transfer of Prostaglandin H_2 Isomerization by Prostacyclin Synthase

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Prostacyclin synthases (PGISs) have been classified as cytochromes P450s with function in isomerization of endoperoxide substrate prostaglandin H_2 (PGH_2) to prostaglandin I_2 (PGI_2). However, these enzymes unlike typical P450s, they catalyze the peroxide isomerization without the need for either molecular oxygen or any external electron donors. Despite the postulated mechanism has been developed, how to abstract the proton of C_6 and protonation C_{11} in PGIS catalytic mechanism remains a critical question. This work examines the issue of enzyme catalysis in terms of enzymatic confinement water dynamical concept and development of the substrate recognition mechanism. We describe the detailed structure dynamics and catalysis by means of Quantum Mechanics (QM) and Molecular Dynamics (MD) simulations. We observed that the nitrogen atom of Trp residue forms hydrogen network with two waters, which in turn form H-bonds to N287 with subsequent water molecule connection to the substrate head endoperoxide. Theoretical insights suggest this water bridge structure as a PCET shuttle delivering proton/electron to confer high product fidelity for PGIS catalysis. Furthermore, even if one of the water moved away, supplemental waters in the surrounding will substitute the position to stabilize the hydrogen-bonding network. This study emphasizes that the preorganized enzyme active site with confinement water dynamics can employ relatively fixed dipoles oriented towards transition state stabilization, as well as directing the PCET to the high fidelity PGI_2 isomerization from PGH_2 in the catalytic mechanism.

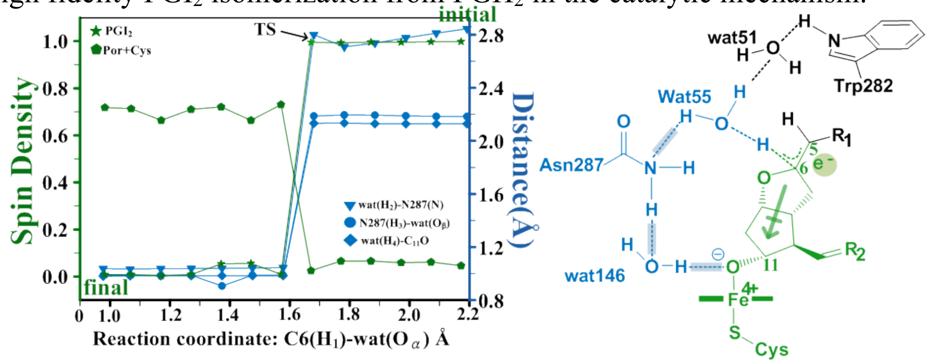

Figure 1 The spin density analysis through proton transfer reaction, and the truncated model of quantum calculation

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Investigation of the Water Coupled Conformational Dynamics of Thromboxane and Prostacyclin Syntheses by Molecular Dynamics Simulation and Small-Angle X-ray Scattering

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Enzymes are dynamical systems that perform homeostatic abilities, in precise control of their local environment through inter-conversions of chemical and mechanical energy and self-regulating feedback connections organized hierarchically across many scales of states. However, little is currently known about the fundamental molecular mechanisms by which enzymes sense mechanical force or deformation, and transducer the mechanical signal into a biological response. In this study, our efforts focus on theoretical and experimental studies of the dynamics and mechanics of thromboxane synthase (TXAS) and prostacyclin synthase (PGIS). They are heme-containing proteins and belong to the cytochrome P450s (CYP450s) family. They are counter proteins in playing crucial roles in cardiovascular homeostasis. Up to date, PGIS have the x-ray structures but the structural information about TXAS is still limited with the lack of X-ray crystallographic structure. We had constructed the TXAS structure with homology modeling and successfully investigated the water-coupled dynamic structures for PGIS and TXAS in solution, by the combination approach of molecular dynamics (MD) simulations and corresponding emission spectrum. We also carefully re-examine the structural information as compare the MD result with the SAXS (small-angle X-ray scattering) experimental resulting data with more insights for the interpretation. Comparison between the MD simulation result and SAXS is great interest to characterize the dynamical structure with the size and shape as well as the flexibility to their bio-functionality. Unlike PGIS, the dynamical behavior of TXAS with characteristic loop domain structure has been observed by simulation and dynamical spectrum. They may play an important role in regulation of the membrane binding interaction or the water-assistant substrate access characteristic loop structure of the proteins in liquid.

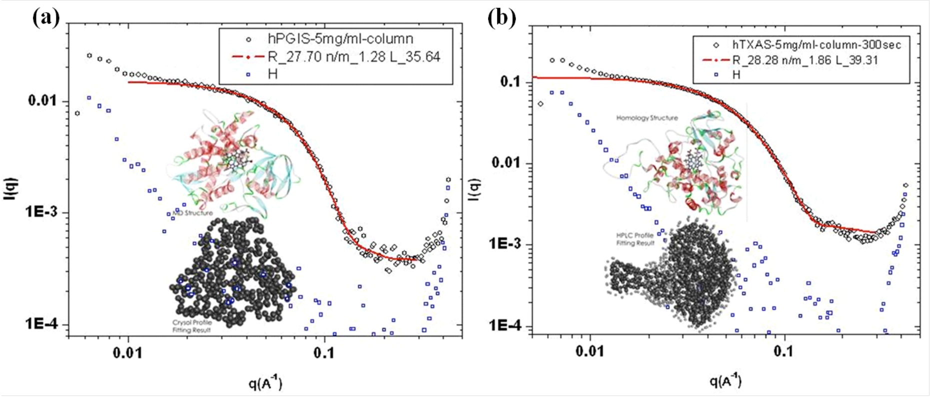

Figure. SAXS profiles and the fits of experimental data by the form factor of elliptical cylinder of the well dissolved (a) hPGIS and (b) hTXAS protein molecules.

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Poster

Boron doped benzene and diphenylacetylene functionalized adamantane networks for hydrogen storage.

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ABSTRACT

Hydrogen is the most abundant element in the universe. It is also the most promising alternative to the carbon based fuels like gasoline. For hydrogen economy to be a reality searching a material capable of storing hydrogen efficiently for vehicular applications is essential.[1] Following our previous study[2], In this work we have studied adamantine based networks by functionalizing boron doped benzene and diphenylacetylene. Using admantane as a ligand and diphenylacetylene as a linker improving hydrogen storage capacity. It is found that, average hydrogen adsorption energies of alkali and transition metals decorated admantane based networks are varying between 0.11-0.42 eV with improved gravimetric densities 8.8- 11.8 wt% respectively.

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Dimerization of Salen-$\text{Co}^{\text{II}\bullet}$: DFT Calculations

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Complexation of cobalt (II) salen dimer was evaluated by various levels of DFT including the M06, M06L, BP86, BP86-D3BJ, B3LYP and B3LYP-D3BJ functionals in conjunction with TZVP basis set. Our results propose two distinct structures of [Co-salen]$_2$ complexes. For the first structure **(1)**, one cobalt atom of Co-salen was bound to oxygen atom of other monomeric unit, corresponding with the inactive form for oxygen binding [1]. On the other hand, the active form of [Co-salen]$_2$ was featured by Co–Co bonding [2], which was represented by complex **(2)**. From the energetic data, the binding energy of complex **(1)** is comparable to **(2)**. The opposite signs of spin densities on each Co center were observed in both complexes **(1)** and **(2)**, proposing antiferromagnetic of [Co-salen]$_2$ complexes.

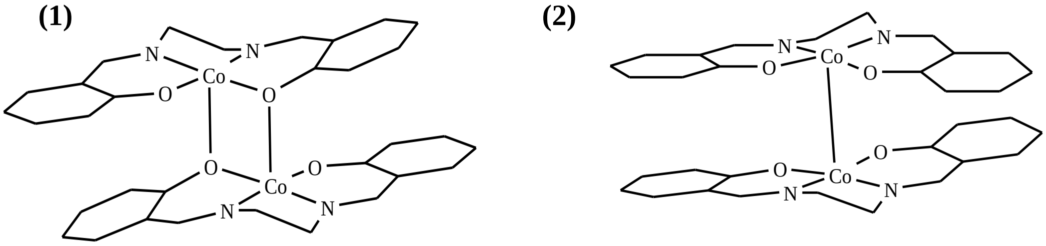

Figure 1: Skelton plots of [Co-salen]$_2$ complexes

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Quantum Transport Through Deformable Conjugated Systems with Lattice Relaxation Theory

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Su-Schrieffer-Heeger model is employed to study electron transport properties through deformable polymethine molecules with different chain lengths, with a focus on the formation of various nonlinear electron-lattice excitations such as polarons and solitons under different biases. To investigate the influences of these large-amplitude lattice relaxations on electron transport, the potential energy curves are constructed in the presence of current. The energy landscapes under certain applied biases show double-minima (see Figure 1), leading to the peculiar current hysteresis phenomenon in the I-V characteristics as shown in figure 2, reminiscent of the first-order phase transition. The hysteresis coercivities and the On-Off ratios (i.e., the current remanences) in the I-V characteristics for polyenes with different chain lengths show a peculiar odd-even effect under the influence of the electrostatic field due to the different nonlinear excitations involved in the charge transport for odd and even chains, respectively.

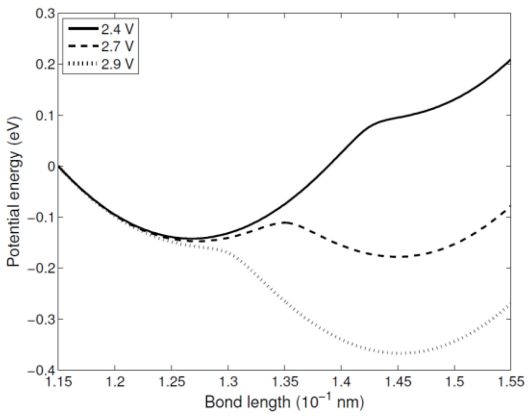

Figure 1

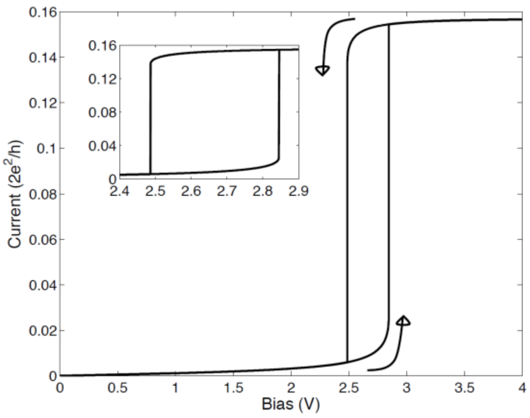

Figure 2

Figure 1: The potential energy curves for a two-site limiting case. Figure 2: The I-V characteristics.

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Computatuinal Study for the Release of Hydrogen Sulfide by Polysulfides, and the pKa Values of Thiol Species

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Hydrogen sulfide (vas been recognized as one of the gasotransmitter molecules exhibiting biological signalling functions (along with nitrogen oxide NO, and carbon oxide CO). It is important in physiological and pathological studies, and is observed in cardiovascular, neuronal, and immune systems. In addition to enzymatic reactions, H_2S was observed in biomimetic solutions. The purpose of this study is to investigate the reaction mechanism involved in the release of H_2S from their donors. We began our investigation with diallyl trisulfide (DATS) and diallyl disulfide (DADS). Glutathione (GSH) and polysulfides were proposed to be involved in these reactions. We calculated pKa values for polysulfides, cysteine and GSH. Our computational data suggest that the reaction involving thiol-disulfide exchange with GSH is more likely than that via α-carbon nucleophilic substitution.

Influence of electron storing, transferring and shuttling assets of reduced grapheme oxide at the interfacial copper doped TiO_2 p-n heterojunction

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Herein we report simple, low-cost and scalable preparation of reduced graphene oxide (rGO) supported surfactant-free Cu_2O–TiO_2 nanocomposite photocatalysts by an ultrasound assisted wet impregnation method. Unlike the conventional preparation techniques, simultaneous reduction of Cu^{2+} (in the precursor) to Cu^{+} (Cu_2O), and graphene oxide (GO) to rGO is achieved by an ultrasonic method without the addition of any external reducing agent; this is ascertained by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses. UV-visible diffused reflectance spectroscopy (DRS) studies (Tauc plots) provide evidence for the loading of Cu_2O tailoring the optical band gap of the photocatalyst from 3.21 eV to 2.87 eV. The photoreactivity of the as-prepared Cu_2O–TiO_2/rGO samples is determined via H_2 evolution from water in the presence of glycerol as a hole (h^+) scavenger under visible light irradiation. Very interestingly, the addition of rGO augments the carrier mobility at the Cu_2O–TiO_2 p–n heterojunction, which is evidenced by the significantly reduced luminescence intensity of the Cu_2O–TiO_2/rGO photocatalyst. Hence rGO astonishingly enhances the photocatalytic activity compared with pristine TiO_2 nanoparticles (NPs) and Cu_2O–TiO_2, by factors of ~ 14 and ~ 7, respectively. A maximum H_2 production rate of 110 968 μmol h^{-1} $gcat^{-1}$ is obtained with a 1.0% Cu and 3.0% GO photocatalyst composition; this is significantly higher than previously reported graphene based photocatalysts. Additionally, the present H_2 production rate is much higher than those of precious/noble metal (especially Pt) assisted (as co-catalysts) graphene based photocatalysts. Moreover, to the best of our knowledge, this is the highest H_2 production rate (110 968 μmol h^{-1} $gcat^{-1}$) achieved by a graphene based photocatalyst through the splitting of water under visible light irradiation.

KEYWORDS
Reduced graphene oxide (rGO); photocatalyst; Cu_2O–TiO_2; water splitting

ACKNOWLEDGMENT
We thank both NCHC and NTUST for their generous provision of computing time.

Reference:
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Improvement of Adsorption Energy and Electronic Properties for Dye-sensitized Solar Cell on Fluorine doped TiO_2: A DFT Study

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Having the advantages of weightless, low-cost, high flexibility and environmental friendly, dye-sensitized solar cell (DSSC) has been becoming one of the most promising photovoltaic technologies nowadays. However, there are still a lot of modifications tried to enhance the photo-to-current efficiency. In this work, density functional theory (DFT) is used to calculate the physical properties and electron distribution of the TiO_2 electrode as well as the dye adsorbs on. Our results show that replaced one outermost O atom by one F atom on the $TiO_2(101)$ surface (anatase), which can not only enhance the adsorption energy of the dye, but also elevate the fermi level of the modified substrate. Both of the features are considered to improve the performance of DSSCs so far as to reserve the electron injection ability. These results suggest that the F modified $TiO_2(101)$ surface can serve as an excellent electrode for DSSCs applications, and we can look forward to a novel brand of DSSCs with better efficiency in the near future.

Enhanced spin-orbit coupling driven by state mixing in organic molecules for OLED applications

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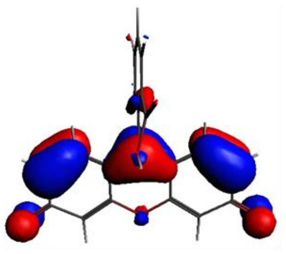
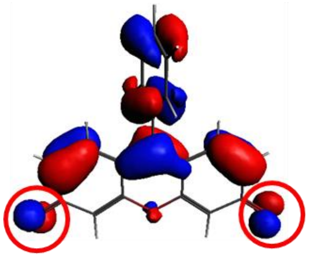
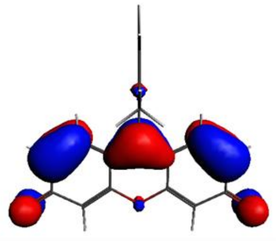
We investigate the energy gap variation as well as spin-orbit coupling (SOC) integrals between various low-lying singlet and triplet excited states for a series of fluorescein derivatives. We find that when the electron-donating property of the substituent group on the benzene moiety of fluorescein is gradually increased, the charge transfer states are lowered in energy and a mixing with nearby ππ* or nπ* states occurs, which causes a twisting in the p orbital on the carbonyl group and a non-zero SOC integral between the originally non-coupled $^1\pi\pi^*$ and $^3\pi\pi^*$ states. We also find an enhancement of about 3 to 4 times in the SOC integrals upon sulfur substitution for the oxygen in the carbonyl groups, and that with substantial energy lowering in ππ* and especially in nπ* states, the SOC between the S_1 state with energetically close triplet states is also increased significantly, signifying the possibility of enhanced phosphorescence or thermally-delayed fluorescence emission.



HOMO-4
-COOH (1)



HOMO-4
-H (2)



HOMO-5
$-CH_3$ (3)

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Unraveling How Water-Microsolvation Channels Drive the Allosteric Interactions of Enzyme Phosphofructokinase-1

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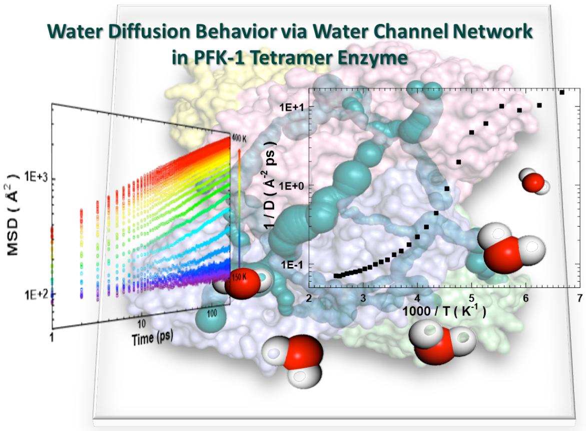
Phosphofructokinase-1 (PFK-1) is the rate-limiting enzyme of glycolysis. It is involved in complex allosteric regulation and PFK mutations have been linked to cancer development. PFK-1 is a tetramer allosteric enzyme that has effector site to bind effector in regulation of the enzyme conformation and active site activity. It catalyzes the phosphorylation of fructose-6-phosphate (F6P) and ATP to fructose-1,6-bisphosphate (F-1,6-bP) and ADP. We report here the characterization of water dynamics between effector and active site in the tetramer protein, in which show some three highest-ranked channel in communication between them. These channels provide water-microsolvation environment in restriction of hydrogen bonding-network. We carry out the molecular dynamic simulation and explore unravel how water-microsolvation channels drive the allosteric interaction between the sites. Our results reveal that channel dynamic water solvation is crucial to conformational reorganization and hence to commute the sites' structures and functionality. The characterization of water dynamics on the active site structures through the early, middle and final state with distinct catalytic activity. In addition, careful analysis led us to propose three structural states associated with the rearrangement of the hydrogen-bond network and the magnesium ion coordinates with water molecules, asparagine and phosphate oxygenated. Briefly, PFK1 acts as a smart mechano-chemical system by regulating the protein cavities enclosing the channel and interface for the trapped water motion and networking the communication between different sites. The hydration water behavior changes reflect the modulation of structural states by locally confined environment and trapped-water collective motions. The temperature dependent diffusion behavior of the PFKI microsolvation water or the channel (and the active, allosteric sites) water thus provides a missing link relevant to the respiration non-Arrhenius behavior measurements and the microscopic MD simulations.



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The catalyst of gold clusters for CO oxidation

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Abstact

The catalysts properties of Au clusters which is supposed on the boron nitrite surface (BN surface) is studied by using density functional theory calculation. The Au clusters become active due to electron transfer from supposed surface. Several reactions are considered between oxygen, carbon oxide and water (wet environment): (1) H_2O+O_2 -> OH+OOH; (2) CO+OH-> COOH; (3) CO+OOH-> CO_2+OH; (4) COOH+O_2-> CO_2+OOH and so on. We are able to observe the UV-Vis and IR spectrum change in the dry and wet environment on the Au/BN both on the experiment and calculation. Then we calculate the adsorption energy of every reaction's initial and final states. And analysis the bond length and molecular vibration. Finally compare the overall reactions with a series of experimental data. So we can infer the possible reaction route from the UV and IR spectrum, adsorption energy and reaction barrier.