

Final Report for the 2011 AC21 Special Project Fund (SPF) Project “Collaborative computational studies of cellulose degradation in ionic liquids for biofuel production”

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Activities

The AC21 SPF has enabled us to initiate collaborative computational studies related to the cellulose degradation in ionic liquids by supporting two workshops. The first meeting was held from June 5-10, 2011 at Nagoya University, and the second one was organized by Kasetsart and Chulalongkorn Universities and held from October 17-18, 2011. During these workshops, attended by the PI, co-PI's, and respective group members, we defined the project activities, exchanged experience on related projects ongoing in the partner research labs. At the visit to Kasetsart University, we agreed to extend our studies on green biofuel production by considering the activities of this university's "Center of Excellence – Oil Palm" (<http://www.coe-op.center.ku.ac.th>). We also used the opportunity of face-to-face discussions at these workshops to discuss joint research between the groups of Profs. Irle and Vudhichai Parasuk on covalent organic frameworks, producing one communications paper in the Journal of American Chemical Society (J. Am. Chem. Soc. **2011**, *133*, 14510). Finally, Prof. Irle had an opportunity to discuss the possibility for a student and researcher exchange program between the Department of Chemistry of Chulalongkorn University and Nagoya University with the Chair of the department at Chulalongkorn.

Activities in Detail

June 5-10, 2011: Workshop at Nagoya University. Attendees: Prof. Vudhichai Parasuk, Prof. Waraporn Parasuk, Prof. Stephan Irle, Dr. Matt Addicoat, Dr. Oraphan Saengsawang, Mr. Syou Fukuoka, and via Skype from Taiwan: Mr. Yoshifumi Nishimura.

Talks:

1. Stephan Irle, “Collaborative computational studies of cellulose degradation in ionic liquids for biofuel production”, plus collaboration discussion
2. Vudhichai Parasuk, “Stabilities and Electronic Properties of Undoped- and B-N Doped Single-wall Carbon Nanotubes”
3. Prof. Waraporn Parasuk, “Proline and Thioproline as Organocatalyst in Mannich Reaction: Theoretical Study”
4. Dr. Matt Addicoat, “Studying molecular ensembles: Step I: Building the tools”, plus collaboration discussion

October 17, 2011: Workshop at Kasetsart University. Attendees: Prof. Supa Hannongbua, Prof. Waraporn Parasuk, faculty members of the Department of Chemistry at Kasetsart University, Dr. Matt Addicoat. Two Special Department Seminars.

Talks:

1. Stephan Irle, “New Insights from Quantum Chemical Molecular Dynamics Simulations on the Formation Mechanism of Metallofullerenes”
2. Matt Addicoat, “Computational chemistry with the roll of a dice: stochastic structure generation from metal clusters to ionic liquids”

October 18, 2011: Workshop at Chulalongkorn University. Attendees: Prof. Vudhichai Parasuk, Prof. Waraporn Parasuk, faculty members of the Computational Chemistry Unit Cell (CCUC) of Chulalongkorn University, students and postdocs.

Talk: Stephan Irle, "Fun with graphenes: theoretical studies of hydrogenation and formation"

Preliminary Results of Scientific Research

Nagoya University: We benchmarked an approximate density functional theory (DFT) method, namely the density-functional tight-binding (DFTB) method in the context of small ionic liquid ionic clusters. This study represents a first step towards the application of the DFTB method in integrated molecular orbital studies of cellulose hydrolysis in ionic liquids in the presence of metal atoms and without. We established that a particular incarnation of the DFTB method, namely the dispersion-augmented third-order DFTB method (DFTB-3rd-D) is particularly suited to reproduce ionic liquid cluster geometries, isomer energies, as well as their electronic structures, as measured by the monopolar charge distribution.

Chulalongkorn University: The minimum energy reaction pathway of the hydrolysis of the glucose dimer was studied using DFT methods in the gas phase. As expected, this pathway involves a very high barrier that cannot be overcome in mild reaction conditions.

Kasetsart University: A model system for lignocellulose is being developed, based on the results of previous studies reported in the scientific literature.

Future Work:

Nagoya University and Chulalongkorn University: We will perform molecular dynamics (MD) simulations of small ionic liquid clusters and analyze the trajectories in terms of the minimum energy structures that have been identified thus far. We then will carry out steered MD simulations for the glucose dimer hydrolysis in such small ionic liquid clusters, using the integrated ONIOM(DFT:DFTB-3rd-D) methods.

Kasetsart University: Finite temperature MD simulations of lignocellulose will be carried out using classical force fields with parameters adjusted for ionic liquids. We will investigate the performance of the monopolar representation of the charge distribution and finally will combine such simulations in a multiscaling MD simulation, where some part of the system will be treated at the aforementioned integrated ONIOM(DFT:DFTB-3rd-D) method.