首都大学東京帰国留学生短期研究支援制度　平成30年度　研究報告書

＜外国人研究者プロフィール/Profile＞

外国人研究者	セバスチャン・ニービン・レメロ
Foreign Researcher	Sebastian Nybin Remello
国　籍	インド
Nationality	India
所属機関	コチン科学技術大学
Affiliation	Cochin University of Science and Technology
現在の職名	助教授
Position	ASSISTANT PROFESSOR
研究期間	2018年5月10日～6月29日
Period of Stay	2018 May 10 ~ June 29
専攻分野	応用化学
Major Field	Applied Chemistry

Professor Sebastian Nybin Remello

受入研究者	井上　晴夫	職名	特別先導教授
Research Advisor	Haruo Inoue	Position	Senior Leading Professor
受入研究科	環境応用化学域		
Graduate School/Department	Appled Chemistry for Environment		

＜外国人研究者からの報告/Foreign Researcher Report＞

①研究課題　/　Theme of Research

Artificial Photosynthesis
Solar energy, based on experimental and theoretical studies will be the most fitting candidate to solve two main challenges of the present day society; clean energy and clean environment. Solar energy can be harvested to either electrical energy as in solar cell or to chemical energy as in photosynthesis, a scientific technology that can recreate the chemical processes in photosynthesis to fix solar energy as fuels is now a hot area of research in the field of sustainable energy and fuels, termed as Artificial Photosynthesis (AP). AP systems split water under visible light irradiation to generate fuels like Hydrogen, Oxygen and Hydrogen peroxide and also an alternative to fix the global warming gas carbon dioxide to form useful fuels.

②研究概要　/　Outline of Research

Water splitting is the potential half-reaction in artificial photosynthesis, but it imposes a significant mechanistic uphill in its requirement for both 4H+/4e- loss and O-O bond formation under visible light irradiation. The stepwise four photon/four electron pathway has to overcome the photon flux density problem, to get through this bottleneck Inoue et.al., proposed one photon induced two electron activation of water as one of the strategy . The proposed concept was established well by performing one photon induced photo oxygenation of alkenes using water as both electron and oxygen donor catalyzed by Ru-Porphyrins. The current research focus on development of efficient molecular catalyst system for direct water oxidation utilizing ubiquitous Silicon as metal center.

③研究成果　/　Results of Research

The second most earth abundant atom incorporated meso-tetrapyridylporphyrinatesilicon(IV) (SiTPyP) as an electrochemical catalyst was newly synthesized. The two axially ligated water molecules on SiTPyP and the four meso-substituted pyridyl nitrogens suffer eight-step protonations and deprotonations. Our detailed pKa study indicated that the two axially ligated water molecules were fully deprotonated to exist as O—Si–O-under the condition of pH > 2. Under basic conditions, SiTPyP(O-)2 exerted the two-electron oxidation of water to form hydrogen peroxide as the primary product in aqueous acetonitrile, which was initiated through a one-electron oxidation process on the electrode with faradaic yield of 84–92%. The details of the result was presented as an invited talk at the 3rd International symposium for hydrogen based society in August 2018, TMU, Japan.

④今後の計画　/　Further Research Plan

The electrochemical water oxidation behavior of silicon porphyrins under neutral and acidic condition have to be investigated to understand the versatility of catalyst to perform in whole pH scale. Once the electrochemical water oxidation is optimized we have to perform the photochemical water oxidation by sensitizing the silicon porphyrins over Titania co-catalyst system by axial coordination. Research in ultrafast LASER spectroscopy for understanding the mechanism of water oxidation should be carried out, which helps us to optimize the reaction condition, also we can get information about the modification in structural properties of the catalyst required to develop efficient Artificial Photosynthesis systems.

⑤東京と海外諸都市との相互理解・友好親善関係の推進についての計画　/
Further Plan of Contribution of Strength of Mutual Understanding/Friendship Between Tokyo and International cities

The Program will initiate exchange of academic and research activity between Kerala and Tokyo. Few steps are already taken in this direction;
Student Exchange Program - A student exchange program has started between Department of Applied Chemistry, TMU and Department of Applied Chemistry, Cochin University of Science and Technology (CUSAT) which will benefit Master/Doctoral Students to perform a Short term research activity in TMU.
Scholor in Residence Program – Planning to bring eminent professor from TMU to CUSAT as part of ERUDITE program instituted by Kerala State Higher Education Council. The Program provide graduates and young researchers with opportunities to interact with Nobel Laureates and other distinguished scholars, who pioneer the frontiers of knowledge.
Collaborate Research Programs – To initiate collaborative research project between TMU and CUSAT under bilateral research funding schemes of Govt. of India.
All these activity will eventually lead to MOU between CUSAT and TMU.

＜受入研究者からの報告/Research Advisor Report＞

①研究概要　/　Outline of Research

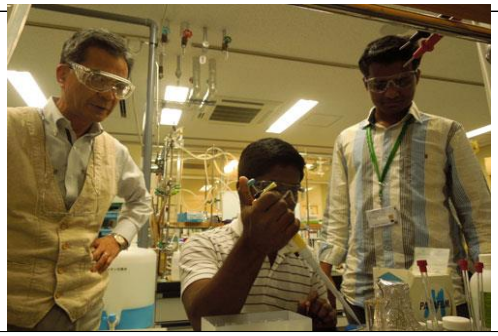
再生可能エネルギーとして期待される人工光合成の要点は、可視光エネルギーを用いて水分子から電子を取り（酸化し）その電子をプロトンや二酸炭素に移動させて水素の発生や二酸化炭素の還元固定を図ることにあるが、金属錯体などの分子触媒を用いた人工光合成研究は如何にして水分子から電子を取るかについては、水分子から段階的に4個の電子を取って酸素を発生させる必要があるため分子触媒は次の光子を待つ間に分解するという大きい困難があった。受入れ研究者等は、この困難を突破する1光子による水分子の2電子酸化反応が地球存在比第2位のシリコンを中心元素とするポルフィリン錯体で誘起されることを見出している。本研究支援制度ではSeabatian Nybin Remello博士との共同研究で本研究の一層の展開を図るよう研究指導した。

②研究成果　/　Results of Research

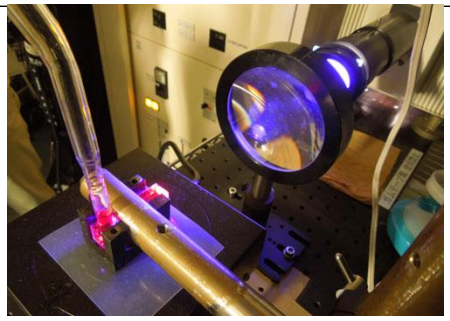
受入れ研究者等が見出したシリコンポルフィリン誘導体を分子触媒とする人工光合成反応において、分子触媒を1電子酸化することにより触媒サイクルを開始し、水分子の2電子酸化による過酸化水素の生成反応の詳細を検討した。電気化学的な手法による1電子酸化では、塩基性条件下で効率よく水が酸化され過酸化水素が生成した。一方、中性、酸性条件下では電極上でシリコンポルフィリンによる急速な2量化、オリゴマー化が進行することを見出した。詳細な検討により液性条件の変化による反応挙動の変化の内容、反応機構を明らかにした。

③今後の計画　/　Further Research Plan

本研究支援制度による共同研究で得られた成果を基礎に、今後は可視光を用いた1光子による水の2電子酸化反応系を組み込んだ人工光合成系の構築研究を展開する。共同研究の実施には、Sebastian Nybin Remello博士が所属するインドのコチン科学技術大学(Cochin University of Science and Technology)と本学の両者の大学院生、研究者が互いに交流し得る2大学覚書協定（MOU）の調印などの協力連携段階に進んで一層の研究推進を図ることが望まれる。



分子触媒による人工光合成の実験風景(1)
Experiment on artificial photosynthesis by molecular catalyst(1)



分子触媒による人工光合成の実験風景(2)
Experiment on artificial photosynthesis by molecular catalyst(2)