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Foreign Researcher	Shahed Rana		
受入研究者	杉浦健一	職名	教授
Research Advisor	Dr. Ken-ichi Sugiura	Position	Professor
受入研究科	理工学研究科・分子物質化学専攻		
Graduate School/Department	Graduate School of Science and Engineering		

<外国人研究者プロフィール/Profile>

国籍	バングラデシュ
Nationality	Bangladeshi
所属機関	ジャハングルナガル大学
Affiliation	Jahangirnagar University, Savar, Dhaka, Bangladesh
現在の職名	助教
Position	Assistant Professor
研究期間	2017年5月27日～7月15日
Period of Stay	27th May 2017 to 15th July 2017
専攻分野	化学
Major Field	Chemistry



研究者

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

①研究課題 / Theme of Research
Synthesis of porphyrin azides and an approach to the "Click Chemistry" for the synthesis new compounds.
②研究概要 / Outline of Research
<p>Metallo-porphyrins plays an important role in the current research, because of their versatile applications in electron transfer, photochemistry and also in material science. Their reactivity depends on the central metal, substituents and the axially coordinated ligands. Several synthetic strategies are applied on the porphyrins for the synthesis of new assemblies of porphyrin analogue. Among these reactions "Click reactions" has recently attracted much attention. "Click Chemistry" is a powerful method for the synthesis of multi-chromophoric array because of the reliability and selectivity of the reaction for linking two chemical moieties together. Moreover, the Click reaction between porphyrin containing terminal azides and various alkynes has considered as one of the most effective tools, because it can be conducted under mild conditions and using various solvent systems. The formation of the desired product in high yield is also a key choice of the Click reaction. In my research, nickel(II)porphyrin monomer and pentamer containing terminal azides have been synthesized and performed the click reaction with phenylacetylene. Both the monomer and pentamer undergoes click reaction with phenylacetylene in high yield. Axially coordinated diazidetin(IV)porphyrin is also synthesized.</p>
③研究成果 / Results of Research
<p>Click reactions was performed using porphyrin having terminal azide with various acetylenes. In this case, we investigated the reactivity between with Ni(II) porphyrin monomer and pentamer with phenylacetylene. The Ni(II) porphyrin monomer and pentamer with terminal azide was synthesized from the precursor having terminal benzaldehyde. In both cases similar reaction conditions were applied. The benzaldehyde was first converted to benzyl alcohol using NaBH4 at 0 oC. The yield of this conversion reaction was 90%. Then the benzaldehyde was converted to azide using 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), Diphenylphosphoryl azide (DPPA). The yield of the reaction was 60% for pentamer and 80% for monomer. Now, using porphyrin azides click reaction was carried out using CuI as catalyst with phenylacetylene. Both the monomer and the pentamer undergoes click reaction with phenylacetylene with the yield of 92% for monomer and 89% for pentamer. Both the products of the click reaction were characterized by TLC, 1H NMR, and IR spectroscopic data. Axially coordinated diazidetin(IV) porphyrin [Sn(IV)TPP] (N3)2 was synthesized using 10.0 eq. NaN3, 10 eq. 18-Crown-6, in refluxing chloroform using [Sn(IV)TPP]Cl2.</p>
④今後の計画 / Further Research Plan
<p>As the Ni(II) porphyrin monomer and pentamer containing terminal azides undergoes click reaction in high yield, our future plan is to perform the click chemistry with 1,3,5 triethynylbenzene and 1,3,5, tris(propynyl)oxy)benzene. Such reactions will afford dendrimeric structure of porphyrin containing three and fifteen porphyrin units. Moreover, Zn(II) porphyrin acts as a promising class of sensitizer. Owing to its light harvesting and photophysical properties, similar click reactions will be performed with Zn(II) porphyrin containing terminal azides with various acetylenes.</p>
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
<p>There is no doubt that, the follow-up research fellowship offered by the Tokyo Metropolitan University will make a great impact on the home country of the foreign researchers. From my point of view, the research knowledge obtained during this period will help my institution, Jahangirnagar University, Dhaka, Bangladesh. My university is situated near the capital city of Bangladesh. I can share my knowledge with my students and through this process my city will be developed. Moreover, Japan is the friend of Bangladesh in the diplomatic level and now through the fellowship financed by Tokyo Metropolitan Government, the students, faculty members of different universities of my country get the opportunity to study in Tokyo Metropolitan University. In this way it makes a mutual understanding between the Tokyo and the Dhaka, Bangladesh.</p>

<受入研究者からの報告/Research Advisor Report>

①研究課題 / Theme of Research

アジ化ポルフィリンを用いたクリック反応の評価とポルフィリン多量体の合成研究

②研究概要 / Outline of Research

ポルフィリンは植物の光合成を担うクロロフィルの母体である。植物の葉緑体の中で、クロロフィルは多量体構造を形成してタンパク質の中に取り込まれている。この多量体構造の役割については未解明なことが多く、逆に、この多量構造の合目的性を明らかにすることができれば、将来、人工光合成実現の手がかりが得られるかもしれない。そこで、本研究では、高い反応性を有し、かつ、選択的な反応を実現することができるアジ化物とアセチレンとのクリック反応に注目し、これを用いて実験室内でポルフィリン多量体を合成することを目指した。

③研究成果 / Results of Research

実験は、合成が容易なテトラフェニルポルフィリン (TPP) を基本骨格として用いることとした。TPPにエステルが一つだけ導入された分子を合成し、これの官能基変換を行い、エステル→ベンジルアルコール→ベンジルハライド→アジ化物とした。これに対応する亜鉛錯体とした後、アセチレンと反応させトリアゾールとするクリック反応を行った。この反応には銅塩を触媒として作用させる必要があるが、顕著な対イオン依存性が観察され、CuIが最も良い結果を与えた。この反応を利用することにより、ポルフィリン5量体や10量体の合成に成功した。

④今後の計画 / Further Research Plan

上記の反応により、構造が明確なポルフィリン多量体を系統的に得ることに成功した。今後は、これらの分子を用いてエネルギー移動反応や電子移動反応を評価し、植物が行っている光合成の同反応と比較を行う。このことは、自然界が行っている光合成のメカニズム解明につながり、将来の人工光合成実現のための手がかりやヒントが得られると期待している。



研究室での実験の様子