様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　４ 年　６ 月 １５ 日現在

機関番号：１４６０３
研究種目：若手研究
研究期間：2019～2021
課題番号：１９Ｋ１５３１２

研究課題名（和文）Exploiting cascade reactions of high performance tearylenes for solar applications.

研究課題名（英文）Exploiting cascade reactions of high performance tearylenes for solar applications.

研究代表者
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研究者番号：７０８３６３６１

交付決定額（研究期間全体）：（直接経費）　　3,300,000円

研究成果の概要（和文）：A　カスケード反応の最適化。合計13分子の2世代にわたる光物理学的、熱的、電気化学的な分析。B　プラスチック/固体媒体中のカスケード反応の研究。このプロジェクトは、NAISTの河合研究室と共同で、ポリマーやゲルから、ミセルやピッカリングエマルションといった他の媒体にも拡大されました．私の研究職の終了に伴い、この研究テーマはNAISTのLouis博士と共同で継続される予定です。C - X線の吸収を高めるために設計された8つのターゲットの第二世代を含む、X線検出のための枠組みの拡張。この部分の研究テーマは、Louis博士との共同研究として継続されます。この分野の論文は多数発表されています.

研究成果の学術的意義や社会的意義
このプロジェクトでは、低濃度でのX線検出に使用する新しい分子の開発に成功した。合計13の分子を調製し、X線検出能力をテストしました。その結果、これらの化合物は、ポリマー、ゲル、液体溶液など、さまざまな媒体で使用され、新しい高感度安全装置の開発が可能になります。この研究は、私が奈良から横浜に赴任した後も、NAISTのM.Louis博士と協力して継続されます。

研究成果の概要（英文）：This grant focused on three research areas (A-C). A - Optimization of the cascade reaction: Analysis of two generations of in total 13 molecules complete with photophysical, thermal and electrochemical analysis. All compounds were prepared and tested as planned B - Studies of the cascade reaction in plastic/solid media: This part of the project was expanded from polymers and gels to also include other media such as micelles and pickering emulsions in conjunction with the Kawai laboratory at NAIST. With the conclusion of my research position this part of the research topic will be continued in conjunction with Dr. Louis in NAIST. C - Expansion of frameworks towards detection of X-rays: Generation two containing 8 targets designed to increase X-Ray absorption were prepared and fully characterized. With the conclusion of my research position this part of the research topic will be continued in conjunction with Dr. Louis in NAIST. A number of papers in these areas have been published.

研究分野：光化学

キーワード：photochemisty　terarylenes　X-Rays　Cascade reactivity

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

In recent years, many terarylenes that undergo exchange between two chemically unique forms, open and closed, upon controlled application of light have been reported (Nakashima et al. *Eur. J. Org. Chem.* **2007**, 3212; Martin et al., *J. Photochem. Photobiol. C*, **2018**, 41). In each of these cases small structural changes have been used to tune the properties of both states of the target molecules and allowed for their use in a number of important physical processes including data storage, photophysical switching and surface conductance control. From these representative examples it was seen that choosing the correct molecule for the correct application is a key component in the development of new applications. One significant recent result we have reported, is the development of a cascade reaction in which a single input, either through oxidation or X-ray induced charge transfer, leads to ring opening of multiple molecules through a domino process (Figure 1) (Calupitan et al., *Chem. Eur. J.*, **2016**, 10002).

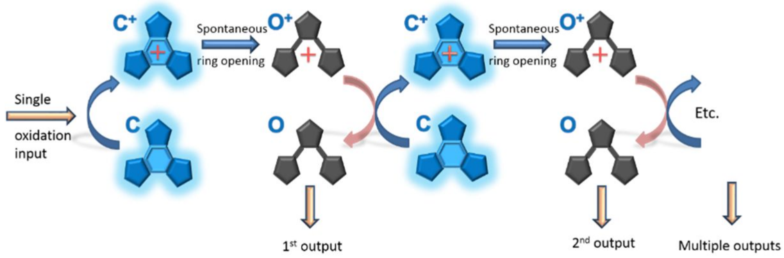


Figure 1: The oxidative cascade system developed within the Kawai lab.

When a small amount of the closed form **C** is oxidized to its cationic radical **C**$^{\cdot+}$ it spontaneously converts to the open form radical **O**$^{\cdot+}$ at room temperature. This rapidly undergoes electron transfer with other **C** species in solution to produce the **O** form and another batch of **C**$^{\cdot+}$ continuing the reaction. This leads to many ring openings occurring from a single initiation and offers an interesting new methodology for many applications as a single input leads to a large response. We proposed to expand the library of compounds that undergo this process in order to allow for its use in a number of novel applications. Among these was the detection of X-rays where this cascading reaction will allow for increasing detection limits beyond those currently available. Examination of the energy levels and kinetic parameters of the cascade reaction offers an idea of the requirements to improve the efficiency of the system (Figure 2):

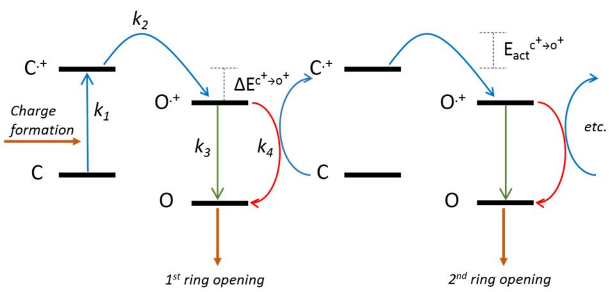


Figure 2: Energy levels and kinetic parameters within the cascade system.

Requirement 1) A large energy difference between the oxidized closed and open forms ($\Delta E^{C+\rightarrow O+}$) to encourage spontaneous ring opening in the oxidized state.
Requirement 2) A small activation energy barrier ($E_{act}^{C+\rightarrow O+}$) and fast reaction rate (k_2) between the oxidized closed and open forms to make the spontaneous ring opening more desirable.
Requirement 3) In the oxidized open state a rate of charge transfer orders of magnitude faster than the rate of relaxation to the ground state ($k_4 >> k_3$)
Requirement 4) Good susceptibility towards oxidization or X-Ray absorption in the closed form to allow for rapid formation of the oxidized closed state (k_1). Terarylene frameworks offered an excellent starting point with existing values for requirements 2, 3 and 4 among the best currently available.

２．研究の目的

We simultaneously developed designs for molecular materials that can undergo the cascade reaction to increase the performance while also optimizing the structures for use in new applications. This was accomplished through a combination of organic synthesis, photo physical analysis and computational calculation methods. This project was based on preliminary results obtained in the Kawai group building on them to deliver high quality original research. Four key areas were focused on to look at answering the questions posed in this project: Short term targets were the optimization of the cascade reactions along with initial tests towards their incorporation reaction in different media which have all been achieved. Longer term aims were the expansion towards the detection of x-rays and to look at other applications suggested by literature reports.

３．研究の方法

Research Item A - Optimization of the cascade reaction: Initial testing has shown that substitution on the thiophene rings (e.g R_1 and R_2 in Figure 3) allows for kinetic control over the cascade reaction. It can be observed that increasing the electron donating ability of the R groups will stabilize the cationic state of the open form more than the closed form as a result of the increased electronic conjugation in the open form. In addition, the steric bulk from the R groups destabilizes the cationic closed form further increasing the likelihood of ring opening in the cationic state. Here investigations into the effect of variations in the electron donating abilities of the R group and the general thiophene framework were carried out to optimize the turnovers seen in the cascade reactions.

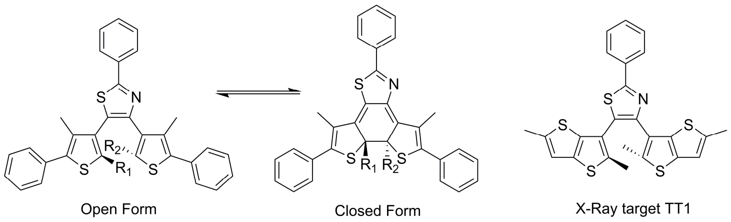


Figure 3: Structure of the cascade molecules (left) and a proposed target for use in X-ray absorption (right).

Research Item B - Studies of the cascade reaction in plastic/solid media: Thus far the cascade systems have only been demonstrated in solution. To allow for their use in an increasing range of applications the expansion to solid media will be investigated. Initially this was examined through studies in solutions containing varying amounts of organic gels and polymers with the effect of increased viscosity and reduced molecular mobility being tested. This was expanded towards micelles in conjunction with Assistant Prof. Louis within the Kawai lab

Research Item C - Expansion of frameworks towards detection of X-rays: Initial detection of X-rays has been successfully accomplished within the group with Grey levels as low as 100's of μGr possible in chloroform (R. Asato, Masters project **2018**, unpublished results). To further improve the sensitivity molecules that can easily undergo formation of radical states, either through direct absorption of X-rays or electron transfer from solvents are required. To this end structures based upon initial target TT1 (Figure 3) were prepared. This compound is predicted to have increased absorption due to its extended thieno-thiophene structure which is more susceptible to absorption of X-rays. Further testing of this system along with expansion of the molecular library to further highly absorbing molecules was carried out.

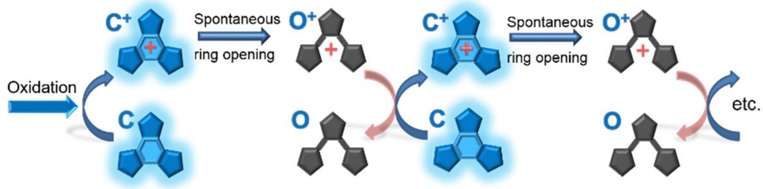
Research Item D - Expansion of applications: Recent work by the groups of Kubo (*J. Phys Chem. C*, **2014**, 118, 5390) and Grzybowski (*J. Am. Chem. Soc.*, **2012**, 134, 7223) has shown that frictional charges on a surface can be detected using chemical color sensors even at values as low as $\mu C/cm^2$. It is proposed the use of suitable cascade molecules will allow for enhancement of the detection limit for charges on the surface. This will allow for the detection of such small amounts of charge that those induced by frictional motion can be observed. Along with this the use of the cascade reactions in molecular energy storage has already been initially investigated within the group (R. Asato, Masters project 2018, unpublished results) and this work was continued with a key publication presented during the course of this project. Towards the later stages of the project it was begun to expand the scope of molecules to other applications.

４．研究成果

(1) Management and Research

Cascade reactivity of Terarylenes

Initial work by showed that the oxidation of some closed isomers can lead to a cascade reaction induced by spontaneous ring opening. Up to 4000 ring openings have been observed for one equivalent of oxidant. A paper on this topic was published in Chemical Science during 2020. A further paper using the same molecules for applications in Energy Storage was published in J. Phys Chem Letters in 2021.



Based on this a further series of compounds were prepared and analysed Five key targets were selected the first three of which were prepared by in conjunction with short term project student in Nara (Bryan Lenoir). The synthesis of all five compounds was completed on 100's of mg scales by the end of 2020. The photoanalysis of all compounds was completed in conjunction with a master's student (Y. Goto) Detailed DFT and electrochemical analysis on these five compounds was also carried out. A paper these studies of the second-generation compounds is under preparation and will be submitted (provisionally to New J. Chem) before the end of summer 2022.
Initial analysis of the X-Ray detection properties in in plastic/solid media: This part of the project was expanded from polymers and gels to also include other media such as micelles and Pickering emulsions in conjunction with Assistant Professor M. Louis in the Kawai laboratory at NAIST. A Masters student has begun work on this topic.

A number of other papers on work carried out as part of the collaborative laboratory running concurrently with this project have also been published:

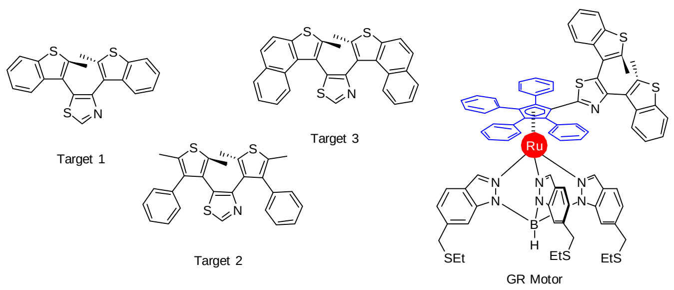
Photohydride generators

<u>Generation one and two</u>

This photohydride project was successfully completed, thirteen key compounds (in two Generations (G1 5-compounds and G2 8-compounds) were prepared and studied during the course of the project. Two papers looking at these photobase release compounds having similar structures to the X-Ray systems have been published in J. Org. Chem and J. Photochem Photobio. A.

Synthesis of new photochromic molecular motors:

A new photoactive molecular motor was designed and developed in collaboration with Prof Rapenne, Dr. Claire Kammerer, Dr. Seifallah Abid and Yohan at CEMES-CNRS in Toulouse, host location of the collaborative laboratory. Initial calculations suggested three targets for incorporation into the motor framework previously prepared by Prof Rapenne (GR):



Target 1 was incorporated into the existing motor framework. This system was prepared on ~30 mg scale. As part of this the existing synthetic methodology was optimized to give a significant increase in the reaction yield.
This sample was split into three parts for spectroscopic (RA in Nara), thermal NMR (RA in Nara) and STM (Prof. Saw Wai Hla, Ohio University and Argonne National Lab., USA) analysis however the COVID-19 outbreak led to significant delays in the delivery of these results, further data is expected in the future.
Two papers in Inorg. Chem. And RSC Advances have been published on this topic.

(2) List of achievements April 2019 – March 2022

Original Papers (*I.F.:Impact Factor, C:Citations, as per Google Scholar 11th March 2022*)

[Peer-Reviewed Journals, First Author]

1) "Systematic studies of structural variations in terarylene photohydride generators", C. J. Martin, J. P. Calupitan, M. Minamide, R. Asato, Y. Goto, G. Rapenne, T. Nakashima and T. Kawai, *J. Photochem. Photobiol. A: Chemistry*, **2020**, 397, 112594 (*I.F.:3.306, C:0*).

2) Terarylenes as Photoactivatable Hydride Donors, C. J. Martin, M. Minamide, J. P. Calupitan, R. Asato, J. Kuno, T. Nakashima, G. Rapenne and T. Kawai, *J. Org. Chem.*, **2018**, 83, 22, 13700-13706 (*I.F.:4.354, C:10*).

[Peer Reviewed Journals, Non-First Author]

3) Nanocars based on Polyaromatic or Porphyrinic Chassis, T. Nishino, C. J. Martin, K. Yasuhara, G. Rapenne, *J. Synth. Org. Chem. Japan.*, **2021**, 79, 11, 1050-1055 (*I.F.:0.362 C:0*).

4) Energy Storage upon Photochromic 6-π Photocyclization and Efficient On-Demand Heat Release with Oxidation Stimuli R. Asato, C.J. Martin, T. Nakashima, J.P. Calupitan, G. Rapenne and T. Kawai, J. Phys. Chem. Lett., **2021**, 12, 46, 11391-11398 (*I.F.:6.475 C:0*).

5) Ruthenium complexes of sterically-hindered pentaphenylcyclopentadienyl ligands, R. Asato, C. J. Martin, Y. Gisbert, S. Abid, T. Kawai, C. Kammerer and G. Rapenne, *RSC Advances*, **2021**, 11, 20207-20215 (*I.F.: 3.361, C: 1*).

6) Molecular Rotor Functionalized with a Photoresponsive Brake, R. Asato, C. J. Martin, S. Abid, Y. Gisbert, F. Asanoma, T. Nakashima, C. Kammerer, T. Kawai, and G. Rapenne, *Inorg. Chem.*, **2021**, 60, 6, 3492–3501 (*I.F.: 5.165, C: 6*).

7) Dipolar Nanocars Based on a Porphyrin Backbone, T. Nishino, C. J. Martin, H. Takeuchi, F. Lim, K. Yasuhara, Y. Gisbert, S. Abid, N. Saffon-Merceron, C. Kammerer and G. Rapenne, *Chem. Eur. J.*, **2020**, 26, 52, 12010-12018 (*I.F.:5.236, C:7*) **Front Cover**.

8) Photosynergetic amplification of radiation input: from efficient UV induced cycloreversion to sensitive X-ray detection, R. Asato, C. J. Martin, J. P. Calupitan, R. Mizutsu, T. Nakashima, G. Okada, N. Kawaguchi, T. Yanagida and T. Kawai, *Chem. Sci.*, **2020**, 11, 9, 2504-2510 (*I.F.:9.825, C:8*).

9) Photo-Lewis Acid Generator Based on Radical-Free 6π Photo-Cyclization Reaction, R. Mizutsu, R. Asato, C. J. Martin, M. Yamada, Y. Nishikawa, S. Katao, M. Yamada, T. Nakashima and T. Kawai, *J. Am. Chem. Soc.*, **2019**, 141, 51, 20043-20047 (*I.F.:15.419, C:11*).

[Peer Reviewed Review Articles, Non-First Author]

10) Advanced functionality in photoacid generators, T. Kawai, C. J. Martin and R. Mizutsu, *Hikarikagaku*, **2019**, 50, 297-104.

[Oral and Poster Presentations]

1) C.J. Martin, Terarylene derivatives for applications in hydride release and as molecular machines, LIA-Nanosynergetics web conference (12th March 2021).

2) "Systematic studies of structural variations in terarylene photohydride generators" C. J. Martin, J. P. Calupitan, G. Rapenne, T. Nakashima and T. Kawai, *RSC Photophysics and Photochemistry Group Early Career Members Meeting, Web meeting* (1st-3rd December 2020).

3) "Systematic studies of structural variations in terarylene photohydride generators" C. J. Martin, J. P. Calupitan, G. Rapenne, T. Nakashima and T. Kawai, *The Japanese Photochemistry Association Annual Meeting 2020, Web meeting* (9th-11th September 2020).

4) "Recent evolutions in terarylene scaffolds using thienothiophene and benzothiazole substituents" C. J. Martin, G. Rapenne and T. Kawai, *9th International Symposium on Photochromism, Paris, France* (23rd-27th September 2019).

5) "Recent evolutions in terarylene scaffolds towards new photo-applications" C. J. Martin, G. Rapenne and T. Kawai, *UK-IT Joint Meeting on Photochemistry 2019, Lipari, Italy* (24th-26th June 2019).

５．主な発表論文等

〔雑誌論文〕　計6件（うち査読付論文　2件／うち国際共著　5件／うちオープンアクセス　1件）

１．著者名 Martin Colin J.、Calupitan Jan Patrick、Minamide Miho、Asato Ryosuke、Goto Yora、Rapenne Gwenael、Nakashima Takuya、Kawai Tsuyoshi	４．巻 397
２．論文標題 Systematic studies of structural variations in terarylene photohydride generators	５．発行年 2020年
３．雑誌名 Journal of Photochemistry and Photobiology A: Chemistry	６．最初と最後の頁 112594～112594
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jphotochem.2020.112594	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Nishino Toshio、Martin Colin J.、Takeuchi Hiroki、Lim Florence、Yasuhara Kazuma、Gisbert Yohan、Abid Seifallah、Saffon‐Merceron Nathalie、Kammerer Claire、Rapenne Gwenael	４．巻 26
２．論文標題 Dipolar Nanocars Based on a Porphyrin Backbone	５．発行年 2020年
３．雑誌名 Chemistry: A European Journal	６．最初と最後の頁 11913～11913
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/chem.202003128	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Asato Ryosuke、Martin Colin J.、Abid Seifallah、Gisbert Yohan、Asanoma Fumio、Nakashima Takuya、Kammerer Claire、Kawai Tsuyoshi、Rapenne Gwenael	４．巻 60
２．論文標題 Molecular Rotor Functionalized with a Photoresponsive Brake	５．発行年 2021年
３．雑誌名 Inorganic Chemistry	６．最初と最後の頁 3492～3501
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.inorgchem.0c03330	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Asato Ryosuke、Martin Colin J.、Calupitan Jan Patrick、Mizutsu Ryo、Nakashima Takuya、Okada Go、Kawaguchi Noriaki、Yanagida Takayuki、Kawai Tsuyoshi	４．巻 11
２．論文標題 Photosynergetic amplification of radiation input: from efficient UV induced cycloreversion to sensitive X-ray detection	５．発行年 2020年
３．雑誌名 Chemical Science	６．最初と最後の頁 2504～2510
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/C9SC05380H	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

1．著者名 Mizutsu Ryo、Asato Ryosuke、Martin Colin J.、Yamada Mihoko、Nishikawa Yoshiko、Katao Shohei、Yamada Miku、Nakashima Takuya、Kawai Tsuyoshi	4．巻 141
2．論文標題 Photo-Lewis Acid Generator Based on Radical-Free 6π Photo-Cyclization Reaction	5．発行年 2019年
3．雑誌名 Journal of the American Chemical Society	6．最初と最後の頁 20043～20047
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/jacs.9b11821	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Kawai Tsuyoshi, Martin Colin J., Mizutsu Ryo	4．巻 50
2．論文標題 Advanced functionality in photoacid generators	5．発行年 2019年
3．雑誌名 The Japanese Photochemistry Association "光化学"	6．最初と最後の頁 97-104
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 無
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〔学会発表〕　計3件（うち招待講演　0件／うち国際学会　2件）

1．発表者名 Colin J. Martin
2．発表標題 Terarylene derivatives for applications in hydride release and as molecular machines
3．学会等名 LIA-Nanosynergetics web conference
4．発表年 2020年

1．発表者名 Colin J. Martin, Jan Patrick Calupitan, Ryosuke Asato, Takuya Nakashima, Gwenael Rapenne and Tsuyoshi Kawai
2．発表標題 Recent evolutions in terarylene scaffolds towards new photo-applications
3．学会等名 UK-IT Joint Meeting on Photochemistry 2019（国際学会）
4．発表年 2019年

１．発表者名 Recent evolutions in terarylene scaffolds using thienothiophene and benzothiazole substituents.
２．発表標題 Colin J. Martin, Takuya Nakashima, Gwenael Rapenne and Tsuyoshi Kawai
３．学会等名 9th International Symposium On Photochromism (ISOP'2019)（国際学会）
４．発表年 2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

－

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関