

Report on the investigation of research misconduct related to GNR research in Itami Laboratory

Summary version

I. Background and Outline

On August 17, 2020, Professor Kenichiro Itami of the Institute of Transformative Bio-Molecules (ITbM) and Associate Professor Hideto Ito of the Graduate School of Science, Nagoya University, filed a complaint with the Nagoya University Misconduct Complaint Desk, alleging that some data in two papers published in *Nature* and *Journal of the American Chemical Society* (JACS), by their group had been fabricated. The Nagoya University Committee for Fair Research (CFR) accepted the complaint and organized a dedicated investigation committee (DIC) to start the investigation on September 30, 2020. The initial targets of the investigation were the two papers (Nature paper and JACS paper) containing the suspected MALDI-TOF/MS data, and the first author of both papers (Former Graduate Student A, Graduate School of Science) and the two corresponding authors (K. Itami and H. Ito). However, as the investigation progressed, the suspicion of research misconduct was expanded to include various data related to GNR synthesis, and in response to this, three more papers, published in *ACS Applied Nano Materials* (ACS Nano), *Journal of Organic Chemistry* (JOC) and *Synlett* on February 26, 2021, and three more people were added in the investigation list on May 31, 2021.

As a result of the investigation, SEC charts, IR and Raman spectra, UV-visible absorption and fluorescence spectra, and MALDI-TOF/MS related to GNR synthesis were identified as research misconduct for the Nature paper (the number of figures identified as misconduct was 10). For the JACS paper, the committee found NMR spectra of monomer molecules, SEC charts of GNRs, IR spectra, and MALDI-TOF/MS data as research misconduct (the number of fraudulent figures is 13). For the ACS Nano paper, they found research misconduct (the number of fraudulent figures is 4) related to ¹H-NMR spectra, SEC charts, and IR spectra related to GNR synthesis.

The committee found that A committed all the above misconduct. Beginning in the fall of 2015, he repeated the research misconduct over a period of more than four years. The volume of fabricated data was extremely large. In addition, he destroyed research information, such as experiment notes, and also engaged in a cover-up, such as replacing the data of a similar polymerization experiment conducted by a co-author.

Professors K. Itami and H. Ito were identified as corresponding authors but not involved in the fraudulent activities. However, they were responsible for the papers and other documents related to the fraudulent research. Although there was no evidence that the two responsible authors led the research misconduct, they were responsible for supervising the fraudulent activities that occurred. Because reproducibility checks and verification of raw data were not conducted properly, research misconduct could not be detected before the paper was published. The two professors failed in their duty of care as responsible authors. The degree of breach of the duty of care is "high" because they failed to perform the necessary checks and failed to prevent the huge number of irregularities in the paper. However, on the other hand, after the situation where the reproduction of GNR synthesis could not be taken was found, they conducted their own investigation to clarify the situation, filed a research misconduct complaint, and cooperated with the investigation from the committee.

II. Investigated persons

1. **A**, Former Graduate Student at Nagoya University.
First author in Nature, JACS, JOC, and Synlett, and Co-author in ACS Nano paper.
2. Kenichiro Itami, Professor, ITbM, Nagoya University.
Corresponding author in Nature, JACS, ACS Nano, JOC, and Synlett.
3. Hideto Ito, Associate Professor, Graduate School of Science, Nagoya University.
Corresponding author in Nature, JACS, ACS Nano, and JOC, and Co-author in Synlett.
4. **B**, Former Researcher, Graduate School of Science, Nagoya University, Former Designated Assistant Professor.
First author in ACS Nano, and co-author in Nature, JACS, and JOC.
5. **C**, Former Designated Associate Professor, Graduate School of Science, Nagoya University.
Corresponding author in ACS Nano, and co-author in Nature, and JACS.
6. **D**, Former Assistant Professor, Research Center for Materials Science, Nagoya University, Former Group Leader and Assistant Research Director, Itami ERATO project, JST.
Co-author in Synlett.

III. Investigation Method of DIC

1. Examination of the allegations: Profs. K. Itami and H. Ito submitted a total of six petitions, and the committee examined them closely.
2. Review of the papers: All the data in the five papers, in which **A** was the first author, were examined for the presence of research misconduct. For the Nature paper, the correspondence between the Nature editor and the corresponding authors was also investigated.
3. Scrutiny of data files: As described in section V, the experimental notebooks of **A** were not left behind, but the DIC found some raw data and some secondary data in the Itami lab. that were created to prepare graphs for submission to the journals. These data were closely investigated.
4. Questionnaires and scrutiny of responses: We sent letters of inquiry to Professors K. Itami and H. Ito (12 times), **A** (twice), a designated lecturer **E** in ITbM (once), Former Graduate Student, **F** (once), and Former Assistant Professor **D**(once), and received their responses in writing.
5. Interviews: Interviews were conducted with investigated persons.
6. On-site investigation in Itami lab. and MALDI-TOF/MS measurement request: The samples left by **A** were found in Itami lab., and the MALDI-TOF/MS spectrum measurements were requested to JEOL.
7. Evaluation of image data: For the STM and AFM images published in Nature, JACS, and ACS Nano papers, image analysis was requested to Lpixel Co.

IV. Accreditation for the investigated papers

The DIC has investigated all the figures and tables in the following five papers, in which **A** was the first author, and has discovered several cases of research misconduct. The list and representative examples of research misconduct are shown in Appendixes I and II, respectively. This section summarizes the evaluations of the five papers.

1. Nature paper

"Living annulative π -extension polymerization for graphene nanoribbon synthesis"

Nature, 571, 387-391 (2019).

This paper reports the bottom-up synthesis of size-selected GNRs by the APEX method, specifically the synthesis of GNR **2** and GNR **7**, called fjord types, and the chemical transformations of GNR **2**→GNR **5** and GNR **2**→GNR **8**. The first author, **A**, was responsible for almost all the experiments from material synthesis to sample identification, and also prepared the first draft of the paper. **F**, a fourth-year undergraduate student in 2018, conducted GNR synthesis experiments using diphenylacetylene as an initiator and its SEC measurements with **A** as her mentor in the laboratory. It should be noted that the SEC data of **F** were replaced by **A**. Associate Professor H. Ito, the corresponding author, advised and supervised the experiments of **A** and **F**, and was in a position to check the raw data of the experiments. He also prepared the manuscript of this paper based on the first draft together with **A**. Professor K. Itami, who was also the corresponding author, supervised the research and checked the experimental data. He revised the manuscript and prepared the final version in discussion with **A** and H. Ito. The other authors were responsible for the STM and AFM measurements and their analysis.

The paper shows SEC charts, IR and Raman spectra, UV-visible absorption and fluorescence spectra, STM and AFM, and MALDI-TOF/MS results, but in all data except STM and AFM, there are obvious fabrications, conducted by **A** (see Appendixes I and II). As for the STM and AFM data which were measured by the other authors, there was no fraud in itself, though the samples supplied by **A** did not have the structures described in the paper.

Furthermore, this paper included a scientific error. An examination of the NMR spectra of the monomer substances revealed that it was a mixture of several isomers, unlike the description in the paper. Although this identification error itself is not research misconduct, Profs. H. Ito and K. Itami had deficiencies in their examination of the compound identification.

2. JACS paper

"Step-Growth Annulative π -Extension Polymerization for Synthesis of Cove-Type Graphene Nanoribbons"

J. Am. Chem. Soc., 142, 1686-1691 (2020).

The synthesis of GNRs **2a** ~ **2d**, called the cove type, by the APEX method, and the synthesis of GNR **6** and GNR **8**, which have copolymer structures by devising the monomer structures, have been reported. The roles of the first author, **A**, and the corresponding authors, K. Itami and H. Ito, are identical to those in the Nature paper. The other authors also played the same

roles as in the Nature paper.

In this paper, there is obvious falsification/fabrication of $^1\text{H-NMR}$ spectra of monomer molecules, SEC charts of GNR, IR spectra, and MALDI-TOF/MS data. We recognize the obvious research misconduct by **A**. On the other hand, although the sample supplied by **A** did not have the structure described in the paper, there was no misconduct in the AFM data itself for this sample.

3. ACS Nano paper

“Graphene Nanoribbon Dielectric Passivation Layers for Graphene Electronics”

ACS Appl. Nano Mater., 2, 4825-4831 (2019)

FET characteristics of a composite system of graphene with cove-type GNR **2a** synthesized in the JACS paper were reported. The first author, Dr. **B**, made this composite system, using the GNR samples synthesized by the second author, **A**. These GNRs were identical to those in the JACS paper. Then, Dr. **B** formed and characterized the field-effect transistors. The roles of Profs. K. Itami and H. Ito were identical to those in the Nature and JACS papers, respectively, and they were responsible for the preparation of the GNR samples while supervising **A**. On the other hand, the other authors were responsible for the fabrication of the GNR/Graphene composite system, its device fabrication, and the measurement of its performance evaluation such as transistor characteristics. In the preparation of this paper, **A**, H. Ito and K. Itami were in charge of the sample synthesis part, while the other authors were in charge of the device fabrication and its performance evaluation part. Although no irregularities were found in the STM/AFM and FET characterization data, the basis for the sample synthesis ($^1\text{H-NMR}$ spectra, SEC charts, and IR spectra), which was allegedly measured by **A**, was clearly falsified or fabricated.

4. JOC paper

“A Quest for Structurally Uniform Graphene Nanoribbons: Synthesis, Properties, and Applications”

J. Org. Chem., 85, 4-33 (2020).

This paper is a review paper and does not contain any original data. Although this may not be research misconduct, the latter half of the paper mentions GNR synthesis by the APEX method, and this part is not true. The first author, **A**, and the second author, **B**, prepared the first draft of the paper, and the corresponding authors, K. Itami and H. Ito, completed the paper.

5. Synlett paper

“Helically Twisted Tetracene: Synthesis, Crystal Structure, and Photophysical Properties of

Hexabenzoc[*a,c,fgj,l,op*]tetracene”
Synlett, 27, 2081–2084 (2016).

This paper reports on the synthesis, crystal structure and optical properties of tetracene derivatives. The first author, **A**, was in charge of almost all the experiments from material synthesis to sample identification, and the third author, **D**, was in charge of X-ray crystallography. Along with H. Ito, both of them prepared the draft of this paper, and K. Itami prepared the final version of this paper. **A** obtained the data, but there was nothing suspicious.

V. Cover-up operations

1. Loss of Research Information

In the Itami laboratory, it was a rule that upon graduation, the raw experimental data and research samples were to be handed over to the staff member in charge (H. Ito in the case of **A**), and either the original experiment notebooks were to be left behind or the notebooks were to be scanned to create a pdf file, which was then left in the lab’s dropbox. After scanning, the students were allowed to dispose of the original notebooks with the permission of the staff. However, in violation of the laboratory rules, **A** did not leave any digitalized experiment notes, and the original experiment notes were discarded. He claimed that he had digitized his experimental notebooks according to the lab rules, uploaded them to the lab's dropbox, and disposed of the original notebooks. However, there was no evidence of digitization even after looking at the data recovery process of his USB drive and the scanning history of the lab’s printer used in the process, and the disposal of the original experimental notebooks was unilateral, in violation of the laboratory rules and without the approval of the staff.

This investigation revealed numerous cases of research misconduct by **A** in the papers under investigation, including SEC charts, IR and Raman spectra, UV-visible absorption and emission spectra, NMR spectra, and MALDI-TOF/MS. The DIC examined the research reports of **A**, and found that he had repeatedly committed misconduct on a daily basis from the very early stage (the fall in 2015) after he joined the Itami laboratory. To cover up these activities, it is possible that he destroyed his experimental notebooks.

2. Replacement of HPLC data

Most of the HPLC data on the synthesis of GNRs using diphenylacetylene as initiator, which was conducted by **F**, a Former Graduate Student who was directly supervised by **A**, had been replaced. Extended Data Fig. 5a in the Nature article shows the SEC charts for the synthesis

of GNR 7 with monomer **M**/initiator **I** = 50/1, 100/1, 300/1, and 500/1. These raw data (.lcd file) are left in the data folder of the measurement PC. Among them, “File G” was supposed to be the result obtained by the HPLC measurement of the sample synthesized by **F** on May 19, 2018, in the experiment called G in the Itami laboratory, in which **A** and **F** collaborated. In the actual operation, the sample synthesized by **F** was injected into the HPLC system under the guidance of **A**, and the measurement was started. **F** left the instrument during the analysis and returned to the instrument when it was finished to verify “File G” created in the data folder of the PC. However, the present examination of “File G” revealed that this was not the original one, but a copy of “File H”, measured by **A**, previously, for a living APEX polymerization using chrysene as an initiator. Further, we found “File G”, which was thought to be the original data that had been replaced, in a PC trash folder used by **A**. This suggests that the original “File G” was replaced with a copy of “File H” by **A** immediately after the measurement, before **F** could confirm the experimental results.

This kind of data replacement was repeated not only once, but every time **F** conducted a reproduction experiment on GNR synthesis (10 times in total). These are classified as an attempted cover-up.

VI. Certification

1. Researchers identified as having been involved in the misconduct:

A (Former Graduate Student at Nagoya University)

The Committees certificated that, in the Nature paper, Y. Yuta, the first author, fabricated the SEC chart, IR spectrum, Raman spectrum, UV-visible absorption spectrum, emission spectrum, and MALDI-TOF/MS data. In addition, he replaced the experimental data (SEC chart) conducted by **F**. For the JACS paper, he also fabricated or falsified the SEC chart, ¹H-NMR spectrum, IR spectrum, Raman spectrum, UV-visible absorption spectrum, emission spectrum, and MALDI-TOF/MS data. In addition, for the ACS Nano paper, he fabricated or falsified the ¹H-NMR spectrum, SEC chart, and IR spectrum. In addition, he destroyed research information such as experimental notes, presumably for the purpose of concealing this research misconduct.

When confronted with the apparent evidence of research misconduct and replacement of the SEC charts of **F**, **A** continued to deny any wrongdoing. He finally admitted to the arbitrary calculation of the proton number in the NMR spectrum analysis, but other than this, he has not shown any reasonable counterevidence. There was no sign of remorse on his part even though his actions were clearly malicious.

Since research misconduct was repeated over a period of more than four years since the fall of 2015, the volume of fabricated data is extremely large. Cover-ups were conducted, leading to an evaluation of the acts as highly malicious. Furthermore, the impact on the progress of research in the field is significant because the fraudulent acts affect the conclusions of the papers, and the contents of the fraudulent acts are highly academic novelties when genuine. In addition, social impact is large because the fraudulent data were published in high-impact journals.

2. Researchers who have not been involved in research misconduct but have been identified as authors responsible for papers related to the research in which misconduct occurred.

Kenichiro Itami

Hideto Ito

There is no indication that K. Itami and H. Ito led this research misconduct. However, they are the ones who are responsible for supervising the misconduct that occurred, and they are responsible for preventing the misconduct or detecting it before the paper was published. Especially in the case where inexperienced graduate students are co-authors, the corresponding authors were expected to detect misconduct at an early stage and instruct them on the correct research ethics. The false judgment that reproducibility had been obtained delayed the discovery of the problem because the results of the replicated experiments by **F** were replaced by **A** in routine laboratory activities. However, the research misconduct could not have been noticed due to the superficial data evaluation. Regarding the sample synthesis and identification of GNRs, Associate Professor H. Ito was obligated to check the raw data of all the measurement data obtained by the paper's co-authors, including **A**, to examine the scientific validity and reproducibility, and to pay attention to the absence of research misconduct, but he did not check the raw data. Professor K. Itami was responsible for overseeing the research, paying attention to the scientific validity and reproducibility of the measurement data through discussions with **A**, other co-authors, and H. Ito, and preventing research misconduct by instructing co-authors to check the raw data, but he failed to detect the misconduct before the paper was published. The amount of fabricated and falsified data is enormous. The period during which it was done spans more than four years, from the fall of 2015, **A**'s first year of his master's course, to the completion of his doctorate. The failure of Professors K. Itami and H. Ito to fulfill their respective responsibilities, and the failure to verify the reproducibility of the data and to go back to the raw data in their daily research life and in the research debriefing sessions, allowed **A** to commit his misconduct unchecked.

However, after it became clear that they could not reproduce the GNR synthesis, Professors K. Itami and H. Ito conducted their own investigation, including repeated interviews

with A, to clarify the situation. They also applied for retraction of the Nature paper at their own discretion. In addition, at the request of the investigative committee, they proceeded to verify various data left in the laboratory by A, and found various falsifications and fabrications of data and even data replacement. They cooperated with the committee's investigation by filing further complaints. During this period, they applied for retraction of the JACS paper and ACS Nano paper at their own discretion.

Professors K. Itami and H. Ito were not involved in the misconduct, but they were the corresponding authors. The degree of the breach of the duty of care is "high" because they failed to prevent the misconduct in the papers by failing to perform necessary checks, which the corresponding authors should have performed.

※ Dedicated Investigation Committee (DIC)

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* Persons who assist the investigation of DIC based on their specialized knowledge as a researcher.