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　３ 年　 ６ 月 １１ 日現在

機関番号：３８００５
研究種目：基盤研究(C)（一般）
研究期間：2018～2020
課題番号：１８Ｋ０５２４７

研究課題名（和文）Stimuli-responsive polymers through new dynamic metal complexes

研究課題名（英文）Stimuli-responsive polymers through new dynamic metal complexes

研究代表者
クスヌディノワ　ジュリア（Khusnutdinova, Julia）

沖縄科学技術大学院大学・錯体化学・触媒ユニット・准教授

研究者番号：９０７４７５４４

交付決定額（研究期間全体）：（直接経費）　　2,000,000円

研究成果の概要（和文）：架橋ポリアクリレートと発光性銅錯体を用いた機械的刺激応答性材料を開発し、そのメカニカルセンサーとしての潜在性の高さを明らかにした。この系の発光強度は、100% 以下の歪みと 0.1 MPa 以下の応力に対して、敏感かつ可逆的に変化し、発光を CCD カメラでとらえることにより、ストレス分布図が得られることを実証した。
また、ピリジノファン Cu(I)(NHC) 錯体の結晶が摩擦発光を示すことを見出した。詳細な研究により、圧電性と非圧電性の両方の結晶が摩擦発光を示すことを明らかにした。さらにアモルファスの PMMA フィルムと混合し、その表面を擦っても摩擦発光が観測されることを実証した。

研究成果の学術的意義や社会的意義
The academic significance arises from development of a new concept of using conformational dynamics in photoluminescent complexes to create new fast and reversible mechanophores for mechanoresponsive polymers. Triboluminescent films can be used for conversion of mechanical energy to light.

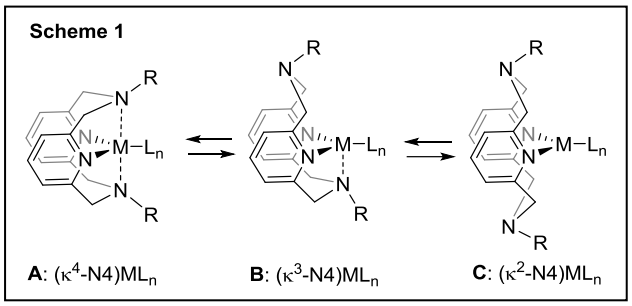
研究成果の概要（英文）：We developed mechanoresponsive material with photoluminecent Cu(I) complex and cross-linked polyacrylate and demonstrated that the system has great potential as mechanical stress sensor. The reversible and sensitive change of photoluminescence intensity is observed in response to applied mechanical stress of less than 0.1 MPa at less than 100% strain. The stress distribution map was obtained by monitoring the photoluminescence intensity by CCD camera.
The pyridinophane Cu(I)(NHC) complexes show intense triboluminescence by grinding the crystals, even in air. Both piezoelectric (centrosymmetric) and non-piezoelectric crystals of pyridinophane Cu(I)(NHC) complex exhibit triboluminescence. Furthermore, amorphous PMMA films containing 1 wt% of the Cu(I) complex showed triboluminescence. The reported examples of triboluminescence of Cu(I) complexes have been extremely limited. Our study gives important insight into the mechanism and design of triboluminescent Cu(I) materials.

研究分野：mechanoresponsive polymers

キーワード：mechanophore　mechanoresponse　polymer　copper

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景




Prior to starting this project, my studies of the conformational dynamics of the **N4**-pyridinophane ligand have shown that this complex can adopt a variety of conformations in metal complexes (Scheme 1).[1,2] I have shown that **N4**-pyridinophane in metal complexes can adopt several conformations, which can interconvert rapidly and easily depending on the metal (Scheme 2). This gave rise to the idea of the general proposal to utilize this property for the stimuli-responsive materials, where conformational change caused by mechanoactivation will trigger changes in reactivity or optical/magnetic properties. Prior to application to this funding, I have shown that this ligand can be used in combination with copper(I) to form luminescent Cu complexes,[3,4] which, when incorporated into polyurethane chain, give rise to the reversible and fast mechanical stress sensing material.[5] Thus, when the polyurethane film containing Cu iodide complexes with **N4** ligand was elongated, photoluminescent intensity increased, and then decreases after film relaxation, over 10 cycles. However, this originally published system suffered from low stability in air and lack of sensitivity (the response could be seen after the film was elongated 4-fold or more). Thus, the key scientific question in the original proposal was whether we can utilize the *reversible conformational dynamics* of metal complexes to create stimuli-responsive materials that have *enhanced reversibility and fast response*.

This approach is different from other approaches commonly used in the literature that typically utilize organic-based mechanophores that undergo covalent chemical bond scission/formation when mechanical stress is applied, leading to slow or irreversible response. In our approach, we utilize highly reversible and facile conformational dynamics of transition metal complexes which is expected to lead to fast and reversible response.

**References**:

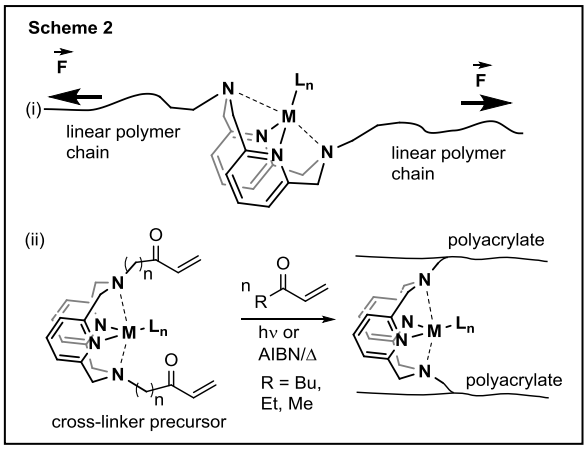
[1] Khusnutdinova, J.R.; Rath, N.P.; Mirica, L.M. *Inorg. Chem.* **2014,** *53*, 13112.
[2] Khusnutdinova, J. K.; Rath, N. P.; Mirica L. M. *J. Am. Chem. Soc.* **2012**, *134*, 2414
[3] Filonenko, G.A.; Fayzullin, R.R.; Khusnutdinova, J.R. *J. Mater. Chem. C* **2017**, *5*, 1638.
[4] Patil, P. H.; Filonenko, G. A.; Lapointe, S.; Fayzullin, R. R.; Khusnutdinova, J. R. *Inorg. Chem.* **2018**, *57,* 10009-10027.
[5] Filonenko, G.A.; Khusnutdinova, J.R. *Adv. Mater.* **2017**, *29*, 1700563.

２．研究の目的

We aimed to create new mechanoresponsive materials that show fast and reversible property change in response to mechanical force. This property can be emission of light, photoluminescence intensity, color etc. We propose that mechanical force can affect conformational dynamics of metal complexes leading to different spectroscopic or photophysical properties. The final goal is to create materials that will show improvement over existing organic mechanophores in terms of sensitivity and reversibility.

３．研究の方法

As a method of attachment of mechanophore to the polymer, we considered two possibilities. One was previously explored by our group and it is attachment of the mechanophore, N4 ligand or corresponding metal complex, to the linear polymer chain (Scheme 2, (i)). Another possibility that we explored in this project was utilization of the **N4**-complex as the cross-linker (Scheme 2, (ii)). This could give additional advantages as we anticipated that such system show improved sensitivity as more mechanical force will be transmitted to a less flexible linker rather than to linear, long polymer chain. This was indeed confirmed by our experiments in this project.



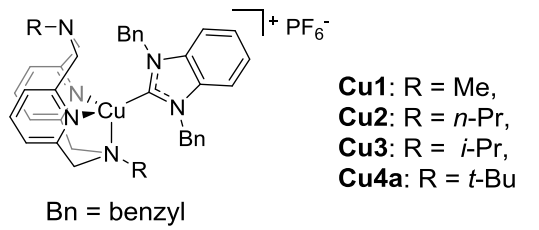

When selecting metals for forming metal complexes, our first target was copper(I) complexes because they show photoluminescent properties that can be easily monitored by a variety of methods.

Our additional purpose was to make stable copper(I) luminophores, because copper(I) complexes often decompose under air. To achieve this goal, we planned to use N-heterocyclic carbene (NHC) complexes of copper.
We also targeted other metals such as Co, Ni etc which could show changes in other properties such as color (or UV-vis absorbance spectrum in the visible or near-IR region, in general).

４．研究成果

In the first part of our study, we synthesized a series of [(**N4**)Cu(NHC)]X complexes (Scheme 3, Figure 1) as model compounds to study their photophysical properties and air stability. All complexes were brightly emissive and showed good air stability in solid state and polymer films.

**Scheme 3**



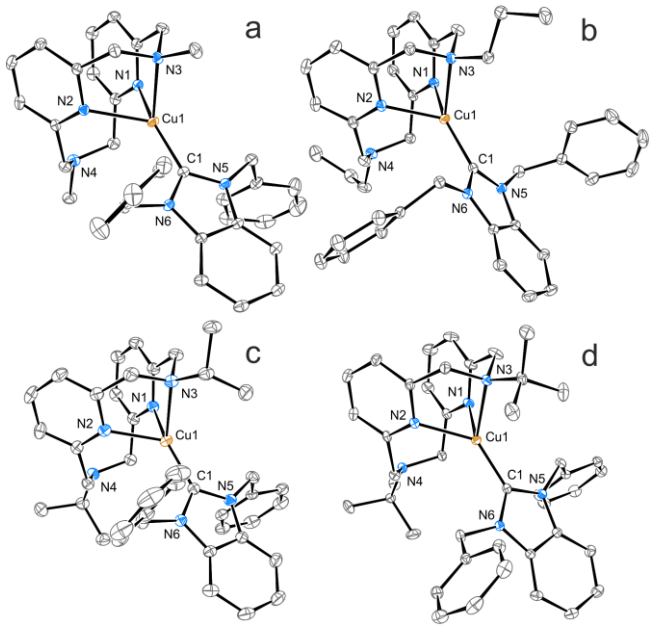




**Figure 1**. ORTEP of the cationic parts of complexes **Cu1** (a), **Cu2** (b), **Cu3** (c), and **Cu4a** (d) at 50 % probability level according to single crystal XRD data.

**Table 1**. Photophysical property of [(N4)Cu$^{I}$(NHC)]X complexes in $CH_2Cl_2$

| Complex | R | PLQY | τ [μs] | $k_r$ $10^{-4}$ [$s^{-1}$] | $k_{nr}$ $10^{-4}$ [$s^{-1}$] |
|---|---|---|---|---|---|
| **Cu1** | Me | 0.06 | 8.20 | 0.732 | 11.5 |
| **Cu2** | $^{n}$Pr | 0.19 | 7.59 | 2.50 | 10.7 |
| **Cu3** | $^{i}$Pr | 0.30 | 9.98 | 3.00 | 7.01 |
| **Cu4a** | $^{t}$Bu | 0.72 | 18.0 | 4.00 | 1.56 |

Their photophysical properties were studied in solid state, solution and blended in PMMA films (Table 1). This study showed that stability and air stability of these complexes make the potential targets to use as cross-linkers in elastomers. We then synthesized an acrylate-functionalized version of the ligand, which was incorporated as a cross-linker in polybutylacrylate films (Scheme 4). After that, the ligand was metalated by treatment with a common Cu(NHC) precursor. The resulting cross-linked, elastomeric polybutylacrylate films were luminescent. When the films were stretched, we observed increase in photoluminescence intensity. When the film was then released, the intensity was decreased. This response was repeatable and could be reproduced up to 30 cycles or longer. The emission intensity could be detected spectroscopically using fiber-optic compact spectrometer. We could also observe directly changes in emission intensity by simply using a CCD camera to record the images under UV light irradiation. The important finding in this study was that the cross-linked showed superior sensitivity as compared to previously published mechanoresponsive polymers with traditional mechanophores and our system showed measurable response even at less than 50% elongation and 0.1 MPa of stress. NMR study of fluxional conformational behavior of these complexes allowed to formulate a hypothesis that the mechanism of mechanoresponse is based on reversible suppression of fluxionality of the ligand.

Scheme 4

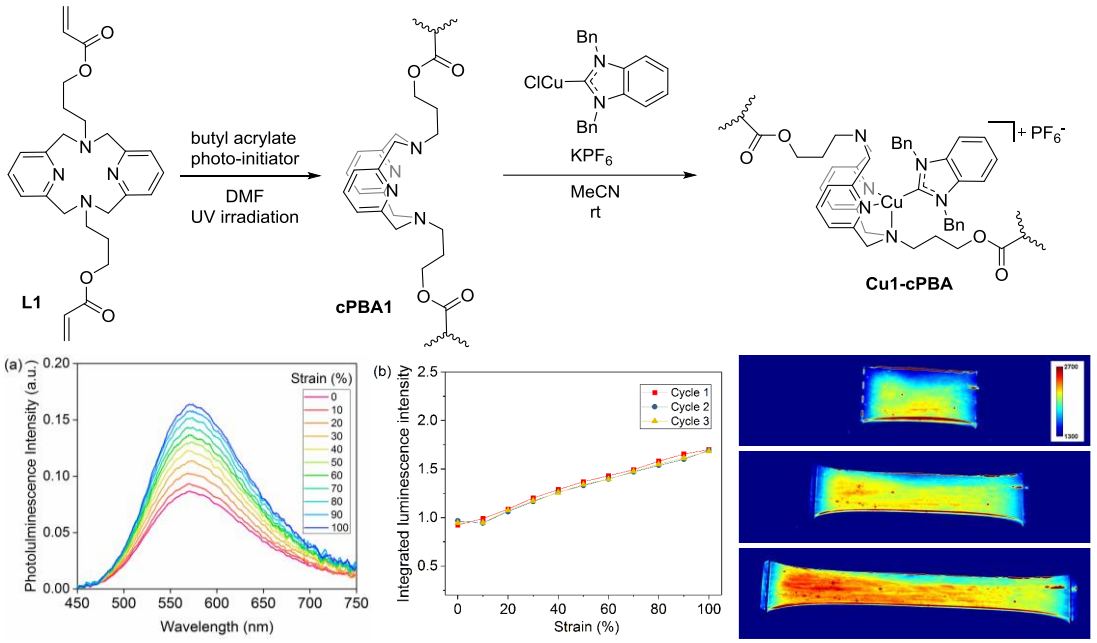
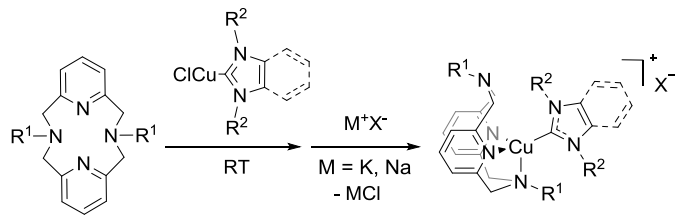



**Figure 2**. Change of photoluminescence of **Cu1-cPBA** during stretching.

To summarize, in this first study we have shown that using [(**N4**)Cu(NHC)]X complexes as cross-linker, we were able to achieve mechanoresponsive elastic material showing reversible changes in emission intensity in response to stretching/release. This finding can be eventually important for mechanical stress detection and mechanical stress mapping using imaging methods in elastic materials, rubbers etc. Based on this study, one publication in Chemical Communications and a patent were published.[6,7]

While studying model [(**N4**)Cu(NHC)]X complexes, we serendipitously found that these complexes show triboluminescence in the crystalline state when the crystals are crushed with a metallic spatula or a glass rod. The bright visible light emission was observed even under air in ambient light. This phenomenon is known as triboluminescence, or mechanoluminescence, which is emission of light directly in response to mechanical action. The difference from photoluminescence is that no external excitation light source is required, and mechanical energy is directly converted to light. Triboluminescent materials are thus ultimately considered as promising components of mechanical damage sensors, athletic and healthcare devices etc. There has been an ongoing discussion regarding explanation of the triboluminescence in crystalline materials, which generally invokes piezoelectric effect and requires non-centrosymmetric crystals to

Scheme 5




Bn = benzyl
Mes = mesityl
Dipp =
OTf = $CF_3SO_3^-$
TFA = $CF_3COO^-$

**Cu4a**: $R^1$ = $^t$Bu, $R^2$ = Bn, X = $PF_6$
**Cu4b**: $R^1$ = $^t$Bu, $R^2$ = Bn, X = OTf
**Cu4d**: $R^1$ = $^t$Bu, $R^2$ = Bn, X = $BPh_4$
**Cu5**: $R^1$ = Me, $R^2$ = Mes, X = $PF_6$
**Cu6**: $R^1$ = Me, $R^2$ = Dipp, X = $PF_6$

**Table 2**. TL properties and space group for crystalline and polymer-blended samples.

| [Cu] | Counter anion | TL (crystal) $\lambda_{max}$ (nm) | TL (PMMA), $\lambda_{max}$ (nm) | Space group in crystal[a] |
|---|---|---|---|---|
| **Cu4a** | $PF_6$ | 544 | 526 | *Pca*2$_1$ (NC) |
| **Cu4b** | OTf | 539 | 530 | *Pca*2$_1$ (NC) |
| **Cu4c** | TFA | 536 | 536 | *Pca*2$_1$ (NC) |
| **Cu4d** | $BPh_4$ | 540 | 527 | *Pbca* (C) |
| **Cu5** | $PF_6$ | 536 | 552 | *P*2$_1$/*n* (C) |
| **Cu6** | $PF_6$ | 527 | 543 | *P*2$_1$2$_1$2$_1$ (NC) |

[a] C: Centrosymmetric, NC: Non-centrosymmetric.

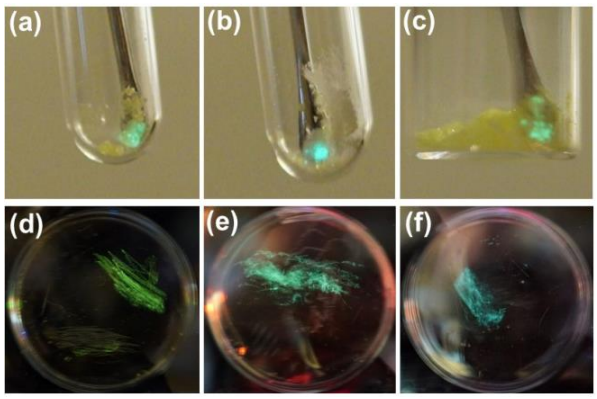



**Figure 3.** Representative images of TL in crystal of **Cu5** (a), **Cu6** (b) and **Cu4a** (c) under air and PMMA film containing 10 wt% of **Cu5** (d), Cu**6** (e), and Cu**4a** (f) under Ar.

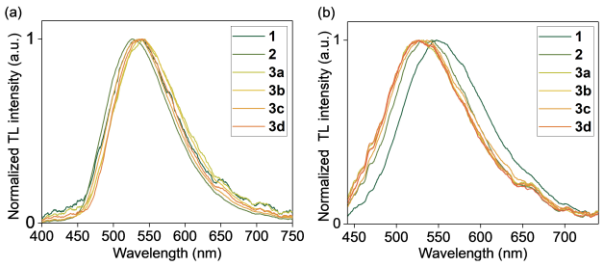
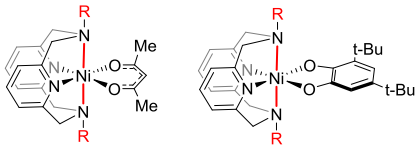



**Figure 4.** Normalized TL emission spectra of complexes **Cu5**, **Cu6**, and **Cu4a-d** (a) in the crystal state and (b) in PMMA films (1 wt%) under $N_2$.

be present.[8] However, our examination of the crystal structures of these complexes showed that both centrosymmetric and non-centrosymmetric crystals showed triboluminescent properties. This is in line with more recent views that conclude that non-centrosymmetricity is not always required to observe triboluminescence.[9]

This observation led us to examine if triboluminescence of these copper complexes can be translated into polymer state. To our surprise, when these complexes were simply physically blended with polymer films (polymethylmethacrylate, polyvinyl chloride, polystyrene), the resulting films also showed triboluminescent properties when the film was rubbed with glass, metal or polymer rod. More detailed investigation using powder XRD and fluorescent microscopy showed that triboluminescence was observed in amorphous films and no microscrystalline phase was required. Further examination of emission spectra showed that gas discharge peaks are present in the spectra and the likely mechanism of emission generation involves triboelectrification of the polymer followed by discharging of surrounding gas leading to excitation of the luminophore.[10, 11]

**Table 3**. Axial bond length of **N4** Ni(II) complexes and its color of the crystals.




R = Me or *t*-Bu

| Ligand | R | Ni – $N_{axi}$ (Å) | color |
|---|---|---|---|
| acac | Me | 2.20, 2.18 | brown |
| | tBu | 2.30, 2.29 | pink |
| catecholate | Me | 2.22 | brown |
| | tBu | 2.46, 2.29 | red |

As a part of ongoing study on complexes of other metals, we examined complexes of N4 ligand with Ni searching for the complexes that would show different coloration while having elongated or shortened Ni-N distances with amine arms of N4 pyridinophane ligands. Once such complexes are identified, we plan to attach amine arms of the N4 ligand to the polymer chain (e.g. as cross-linkers). We have found several Ni complexes with acac or catecholate ligands that show different color depending on the strength of Ni-N binding and the Ni-N bond length (Table 3). We expect that application of mechanical force may perturb Ni-N as the weakest bond present in the complex, which might eventually lead to the color change in response to mechanical force.

**References**:

[6] Karimata, A.; Patil, P. H.; Khaskin, E.; Lapointe, S.; Fayzullin, R. R.; Stampoulis, P.; Khusnutdinova, J. R. *Chem. Commun.* **2020**, *56*, 50-53.

[7] Provisional patent, Japan, Application/Provisional number 2020-103434, J. R. Khusnutdinova, A. Karimata, "Mechanoresponsive polymers containing photoluminescent copper(I)-containing cross-linkers".

[8] J. I. Zink, *Acc. Chem. Res.*, 1978, **11**, 289-295

[9] Y. Xie and Z. Li, *Chem*, 2018, **4**, 943-971

[10] Karimata, A.; Patil, P. H.; Fayzullin, R. R.; Khaskin, E.; Lapointe, S.; Khusnutdinova, J R. *Chem. Sci.* **2020**, *11*, 10814-10829.

[11] Provisional patent, Japan, Application/Provisional number 2020-120094, J. R. Khusnutdinova, A. Karimata, P. H. Patil, "Triboluminescence of Cu-NHC complexes in solid state and in polymer films".

５．主な発表論文等

〔雑誌論文〕　計3件（うち査読付論文　3件／うち国際共著　3件／うちオープンアクセス　0件）

| | |
|---|---|
| １．著者名<br>Karimata, A.; Patil, P. H.; Khaskin, E.; Lapointe, S.; Fayzullin, R. R.; Stampoulis, P.; Khusnutdinova, J. R. | ４．巻<br>56 |
| ２．論文標題<br>Highly sensitive mechano-controlled luminescence in polymer films modified by dynamic CuI-based cross-linkers | ５．発行年<br>2020年 |
| ３．雑誌名<br>Chemical Communications | ６．最初と最後の頁<br>50-53 |
| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.1039/C9CC08354E | 査読の有無<br>有 |
| オープンアクセス<br>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<br>該当する |

| | |
|---|---|
| １．著者名<br>Patil, P. H.; Filonenko, G. A.; Lapointe, S.; Fayzullin, R. R.; Khusnutdinova, J. R. | ４．巻<br>57 |
| ２．論文標題<br>Interplay between conformational flexibility and photoluminescent properties of mononuclear pyridinophane copper(I) complexes | ５．発行年<br>2018年 |
| ３．雑誌名<br>Inorganic Chemistry | ６．最初と最後の頁<br>10009-10027 |
| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.1021/acs.inorgchem.8b01181 | 査読の有無<br>有 |
| オープンアクセス<br>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<br>該当する |

| | |
|---|---|
| １．著者名<br>Karimata, A.; Patil, P. H.; Fayzullin, R. R.; Khaskin, E.; Lapointe, S.; Khusnutdinova, J R. | ４．巻<br>11 |
| ２．論文標題<br>Triboluminescence of a new family of CuINHC complexes in crystalline solid and in amorphous polymer films | ５．発行年<br>2020年 |
| ３．雑誌名<br>Chemical Science | ６．最初と最後の頁<br>10814-10829 |
| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.1039/D0SC04442C | 査読の有無<br>有 |
| オープンアクセス<br>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<br>該当する |

〔学会発表〕　計8件（うち招待講演　2件／うち国際学会　1件）

| |
|---|
| １．発表者名<br>Karimata, A., Patil. P., Lapointe, S., Khaskin, E., Fayzullin, R. R., & Khusnutdinova, J. R. |
| ２．発表標題<br>Photoluminescent pyridinophane copper(I) complexes bearing NHC ligand and their applications in mechanical-stimuli responsive cross-linked polymer materials |
| ３．学会等名<br>Japanese Society of Coordination Chemistry |
| ４．発表年<br>2019年 |

１．発表者名
Karimata, A., Patil. P., Lapointe, S., Khaskin, E., Fayzullin, R. R., & Khusnutdinova, J. R.

２．発表標題
Mechanoresponsive photoluminescence in cross-linked polybutylacrylates containing flexible (pyridinophane)Cu(NHC) complexes as mechanophores

３．学会等名
100th Annual Meeting 2020 of the Chemical Society of Japan

４．発表年
2020年

１．発表者名
Patil, P. H.; Khusnutdinova, J. R.

２．発表標題
Influence of Tetradentate Macroclic Ligand Sterics on the Conformational Flexibility and Photoluminescent Properties of Copper(I) Complexes

３．学会等名
255th American Chemical Society National Meeting（国際学会）

４．発表年
2018年

１．発表者名
Khusnutdinova, J. R., Karimata, A.; Patil, P. H.

２．発表標題
Stimuli-responsive polymers through dynamic coordination compounds

３．学会等名
International Conference on Coordination Chemistry (ICCC)

４．発表年
2018年

１．発表者名
Khusnutdinova, J. R.

２．発表標題
Dynamic coordination compounds of CuI: new mechanophores and extended metal atom chains

３．学会等名
the 25th International SPACC Symposium（招待講演）

４．発表年
2018年

| |
|---|
| １．発表者名<br>Karimata, A., Patil, P., Fayzullin, R. R., Khaskin, E., Lapointe, S., & Khusnutdinova, J. |
| ２．発表標題<br>Triboluminescence of pyridinophane CuI(NHC)complexes in crystals and amorphous polymers |
| ３．学会等名<br>Conference of Japan Society of Coordination Chemistry |
| ４．発表年<br>2020年 |

| |
|---|
| １．発表者名<br>Karimata, A., Patil, P.; Fayzullin, R. R., Khaskin, E., Lapointe, S. & Khusnutdinova, J. |
| ２．発表標題<br>Triboluminescence of pyridinophane copper complexes in crystals and polymers |
| ３．学会等名<br>101st CSJ Annual Meeting |
| ４．発表年<br>2021年 |

| |
|---|
| １．発表者名<br>Khusnutdinova, J. R.; Karimata, A. |
| ２．発表標題<br>Using tribo- and photoluminescent Cu complexes to detect mechanical stress in polymers |
| ３．学会等名<br>IEICE General Conference（招待講演） |
| ４．発表年<br>2021年 |

〔図書〕　計0件

〔出願〕　計2件

| 産業財産権の名称 | 発明者 | 権利者 |
|---|---|---|
| Provisional patent "Mechanoresponsive polymers containing photoluminescent copper(I)-containing cross-linkers" | Khusnutdinova, Karimata | 同左 |
| **産業財産権の種類、番号** | **出願年** | **国内・外国の別** |
| 特許、2020-103434 | 2020年 | 国内 |

| 産業財産権の名称 | 発明者 | 権利者 |
|---|---|---|
| Provisional patent “Triboluminescence of Cu-NHC complexes in solid state and in polymer films” | Khusnutdinova, Karimata, Patil | 同左 |
| **産業財産権の種類、番号** | **出願年** | **国内・外国の別** |
| 特許、2020-120094 | 2020年 | 国内 |

〔取得〕　計0件

〔その他〕

機械的力で Cu(I) 錯体の発光強度を制御する
https://www.chem-station.com/blog/2020/04/cu.html
Nnew “ smart ” polymer glows brighter when stretched
https://www.oist.jp/news-center/news/2020/1/23/feel-force-new-%E2%80%9Csmart%E2%80%9D-polymer-glows-brighter-when-stretched
機械的な力を感じてより強く発光する「スマート」ポリマー
https://www.oist.jp/ja/news-center/news/2020/1/23/34675
Highlight for general public, Japanese version
https://www.oist.jp/ja/news-center/news/2018/11/7/33291
Highlight for general public, English version
https://www.oist.jp/news-center/news/2018/11/7/slower-they-turn-brighter-they-glow
FY2018 annual report, see Section 3.1
https://groups.oist.jp/cccu/fy2018-annual-report

６．研究組織

| | 氏名<br>（ローマ字氏名）<br>（研究者番号） | 所属研究機関・部局・職<br>（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 |
|---|---|