HOKKAIDO UNIVERSITY

| | |
|---|---|
| Title | Multidynamic Crystalline Molecular Rotors Comprising an N-Heterocyclic Carbene Binuclear Au(I) Complex Bearing Multiple Rotators |
| Author(s) | Jin, Mingoo; Matsuura, Satsuki; Yamamoto, Hikaru et al. |
| Citation | European journal of organic chemistry, 26(12), e202201468<br>https://doi.org/10.1002/ejoc.202201468 |
| Issue Date | 2023-03-21 |
| Doc URL | https://hdl.handle.net/2115/91734 |
| Rights | This is the peer reviewed version of the following article: [Jin, M., Matsuura, S., Yamamoto, H., Mizuno, M., Ito, H., Eur. J. Org. Chem. 2023, 26, e202201468], which has been published in final form at https://doi.org/10.1002/ejoc.202201468. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley' s version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited. |
| Type | journal article |
| File Information | EurJOC-manuscript-final.pdf |

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

RESEARCH ARTICLE

# Multidynamic Crystalline Molecular Rotors Comprising an N-Heterocyclic Carbene Binuclear Au(I) Complex Bearing Multiple Rotators

Mingoo Jin*,[a] Satsuki Matsuura,[b] Hikaru Yamamoto,[b] Motohiro Mizuno[c] and Hajime Ito*[a,b]

[a] Prof. Dr. Mingoo Jin (Corresponding author), Prof. Dr. Hajime Ito (Corresponding author)
Institution for Chemical Reaction Design and Discovery (WPI-ICReDD)
Hokkaido University
Sapporo, Hokkaido 060-8628, Japan

[b] Prof. Dr. Hajime Ito, Satsuki Matsuura, Hikaru Yamamoto
Division of Applied Chemistry and Frontier Chemistry Center (FCC), Faculty of Engineering,
Hokkaido University
Sapporo, Hokkaido 060-8628, Japan
E-mail: mingoo@icredd.hokudai.ac.jp; hajito@eng.hokudai.ac.jp

[c] Prof. Dr. Motohiro Mizuno
Division of Material Chemistry, Graduate School of Natural Science and Technology,
Nanomaterials Research Institute, Kanazawa University
Kakuma-machi, Kanazawa, 920-1192, Japan

Supporting Information for this article is provided via a link at the end of the document.

**Abstract:** We report multi-dynamic molecular rotations in crystals using a concave-shape *N*-heterocyclic carbene (NHC) binuclear Au(I) complex rotor bearing pyrazine and tetrahydrofuran (THF) molecules as multicomponent rotators. Single-crystal X-ray diffraction (XRD) measurements revealed that two THF molecules are located near the central pyrazine encapsulated by two bulky NHC ligands. From $^{2}$H solid-state NMR analysis, it was observed that the pyrazine rotated in a 2-fold site exchange with a 180° rotational angle and a 31 kJ mol$^{-1}$ energy barrier, while the THF molecules showed a 23°–38° libration with a lower energy barrier (14 kJ mol$^{-1}$). Interestingly, the pyrazine rotation was accelerated when the THF molecules rotated in fast site exchange with a large angle of libration, suggesting that the rotators exhibit multi-dynamics in a correlated manner.

## Introduction

The design of molecular rotation in crystalline media has attracted much interest not only in the field of molecular machines but also in solid-state functional materials, because the rotation-induced molecular geometry alteration can provide an avenue for switching the physical properties of solid compounds.[1–8] To construct the crystalline materials, known as crystalline molecular rotors, gyroscope-like molecular rotors,[2–4,9–11] dumbbell-shaped molecules,[2–3,12–17] and porous solid-state materials such as metal-organic frameworks (MOFs)[5–8,18-23] have been utilized. The general blueprint of this design is based on the combination of a rotator moiety with a bulky and rigid domain as a stator that is used to construct the ordered frame as well as the local space that can undergoes molecular rotation. Many examples have utilized a single-component rotator that generally shows a simple rotational dynamics.[1–8] To broaden the application of crystalline molecular rotors, realizing larger complexity of molecular motions in the solid-state is important because the multiple molecular dynamics in crystals have a high potential to integrate various functions such as photophysical or dielectric properties (Figure 1a).[24]

One way to obtain multi-dynamic crystalline rotors is to employ a multicomponent as a rotator bearing different molecular structures. Recently, Sozzani and Comotti *et al.* realized cascade dynamics in a crystal by utilizing a MOF bearing two distinct ligands, 4,4′-bipyridine and bicyclo[1.1.1]pentanedicarboxylate, as the multicomponent molecular rotators (Figure 1b).[19] In another example, Merino and Rodriguez-Molina *et al.* demonstrated multicomponent crystals with two fast reorienting motions of 1,4-diazabicyclo[2.2.2]octane (DABCO) and tetrahydrofuran (THF) over perpendicular non-covalent axes formed with bulky carbazole (Figure 1b).[25] However, it is still challenging to construct crystalline rotors possessing multi-rotators with distinct shapes as well as nearly arranged geometry because of the difficulty in the rational design of the crystalline structure.

Recently, we developed luminescent crystalline molecular rotors by encapsulating a central pyrazine rotator using 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr-*N*-heterocyclic carbene (NHC)) Cu(I) or Au(I) complexes, as shown in Figure 1c.[26] The concave-shaped NHC ligands sterically shield the central rotator from the packing environment in the crystal and form a local volume near the rotator. We envisioned that such a local space could accommodate small organic molecules, which may show intercorrelated molecular rotation with the central pyrazine.

To investigate this concept, we prepared the crystalline molecular rotor **1**-$d_4$-2(THF), which includes THF molecules in the local space near the central pyrazine. Single-crystal X-ray diffraction (XRD) analysis revealed that two THF molecules are located near the pyrazine with a tilted geometry, as shown in Figure 1c. Solid-state $^{2}$H NMR spin-echo measurements at variable temperatures indicated that the central pyrazine and THF showed distinct rotational motions. The pyrazine rotated in 180° of a 2-fold motion while the THF molecules show a 23°–38°

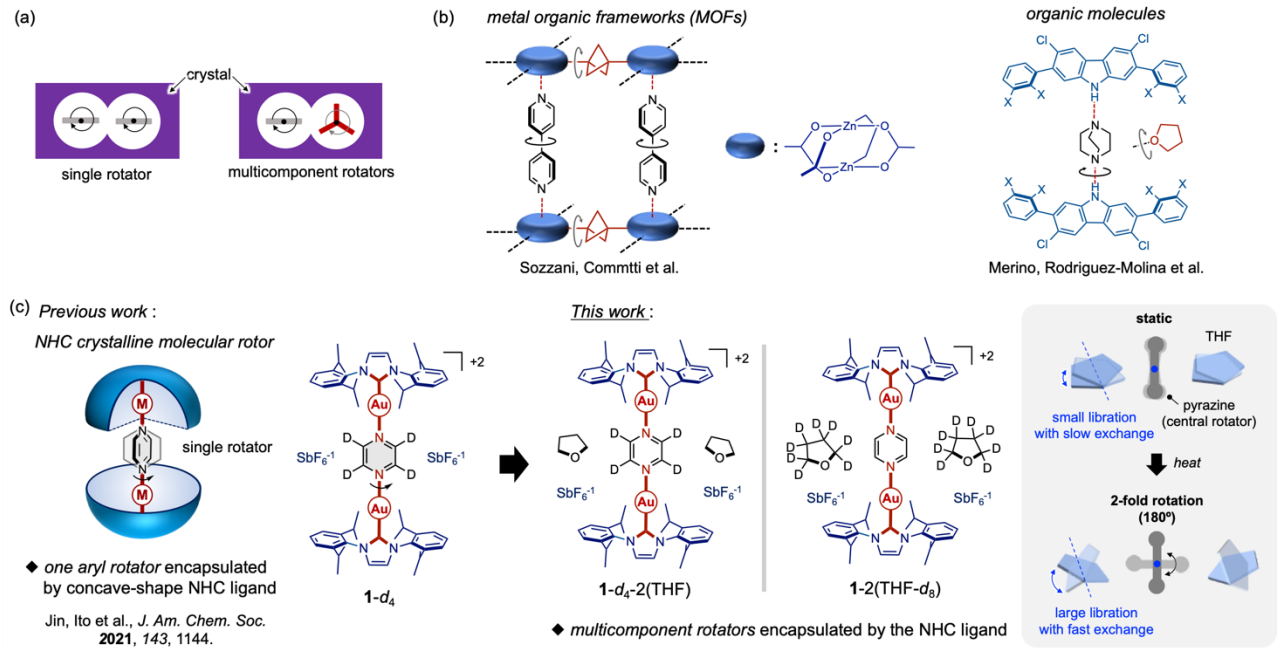



**Figure 1.** (a) Illustration of crystalline molecular rotors bearing (left) single and (right) multicomponent rotators. (b) Examples of amphidynamic crystals possessing multicomponent rotators. (c) Illustration of the NHC Au(I) complex rotor (left) **1**-$d_4$ and (right) the THF or deuterated THF molecules included crystalline rotors **1**-$d_4$-2(THF) and **1**-2(THF-$d_8$), respectively. The observed multi-motions of the central pyrazine and THF molecules with thermally induced rotation, described in gray-box.

libration in the crystals (Figure 1c). Interestingly, we observed that pyrazine rotation was accelerated when the THF molecules rotated in fast site exchange with large libration, indicating that the motions of the two rotators are intercorrelated.

## Results and Discussion

### Preparation of 1-$d_4$-2(THF) and 1-2(THF-$d_8$) single crystals

The cationic NHC Au(I) complex **1**-$d_4$ possessing deuterated pyrazine as the central rotator was synthesized by our previously reported procedure (Figure 1c, see Supporting Information).[26] Then, the obtained Au(I) complex **1**-$d_4$ was crystallized using THF as a solvent, yielding crystals of **1**-$d_4$-2(THF) that allowed the evaluation of the molecular motion of pyrazine by $^2$H-solid-state NMR measurements. To investigate the rotational dynamics of the THF molecules included in the crystal, we also prepared crystal of **1**-2(THF-$d_8$) which possesses non-deuterated pyrazine and deuterated THF molecules (Figure 1c, see Supporting Information). The crystalline samples were dissolved in $CD_2Cl_2$ and characterized using $^1$H and $^{13}$C NMR spectroscopy. Further characterization of the samples was conducted using thermogravimetric analysis (TGA) and single-crystal XRD, indicating that THF solvent was included in all the crystals (see Supporting Information, Figure S1).

### Crystal structure of 1-$d_4$-2(THF)

Single-crystal XRD measurements of crystal **1**-$d_4$-2(THF) at 153 K revealed that the Au(I) complex **1**-$d_4$ and THF molecules were packed in the space group $P2_1/n$ (Table S1). The central pyrazine was encapsulated by two NHC Au(I) moieties and surrounded by the $SbF_6^{-1}$ counter anion in the crystal structure (Figure 2a). Interestingly, THF molecules were included in the center of the two IPr-NHC ligands and were located near the pyrazine, as shown in Figure 2a–b. The distances between the protons of the THF molecule and the NHC ligands ranged from ca. 3.030 to 3.222 Å. The THF carbon atom was close to the pyrazine plane at a distance of 2.827 Å, and the distances between the THF carbon atom and carbon or nitrogen atoms of the pyrazine were 3.111–3.262 Å that is shorter than sum of van der Waals radius of the atoms (Figures 2b and S3). This indicates that the THF molecules may occur steric effect to the pyrazine rotator. The THF and pyrazine encapsulated by the IPr-NHC ligands were clearly shielded from the nearby intermolecular packing environment by the NHC ligand and $SbF_6^{-1}$ counter anion (Figures 2c and S3). The molecular packing mode of crystal **1**-$d_4$-2(THF) was clearly different from that of the previously reported crystal **1**-$d_4$ containing no THF molecules in the crystal which showed $P2_1/c$ space group.[26] Additionally, the dihedral angle between the NHC ring and the central pyrazine in crystal **1**-$d_4$-2(THF) was larger than the crystal **1**-$d_4$.

To investigate the effect of temperature on the crystal structure, we conducted single-crystal XRD measurements of **1**-$d_4$-2(THF) at variable temperature ranging in 295, 273, 260, 230, 200 and 123 K (Table S1 and Figures S3–S4).[27] The crystal structures were identical, and a slight expansion of the unit cell volume upon heating was observed (Table S1 and Figure S4). This observation indicated that the crystals had no thermally triggered solid-state phase transitions. The powder crystalline sample showed clearly matched PXRD patterns with the simulated pattern obtained by the single crystal XRD, which were measured at the room temperature, indicating that the powder crystal is corresponding to the single crystal (Figure S4). Differential scanning calorimetry (DSC) profiles showed no significant thermal exchange peaks during cooling from 295 to 173 K (Figure S2). In contrast, a small exothermic peak appeared at ca. 230 K, followed by two small endothermic peaks near 250 K during the heating process. We expect that these small thermal exchange peaks are related to the alteration of the molecular dynamics in the crystal.

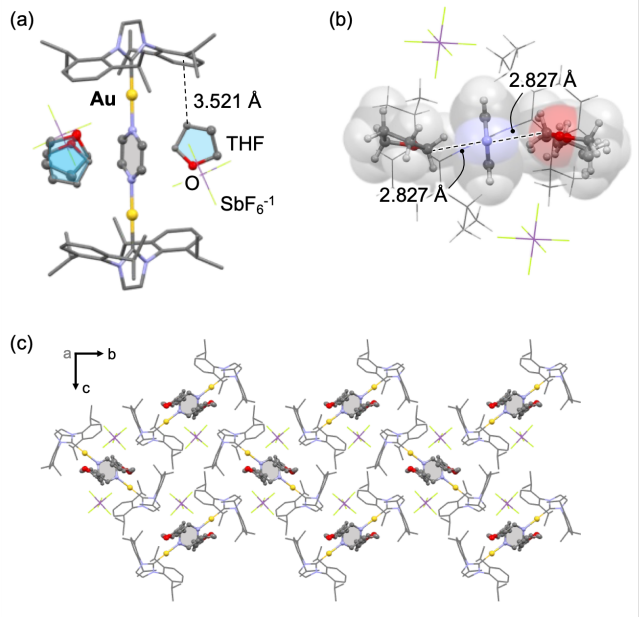



**Figure 2.** Crystal structure of **1**-$d_4$-2(THF). (a) The NHC Au(I) complex **1**-$d_4$ with included THF molecules near the central pyrazine. (b) View from the top of the rotational axis of the pyrazine. (c) Packing diagram.

### Variable-temperature solid-state $^2$H NMR spin-echo study

To explore the molecular dynamics of the central pyrazine and included THF molecules, we carried out variable-temperature solid-state $^2$H NMR spin-echo measurements of **1**-$d_4$-2(THF) and **1**-2(THF-$d_8$), respectively, and explored the site-exchange dynamics using broad-line shape simulations. This method is a well-established technique for deuterium-enriched moieties with varying exchange rates and rotational trajectories.[1–8,28]

Measurements of **1**-$d_4$-2(THF) revealed that the central pyrazine exhibit 180° of a 2-fold rotation in the MHz time scale in the temperature range of 243–300 K (Figure 3a). Figure 3b shows the experimentally obtained spectra measured in the 193–300 K temperature range. Well-matching simulated spectra were obtained using a quadrupolar coupling constant (QCC) of 176 kHz and a cone angle of 60° formed between the rotational 1,4-axis and the C–D bond vector with a 2-fold 180° Brownian jumping model (Figure 3a). The frequency $k_{rot.}$ of the 2-fold rotation at 300 K was 6.0 MHz, and spectra measured at 283, 273, 243, and 193 K were simulated by the same 2-fold rotation model with a $k_{rot}$ of 2.0 MHz, 1.0 MHz, 0.3 MHz, and <10 kHz, respectively (Figure 3b). As shown in Figure 3c, the Arrhenius plot constructed from the $k_{rot}$ of **1**-$d_4$-2(THF) revealed that the central pyrazine has a rotation barrier ($E_a$) of ca. 31 kJ mol$^{-1}$ and a pre-exponential factor ($A$) of 1.1 × 10$^{12}$ s$^{-1}$. The $E_a$ of crystalline rotor **1**-$d_4$-2(THF) was similar with that of crystal **1**-$d_4$ (32 kJ mol$^{-1}$).[26] By applying the Eyring plot, we can extract the entropy change during the rotational motion. As shown in Figure 3d, the pyrazine rotor showed a negative value of –22 J mol$^{-1}$ K$^{-1}$ which is smaller magnitude than that of the reported crystalline rotors occurring correlated motions.[19,29] In addition, a rotational frequency at infinite temperature $k_o$ of the pyrazine was 1.1 x 10$^{12}$ Hz that is slightly lower than that expected from the inertial mass of the rotator (ca. 4 x 10$^{12}$ Hz). These indicates that the pyrazine rotator may operates partially cooperative motion with the neighboring THF molecules.

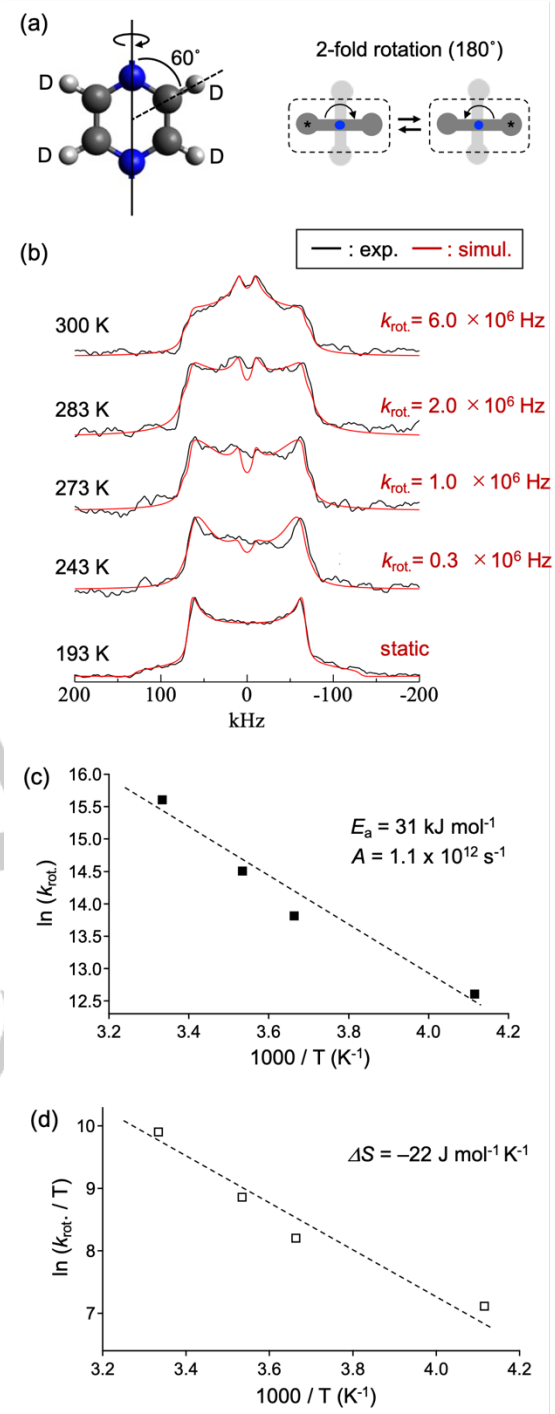



**Figure 3.** Variable-temperature solid-state $^2$H NMR study of **1**-$d_4$-2(THF). (a) Illustration of the 180° of 2-fold site-exchange rotation model for the central pyrazine. (b) Experimental (black) and simulated (red) spectra of crystal **1**-$d_4$-2(THF). (c) Arrhenius plot with evaluated energy barrier ($E_a$) and pre-exponential factor ($A$) of the rotation of the pyrazine. (d) Eyring plot with evaluated the change of entropy for the pyrazine rotation.

On the other hand, the THF molecules near the central pyrazine showed librational motion with faster site exchange than the 2-fold rotation of the pyrazine, which was elucidated by variable-temperature solid-state $^2$H NMR spin-echo measurements of **1**-2(THF-$d_8$). The measurements were performed in the 123–295 K temperature range, and the

simulation spectra were only successfully obtained for temperatures below 223 K owing to the fast motion of THF, which is out of the time scale range of the $^2$H NMR measurement (Figure 4a–b). The simulation was conducted using a QCC of 170 kHz, and a combination of two cone angles of 55° and 68° formed between the axis centered from the oxygen atom and the two C–D bond vectors (C–D1 and C–D2, respectively) with some angle Φ of libration from the axis (Figure 4a). The spectrum obtained at 223 K matched the simulation for a libration of 38° and a $k_{lib.}$ of $2.0 \times 10^7$ Hz (Figure 4b). Lowering the temperature to 213, 193, 183, 158, and 123 K decreased $k_{lib.}$ for the libration exchange to $6.0 \times 10^6$, $5.0 \times 10^6$, $2.0 \times 10^6$, $7.0 \times 10^5$, and $3.0 \times 10^4$ Hz, respectively (Figure 4b). The Arrhenius plot constructed from the $k_{lib.}$ of THF-$d_8$ indicated that the $E_a$ for the modeled rotation was 14 kJ mol$^{-1}$ with $A = 2.4 \times 10^{10}$ s$^{-1}$ of (Figure 4c). This suggests that the THF molecule has a lower energy barrier to rotation than that of the pyrazine rotator. In addition, we noted that the libration angle Φ decreased from 38° to 23° as the temperature was lowered. The entropy change of the libration of THF molecule was –49 J mol$^{-1}$ K$^{-1}$, evaluated by the Eyring plot, indicating that the THF libration occurred in cooperative manner with the neighboring pyrazine rotator (Figure 4d).

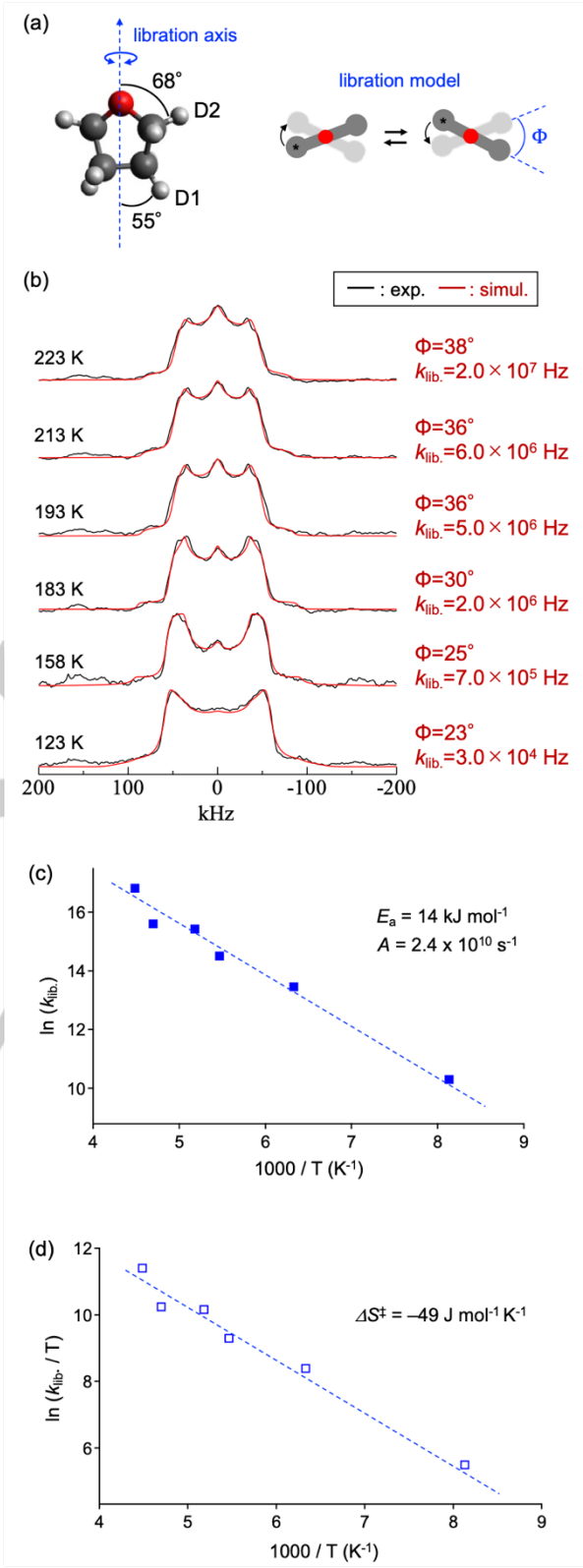



**Figure 4.** Variable-temperature solid-state $^2$H NMR study of **1**-2(THF-$d_8$). (a) Illustration of the libration model for the THF molecule. (b) Experimental (black) and simulated (red) spectra of **1**-2(THF-$d_8$). (c) Arrhenius plot with evaluated energy barrier ($E_a$) and pre-exponential factor ($A$) of the libration of the THF molecule. (d) Eyring plot evaluated the change of entropy for the THF motion.

From the observed rotational motions of the central pyrazine and THF molecules, we know that the large liberational motion with fast dynamics of THF molecules allows pyrazine to rotate at 180° with fast site exchange. As depicted in Figure 5, pyrazine showed static motion at 193 K, while THF located near pyrazine rotated with 23° libration from the axis. On the other hand, pyrazine started to exhibit a 180° 2-fold rotation with a MHz timescale of $k_{rot.}$ when THF showed a larger libration with fast site exchange with increasing temperature (Figure 5). From our previous work, we noted that the pyrazine in crystal **1**-$d_4$, including no THF molecules, showed less than 10 kHz of rotation at 225 K, indicating that the 180° flipping motion barely occurred.[26] This suggest that the central pyrazine in crystal **1**-$d_4$-2(THF), including THF molecules, could clearly rotate at 180° when the nearly located THF molecules undergo a fast large-angle libration, affording local space that allows for the pyrazine rotation. Furthermore, the pyrazine 2-fold rotation occurred in a cooperative manner with the fast libration of neighboring the THF molecules. The observed calorimetric phenomena by DSC measurement during the heating sample suggest that the small exo- and endothermic process may occur by the motion manner alternation and the increasing movement speed, respectively.

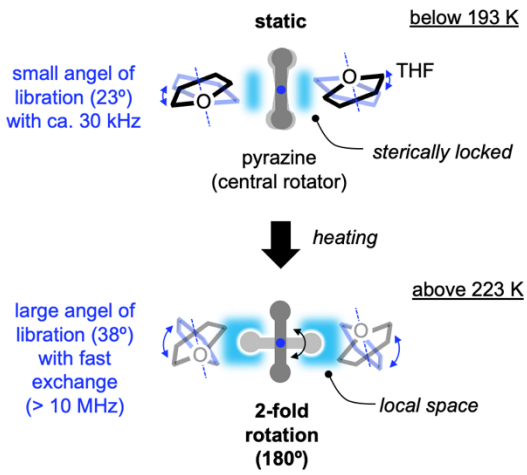



**Figure 5.** Illustration of the observed multiple rotational motions of the central pyrazine and THF molecules at different temperatures.

## Conclusion

Herein, we reported a new multi-dynamic crystalline molecular rotor that bears pyrazine and THF molecules as distinct rotators encapsulated by two bulky NHC Au(I) complexes. The motion of the central pyrazine and two THF molecules are characterized by 180° of a 2-fold rotation with MHz site exchange and libration, respectively. In particular, the larger libration motion of THF with fast exchange allows pyrazine to rotate 180° with fast dynamics. The results of this study suggest that the encapsulation design utilizing a concave-shaped bulky NHC metal complex can lead to the realization of multicomponent rotators in crystals toward the development of multi-functional solid-state materials originating from multi-dynamic molecular motions.

## Acknowledgements

This work was financially supported by the Japan Society for the Promotion of Science (JSPS) via KAKENHI grants JP17H06370, JP20H04666, JP21K14637, JP22K18333 and JP22H00318; by the JST via CREST grant JPMJCR19R1; and by the Institute for Chemical Reaction Design and Discovery (ICReDD) established by the World Premier International Research Initiative (WPI), MEXT, Japan.

**Keywords:** Crystalline molecular rotor · NHC metal complex · Multicomponent crystal · Correlated motion · Molecular dynamics

[1] a) S. Erbas-Cakmak, D. A. Leigh, C. T. McTernan, A. L. Nussbaumer, *Chem. Rev.* **2015**, *115*, 10081–10206. b) R. Costil, M. Holzheimer, S. Crespi, N. A. Simeth, B. L. Feringa, *Chem. Rev.* **2021**, *121*, 13213–13237.

[2] C. S. Vogelsberg, M. A. Garcia-Garibay, *Chem. Soc. Rev.* **2012**, *41*, 1892–1910.

[3] T. A. V. Khoung, J. E. Nunez, C. E. Godinez, M. A. Garcia-Garibay, *Acc. Chem. Res.* **2006**, *39*, 413–422.

[4] L. Catalano, P. Naumov, *CrystEngComm.* **2018**, *20*, 5872.

[5] A. Comotti, S. Bracco, P. Sozzani, *Acc. Chem. Res.* **2016**, *49*, 1701–1710.

[6] A. Gonzalez-Nelson, F. X. Coudert, M. A. van der Veen, *Nanomaterials* **2019**, *9*, 330.

[7] J. Dong, V. Wee, S. B. Peh, D. Zhao, *Angew. Chemie - Int. Ed.* **2021**, *60*, 16279–16292.

[8] J. Dong, V. Wee, D. Zhao, *Nat. Mater.* **2022**, *21*, DOI 10.1038/s41563-022-01317-y.

[9] W. Setaka, K. Yamaguchi, *J. Am. Chem. Soc.* **2013**, *135*, 14560–14563.

[10] J. E. Nuñez, A. Natarajan, S. I. Khan, M. A. Garcia-Garibay, *Org. Lett.* **2007**, *9*, 3559–3561.

[11] G. M. Lang, T. Shima, L. Wang, K. J. Cluff, K. Skopek, F. Hampel, J. Blümel, J. A. Gladysz, *J. Am. Chem. Soc.* **2016**, *138*, 7649–7663.

[12] M. Jin, T. S. Chung, T. Seki, H. Ito, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2017**, *139*, 18115–18121.

[13] M. Jin, S. Yamamoto, T. Seki, H. Ito, M. A. Garcia-Garibay, *Angew. Chemie - Int. Ed.* **2019**, *58*, 18003–18010.

[14] A. Colin-Molina, M. J. Jellen, E. García-Quezada, M. E. Cifuentes-Quintal, F. Murillo, J. Barroso, S. Pérez-Estrada, R. A. Toscano, G. Merino, B. Rodríguez-Molina, *Chem. Sci.* **2019**, *10*, 4422–4429.

[15] A. Colin-Molina, M. J. Jellen, J. Rodríguez-Hernández, M. E. Cifuentes-Quintal, J. Barroso, R. A. Toscano, G. Merino, B. Rodríguez-Molina, *Chem. - A Eur. J.* **2020**, *26*, 11727–11733.

[16] E. C. Vargas-Olvera, F. J. Salas-Sánchez, A. Colin-Molina, S. Pérez-Estrada, B. Rodríguez-Molina, J. Alejandre, G. Campillo-Alvarado, L. R. MacGillivray, H. Höpfl, *Cryst. Growth Des.* **2022**, *22*, 570–584.

[17] P. Labra-Vázquez, M. E. Ochoa, L. A. Alfonso-Herrera, M. A. Vera, N. Farfán, R. Santillan, *Eur. J. Org. Chem.* **2022**, *38*, e202200351.

[18] A. Gonzalez-Nelson, S. Mula, M. Šimėnas, S. Balčiū Nas, A. R. Altenhof, C. S. Vojvodin, S. Canossa, J. R. Banys, R. W. Schurko, F. X. Coudert, M. A. Van Der Veen, *J. Am. Chem. Soc.* **2021**, *143*, 12053–12062.

[19] a) J. Perego, C. X. Bezuidenhout, S. Bracco, G. Prando, L. Marchiò, M. Negroni, P. Carretta, P. Sozzani, A. Comotti, *J. Am. Chem. Soc.* **2021**, *143*, 13082–13090. b) J. Perego, C. X. Bezuidenhout, S. Bracco, S. Piva, G. Prando, C. Aloisi, P. Carretta, J. Kaleta, T. P. Le, P. Sozzani, A. Daolio, A. Comotti, *Angew. Chem. Int. Ed.* **2023**, *62*, e202215893.

[20] L. Samperisi, A. Jaworski, G. Kaur, K. P. Lillerud, X. Zou, Z. Huang, *J. Am. Chem. Soc.* **2021**, *143*, 17947–17952.

[21] W. J. F. Trenholme, D. I. Kolokolov, M. Bound, S. P. Argent, J. A. Gould, J. Li, S. A. Barnett, A. J. Blake, A. G. Stepanov, E. Besley, T. L. Easun, S. Yang, M. Schröder, *J. Am. Chem. Soc.* **2021**, *143*, 3348–3358.

[22] A. Torres-Huerta, D. Galicia-Badillo, A. Aguilar-Granda, J. T. Bryant, F. J. Uribe-Romo, B. Rodríguez-Molina, *Chem. Sci.* **2020**, *11*, 11579–11583.

[23] J. Perego, S. Bracco, M. Negroni, C. X. Bezuidenhout, G. Prando, P. Carretta, A. Comotti, P. Sozzani, *Nat. Chem.* **2020**, *12*, 845–851.

[24] S. Bracco, M. Beretta, A. Cattaneo, A. Comotti, A. Falqui, K. Zhao, C. Rogers, P. Sozzani, *Angew. Chem. Int. Ed.* **2015**, *54*, 4773–4777.

[25] A. Colin-Molina, J. Arcudia, E. R. López-López, M. J. Jellen, M. C. García-González, G. Merino, B. Rodríguez-Molina, *Cryst. Growth Des.* **2022**, *22*, 673–680.

[26] M. Jin, R. Ando, M. J. Jellen, M. A. Garcia-Garibay, H. Ito, *J. Am. Chem. Soc.* **2021**, *143*, 1144–1153.

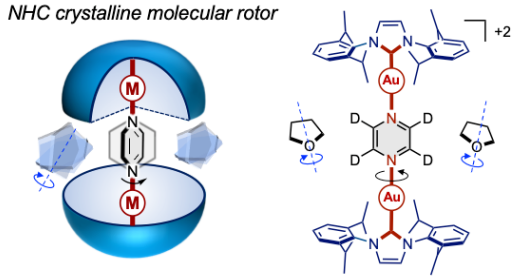
[27] Deposition Numbers 2225161 [for **1**-$d_4$-2(THF) at 295 K], 2237567 [for **1**-$d_4$-2(THF) at 273 K], 2237565 [for **1**-$d_4$-2(THF) at 260 K], 2237564 [for **1**-$d_4$-2(THF) at 230 K], 2237563 [for **1**-$d_4$-2(THF) at 200 K], 2225160 [for **1**-$d_4$-2(THF) at 123 K] contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

[28] V. Macho, L. Brombacher, H. W. Spiess, *Applied Magnetic Resonance The NMR-WEBLAB: An Internet Approach to NMR Lineshape Analysis*, **2001**.

[29] I. Liepuoniute, M. J. Jellen, M. A. Garcia-Garibay, *Chem. Sci.* **2020**, *11*, 12994–13007.

WILEY-VCH

## Entry for the Table of Contents




***Multi-component rotators*** encapsulated by NHC ligand

Herein, we report novel multi-rotational solid-state dynamics utilizing a crystalline molecular rotor bearing multicomponent rotators encapsulated by a concave-shaped NHC Au(I) complex. The motion of the central pyrazine and neighboring THF molecules are characterized, and it is observed that a larger libration of THF with fast exchange allows pyrazine to undergo 180° of 2-fold rotation.

Institute and/or researcher Twitter usernames: @MingooJin, @haj19932469, @ICReDDconnect

WILEY-VCH

## Author biographies

**Prof. Dr. Mingoo Jin**

Mingoo Jin was born in 1989 in Suwon (South Korea). He got a Ph.D. under supervision from Professor Hajime Ito from Hokkaido University in 2018. After his graduation, he joined as a postdoctoral researcher in Professor Miguel A. Garcia-Garibay Laboratory the University of California Los Angeles. In 2019, he started his academic career as a specially appointed assistant professor at WPI-ICReDD, Hokkaido University, and got a promotion to Associate Professor (Junior PI) at the same institute in 2022. His research has been focused on developing a novel platform for crystalline molecular rotors & gears with functional properties. His research interests are Organometallic Chemistry, Coordination Chemistry, Polymer Chemistry, Computational Chemistry and Luminescent Solid-State Materials.

WILEY-VCH