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Ph.D. Thesis

**Development of Functional Crystalline
Materials Based on NHC Metal Complexes**

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Graduated School of Chemical Science and Engineering

Organoelement Laboratory

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Chapter 1.

General Introduction

1.1 Crystalline Molecular Materials

Crystalline molecular materials are a class of substances in which molecules are arranged in a well-ordered, periodic structure, forming a crystalline lattice. These materials exhibit unique physicochemical properties due to their highly organized molecular structures, making them invaluable for various applications in electronics^{1,2}, optics³, and pharmaceuticals⁴. A key category of crystalline molecular materials is organic molecular crystals, which are composed of purely organic molecules that self-assemble into a crystalline structure. These materials have garnered attention in organic electronics due to their potential use in organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic photovoltaics (OPVs). Notable examples include pentacene⁵ and fullerene-based crystals⁶, which exhibit high charge carrier mobility and are widely used in flexible electronic devices. For instance, in the field of organic electronics, a variety of organic light-emitting diode (OLED) materials rely on the precise control of molecular packing within the crystal¹. Another significant class of crystalline molecular materials is hybrid materials such as metal-organic frameworks (MOFs)⁷⁻⁹ and perovskite crystals¹⁰. MOFs consist of metal ions coordinated with organic ligands, forming highly porous crystalline structures that are ideal for gas adsorption, separation, and catalysis. Similarly, perovskite materials, such as methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), have revolutionized the field of photovoltaics due to their exceptional light-harvesting efficiency and ease of fabrication.

The orderly arrangement of molecules is known to improve charge transport, thereby enhancing overall emission efficiency and extending device lifetimes. Researchers have demonstrated that minor changes in molecular conformation and arrangement can bring about remarkable differences in optoelectronic performance, underscoring the importance of crystal engineering at the molecular level. The ability to design and synthesize molecular structures with specific electronic properties allows for the development of next-generation semiconducting materials that combine mechanical flexibility with excellent charge transport characteristics. Meanwhile, in the pharmaceutical industry, crystalline polymorphism has been an object of intense study⁴. Different polymorphs of the same drug molecule can display distinct solubilities and stabilities, drastically affecting bioavailability and shelf life. A classic example is found in certain widely used pharmaceutical agents, where a single compound can crystallize into multiple polymorphs with substantially different dissolution rates. Such polymorphism poses a challenge for patent rights and regulatory approval, prompting researchers to pursue new strategies for systematically controlling crystal forms and ensuring that the most favorable polymorph is obtained and maintained.

One of the fundamental characteristics of crystalline molecular materials is their ability to form well-defined structures through intermolecular interactions such as hydrogen bonding, van der Waals forces, and π - π stacking. These interactions determine the packing of molecules within the crystal lattice, influencing properties such as electrical conductivity, optical response, and thermal stability. Unlike amorphous materials, where molecular arrangement lacks long-range order, crystalline molecular materials benefit from predictable and tunable properties that can be engineered through molecular design and crystal engineering. Over the years, several strategies have been developed to control and design both the molecular conformation and the packing arrangement in crystalline materials¹¹⁻¹³. One commonly employed method is to manipulate crystallization conditions to create or select specific polymorphs. By systematically varying factors such as temperature, solvent type, concentration, and rate of cooling or evaporation, researchers can often direct the crystallization pathway toward a desired polymorph. This approach has been widely used in both academic and industrial settings, particularly for high-value materials such as active pharmaceutical ingredients (APIs).

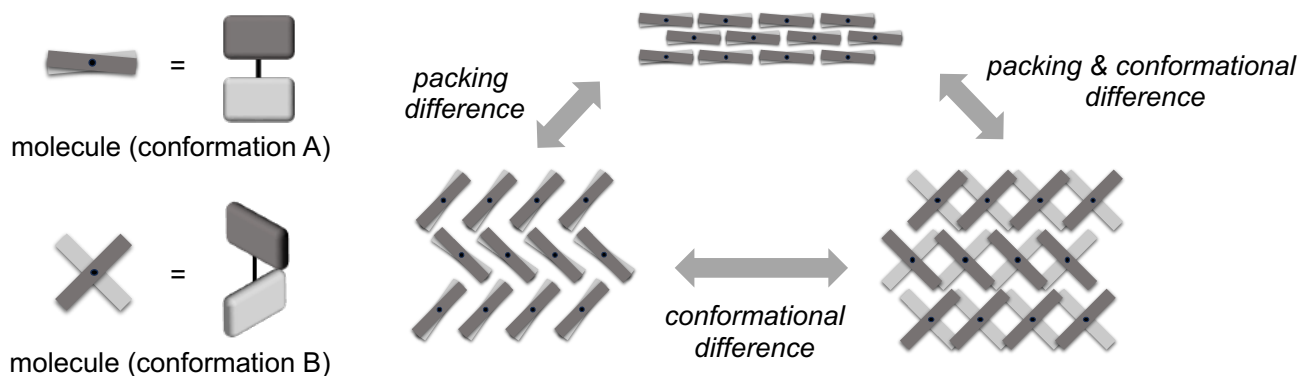


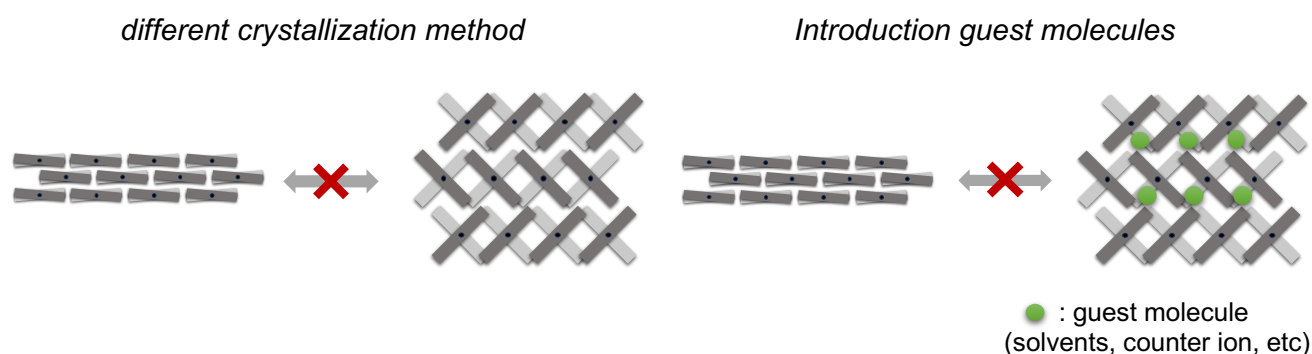
Figure 1-1. Schematic image for crystal packing and molecular conformational differences.

Another exciting research direction lies in phase-transition materials. These substances can undergo changes in their crystalline phases in response to external stimuli such as light, temperature, or pressure. By controlling molecular conformation in the crystal, it becomes possible to optimize quantum efficiencies and achieve high-performance light-emitting devices. Such phase transitions can also lead to interesting phenomena such as color changes, switching behaviors, or variations in mechanical properties, which hold promise for advanced sensing and display technologies.

Despite these advancements, a core challenge remains: in many crystal engineering approaches, changes in molecular conformation and crystal packing often occur simultaneously. When crystallization

conditions are modified or when guests are introduced into the lattice, both conformation and packing arrangement can shift in ways that are not always easily predicted or controlled. Distinguishing the individual contributions of conformation versus arrangement to the overall material properties thus becomes difficult.

- Polymorph design



- Phase transition



Figure 1-2. Schematic example for conformational design of crystal.

This conflation of structural factors is particularly problematic when attempting to establish clear structure–property relationships. For example, an apparent improvement in the photoluminescence efficiency of a newly formed polymorph could be attributed to a more favorable molecular conformation, a tighter molecular packing, or an interplay of both. Unless these factors can be decoupled experimentally, drawing definitive conclusions about the sole effect of conformation can be misleading. In cases where the goal is to purely isolate conformational effects, it may be necessary to employ more refined synthetic techniques or to design molecules with intrinsic rigidity and limited degrees of freedom, thus minimizing potential packing differences.

1.2 Amphidynamic crystals

Molecular crystals are highly ordered three-dimensional assemblies of molecules held together by relatively weak non-bonding interactions. Typically, these crystals adopt close-packed structures that minimize empty space, consequently restricting the degrees of freedom of individual molecules within the crystal lattice. To gain insight into molecular freedom in the assembled phase, it is useful to examine the relationship between molecular motion and long-range phase order¹⁴. This correlation can be visualized in a conceptual diagram (Figure 1-3), where the vertical axis represents phase order, and the horizontal axis represents molecular motion. In this framework, the liquid phase is positioned in the lower right corner of the plot, as it exhibits minimal long-range order. In liquids, molecules undergo rapid, unrestricted rotational motion, resulting in a homogeneous structure when averaged over time. Conversely, molecular crystals, found in the upper left corner of the plot, are characterized by their rigidity, periodicity, and macroscopic anisotropy. These structures maintain long-range order, with molecular motion largely restricted to small-amplitude displacements associated with lattice vibrations. Building on this concept, intermediate phases such as plastic crystals and liquid crystals can be positioned within the plot, reflecting their distinct balance between molecular motion and structural order. The molecular structure plays a crucial role in determining the formation, properties, and dynamics of plastic and liquid crystals. This observation suggests that appropriate molecular designs can lead to the formation of a highly ordered, rigid lattice while simultaneously supporting the rapid motion of specifically designed molecular components. In this context, certain crystals, positioned in the upper right corner of the conceptual plot, exhibit a unique combination of structural rigidity and localized molecular mobility. While some molecular components remain fixed in specific lattice positions, others undergo rapid motion. This distinctive phase, characterized by the coexistence of a rigid ordered framework and highly mobile molecular components, has been termed an "amphidynamic crystal."¹⁴⁻²² This emerging class of solid-phase materials presents exciting opportunities in materials science, offering potential applications that leverage both structural order and dynamic molecular behavior.

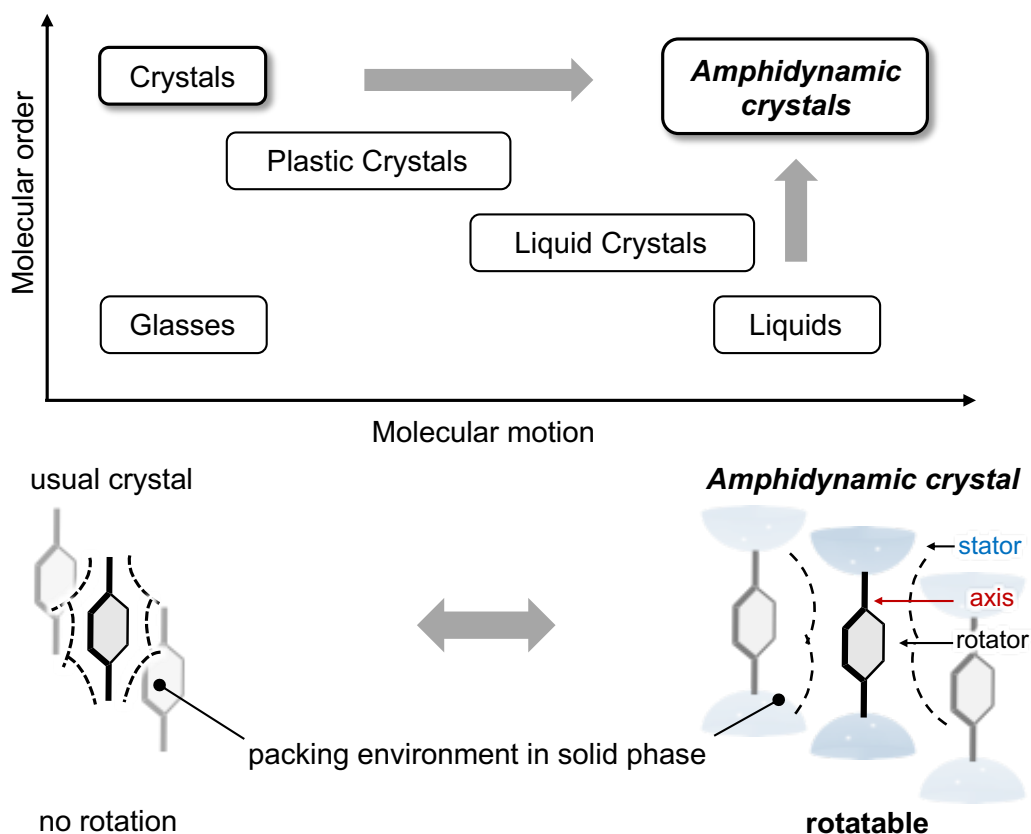


Figure 1-3. Plot of phase order versus molecular motion with schematic representation of each assembly phase.

When investigate these types of the crystals, we can have precise crystal structure information from single crystal XRDs. However, the result from the single crystal XRD analysis give no direct information for molecular dynamics in the crystal. Thus, coupling of complementary techniques that span much wider range of frequencies, such as variable-temperature solid-state NMR (CP-MAS, wide-line analysis of ^2H spin echo and T_1 spin-lattice relaxation) can provide access to the amplitude and frequency of motion, as well as the energy of activation of the dynamic process within the crystal lattice. For the construction of amphidynamic crystals, the components working as static frames designed to support the dynamic portions of the system should be needed. Highly mobile components, defined as rotator, may be isolated from each other, and may have free volume around itself within the crystal lattice. The stator should connect to the rotators through suitable axes that support their rotary motion, or through pivots that support an oscillatory movement. Based on this idea, several molecular or material

designs for constructing the amphidynamic crystals have been reported such as macroscopic gyroscopes²⁰, metal-organic frameworks (MOFs)^{15,17}, and Cocrystal^{23,24}. (figure 1-4) Focusing on molecular crystals, macroscopic gyroscopes, possessing rotator, axel, and stator, have provided the promising designs for the realization of amphidynamic crystals. In particular, Garcia-Garibay M.A. and co-workers have revealed that dumbbell-shaped molecules designed for having gyroscope properties could form many types of amphidynamic crystals.

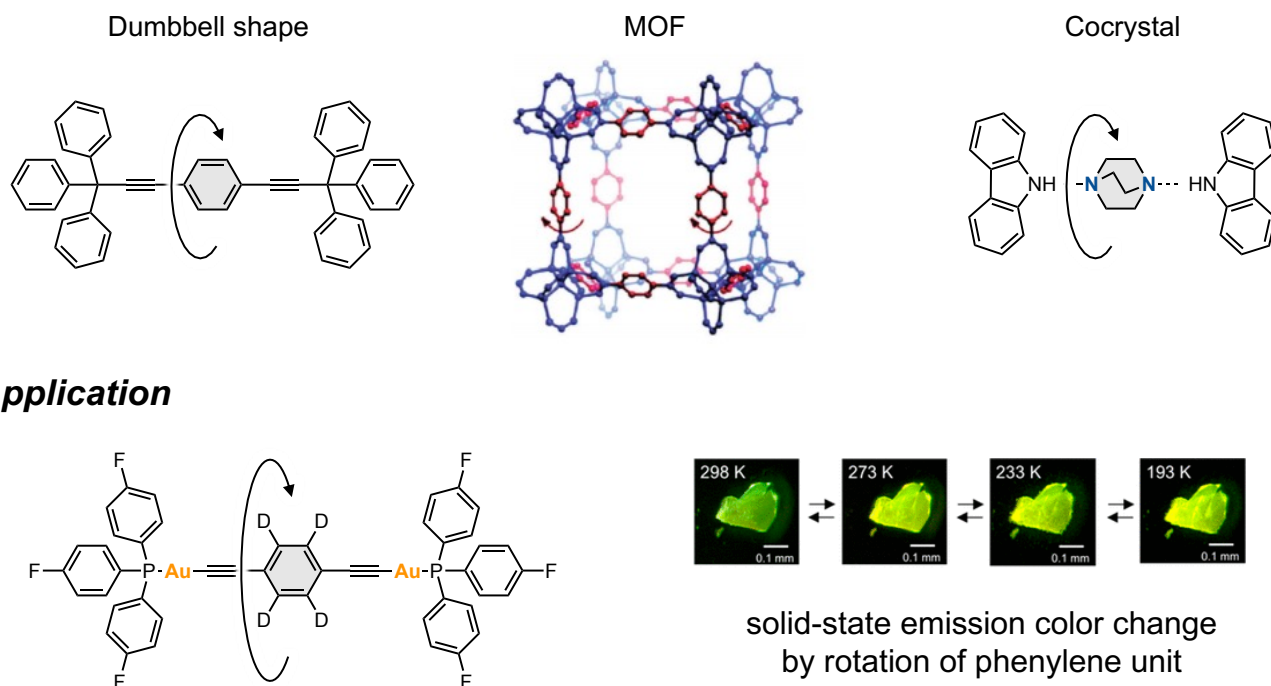


Figure 1-4. Several examples of amphidynamic crystals possessing functional properties.

Several functions in solid phase taking advantage of amphidynamic crystals have been reported¹⁶. For instance, amphidynamic crystals from Au(I) complex exhibit the phosphorescence color change by the result of changes in the rotational motion of phenylene.²⁵

1.3 NHC metal complex

Carbenes, defined as neutral compounds containing a divalent carbon atom with a six-electron valence shell, are a fascinating class of carbon-containing compounds. Their unique electronic structure and incomplete electron octet make them highly reactive and inherently unstable, traditionally classifying free carbenes as transient intermediates in organic reactions such as cyclopropanation. Attempts to synthesize free carbenes date back to 1835²⁶, but their isolation and characterization remained elusive until groundbreaking work in the late 20th century.²⁷ In 1988, Bertrand and colleagues synthesized the first isolable carbene stabilized by adjacent phosphorus and silicon substituents.²⁸ Three years later, Arduengo and coworkers introduced the first isolable, "bottleable" carbene, 1,3-di(adamantyl)imidazol-2-ylidene (IAd), marking the discovery of the first N-heterocyclic carbene (NHC).²⁹

N-heterocyclic carbene (NHC)

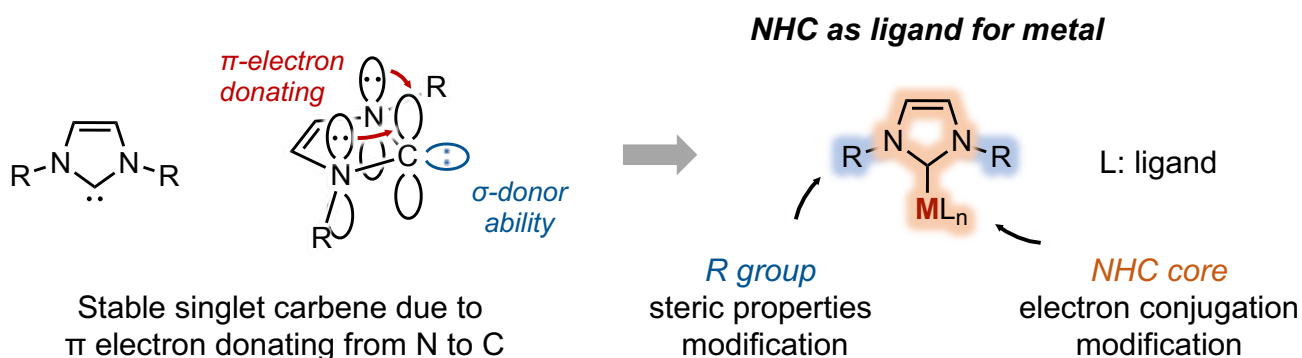
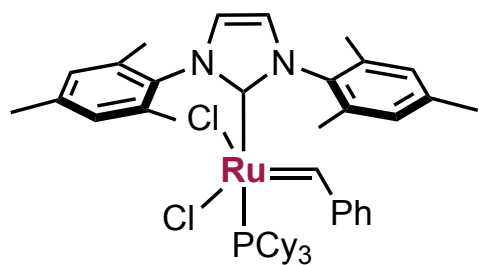


Figure 1-5. Structure of NHC and NHC metal complex.

NHCs are heterocyclic species containing a carbene carbon and at least one nitrogen atom within the ring structure. Their stability arises from both steric and electronic effects. Bulky substituents adjacent to the carbene carbon, such as adamantyl or mesityl groups, sterically inhibit dimerization to the corresponding olefin. Electronic stabilization is provided by nitrogen atoms that inductively lower the energy of the carbene's σ -orbital and mesomerically donate electron density into the vacant p-orbital. This stabilization shifts the electronic ground state to a singlet configuration, distinguishing NHCs from other carbenes.

The steric and electronic properties of NHCs can be fine-tuned by altering the substituents on the nitrogen atoms or the ring backbone. For example, the simple NHC 1,3-dimethylimidazol-2-ylidene (IMe) is stable in solution due to its partial aromaticity, despite having less steric bulk compared to IAd. This tunability has enabled the development of NHCs with specific properties for targeted applications.

· **Organometallic catalyst**



· **Luminescent material for OLED**

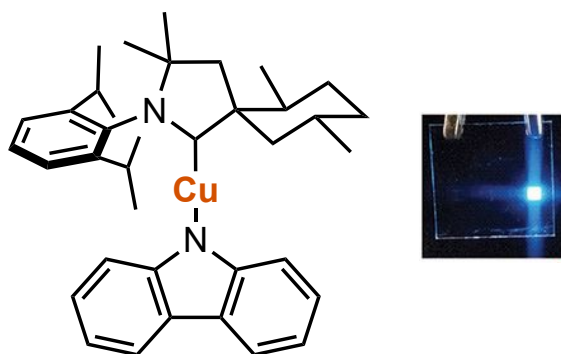
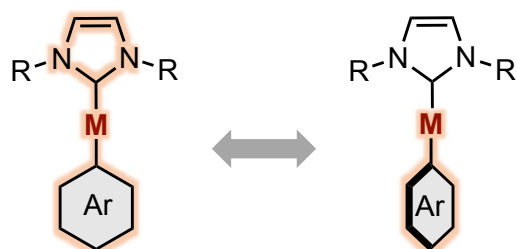


Figure 1-6. Example for NHC metal complex.

The unique stability and straightforward synthesis of NHCs inspired a surge in experimental and theoretical research. NHCs have transitioned from laboratory curiosities to pivotal compounds with broad practical applications. The suitability of NHCs as ligands for transition metals can be rationalized by their inherent σ -donor ability with a formal sp^2 -hybridized lone pair available for donation into a σ -accepting orbital of the transition metal.³⁰ Their exceptional ability to act as ligands for transition metals has made them indispensable in catalysis³¹, with significant contributions to industrial processes such as cross-coupling reactions³², olefin metathesis³³, and hydrogenation. Additionally, NHCs have opened new frontiers in material chemistry^{34,35,36,37}. Especially, NHC metal complexes have attracted significant attention due to their remarkable photophysical properties, including high quantum yields, tunable emission wavelengths, and excellent stability.^{35,37} These characteristics make them promising candidates for applications in organic light-emitting diodes (OLEDs), bioimaging, and photocatalysis. The strong σ -donating and weak π -accepting nature of NHC ligands significantly influence the electronic structure of metal complexes, leading to enhanced metal-ligand interactions. This often results in improved photoluminescence efficiency and longer excited-state lifetimes. Moreover, the rigid nature of NHC ligands reduces non-radiative decay pathways, thereby enhancing emission intensity. Various transition metals, including Ir(III)³⁸, Pt(II)^{39,40}, Cu(I)^{41,42} and Au(I)⁴³, have been explored in NHC-based complexes to achieve diverse emission characteristics. Ir(III) NHC complexes, for instance, exhibit high phosphorescence quantum yields due to efficient spin-orbit coupling. Pt(II) complexes demonstrate strong phosphorescence with distinct color tunability, while Cu(I) or Au(I) complexes have drawn interest for their unique thermally activated delayed fluorescence (TADF) properties. By fine-tuning the

ligand structure and metal center, researchers continue to develop NHC metal complexes with superior emission properties, expanding their potential in advanced optoelectronic and photofunctional materials.

· *NHC metal aryl complex*



example

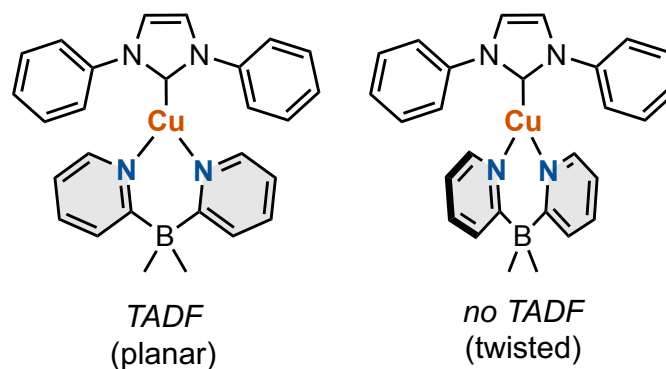


Figure 1-7. NHC metal aryl complex and example for different photophysical properties related to dihedral angle.

The photoluminescence properties of NHC aryl metal complexes are significantly influenced by their molecular conformation, which governs electronic interactions, excited-state dynamics, and emission efficiency. The rigidity and spatial arrangement of the aryl substituents, as well as the overall molecular geometry, play a crucial role in determining emission characteristics. In these complexes, the conformation of the aryl group affects intramolecular charge transfer and π -conjugation. (figure 1-7) A coplanar arrangement between the NHC ligand and the aryl moiety enhances π -electron delocalization, leading to red-shifted emission and higher quantum yields. Conversely, steric hindrance or twisting of the aryl group can reduce electronic communication, resulting in blue-shifted emission and lower luminescence efficiency. Furthermore, the conformational flexibility of the complex impacts non-radiative decay pathways. A rigid molecular structure suppresses vibrational relaxation and internal conversion, thereby prolonging excited-state lifetimes and improving phosphorescence efficiency. On the other hand, increased conformational freedom can introduce additional relaxation channels, leading to emission quenching. For instance, Hartmut Yasin and coworkers reported that these dihedral angle change is crucial for the TADF.⁴⁴

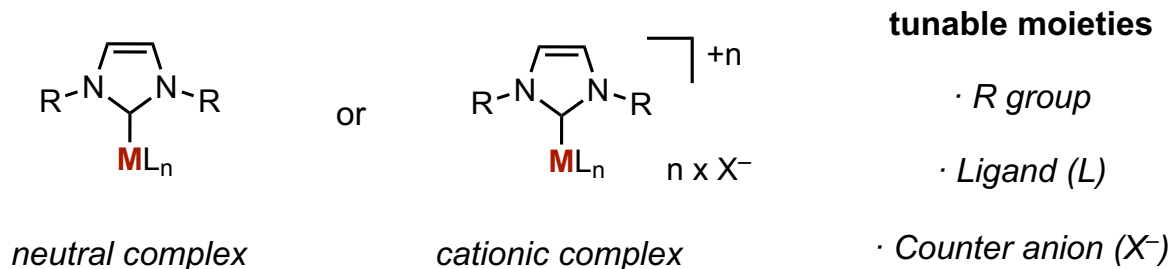


Figure 1-8. NHC metal complex as good molecular units for crystal design.

NHC metal complexes offer significant advantages as crystalline materials due to their tunable structural and electronic properties. (Figure 1-8) By modifying R groups, ligands, and counter anions, these complexes can be systematically designed to control crystal packing and molecular conformation, enabling the precise tailoring of material properties. Substituent modifications on the NHC ligand influence steric and electronic effects, allowing fine-tuning of intermolecular interactions such as π - π stacking, hydrogen bonding, and van der Waals forces. This facilitates the engineering of crystal packing arrangements, optimizing properties like mechanical robustness, porosity, and optical behavior.

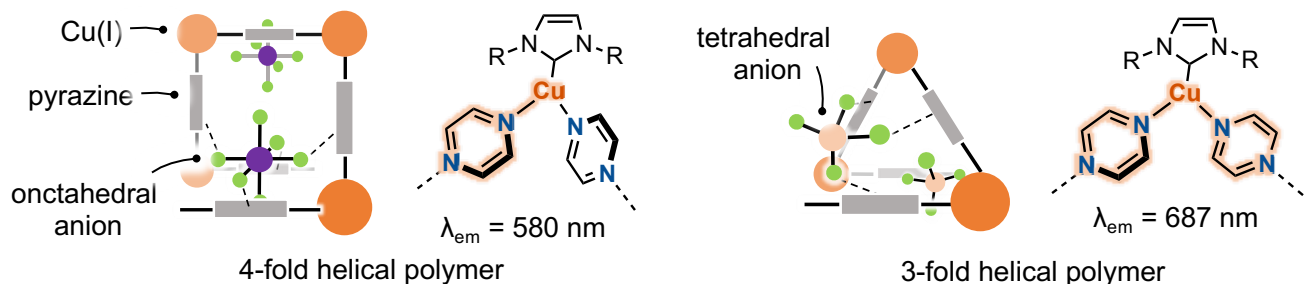
The choice of coordinating ligands affects the molecular geometry and rigidity of the complex, which in turn dictates its conformational preferences in the solid state. For example, rigid ligands can enforce specific molecular alignments, enhancing anisotropic interactions and leading to ordered supramolecular architectures. Counter anions also play a crucial role in crystal design by modulating electrostatic interactions and influencing the overall packing motif. Large or flexible anions can introduce voids or channels within the crystal structure, whereas small, rigid anions may lead to denser packing with enhanced stability. By strategically designing these molecular components, NHC metal complexes can be tailored for advanced crystalline materials with desirable properties, such as tunable luminescence, conductivity, or catalytic activity, broadening their potential applications in functional materials and optoelectronics.

1.4 Overview

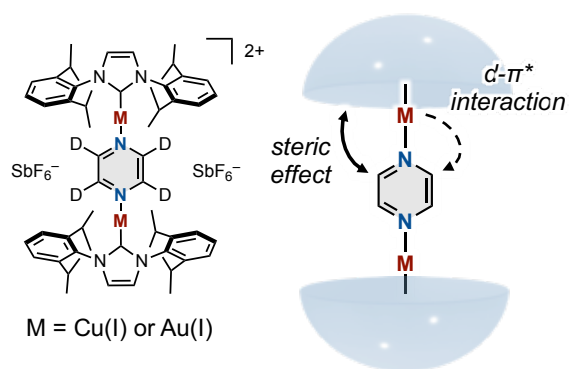
In this Ph.D. studies, the wide molecular design capability and the steric and electronic properties of NHC ligands were utilized to rationally design molecular conformations in crystals and investigate the solid-state optical properties arising from these conformations. This dissertation consists of seven chapters, with Chapter 1 covering the research background and Chapters 2 to 4 presenting the research findings. In Chapter 2, the helical structures and changes in solid-state luminescence properties of cationic coordination polymers consisting of NHC copper(I) complexes and pyrazine in crystals were discussed. It was revealed that the helical structures of cationic coordination polymers composed of NHC copper(I) complexes and pyrazine vary depending on the type of counteranion. Octahedral-type SbF_6^- and PF_6^- counteranions formed quadruple helices (crystals **1** and **2**), whereas tetrahedral-type BF_4^- counteranions formed triple helices (crystal **3**). The differences in helical structure resulted in a redshift of the emission wavelength from 580 nm (crystals **1** and **2**) to 687 nm (crystal **3**). Chapter 3 describes the synthesis of cationic complexes composed of NHC copper(I) or gold(I) complexes, pyrazine, and SbF_6^- , and the investigation of molecular rotational motion of pyrazine and solid-state luminescence properties within crystals. Complexes **4** and **5** were synthesized using Au(I) or Cu(I), and the activation energy for pyrazine rotation was successfully designed. Single-crystal X-ray structure analysis revealed that both complexes had similar structures. Variable-temperature solid-state ^2H NMR measurements confirmed 180° rotational motion of pyrazine, and the activation energy for rotation was lower for Cu(I) complex **4** than for Au(I) complex **5**. Computational studies suggested that the difference in activation energy between complexes **4** and **5** was due to destabilization caused by steric repulsion between pyrazine and NHC in the transition state and stabilization due to π -back donation between pyrazine and the metal. Furthermore, UV-irradiated crystals of complexes **4** and **5** exhibited orange and blue luminescence, respectively, with a decrease in luminescence intensity from low to high temperatures. Chapter 4 describes the molecular rotational motion of molecules with large rotational diameters within crystals, using bulkier NHC ligands compared to those used in Chapters 2 and 3. NHC gold(I) complexes were used to investigate the rotational motion of giant rotators (tritycene **6** and pentitrycene **7**) within crystals. Pentitrycene has a rotational diameter of 13.0 Å, about 3.0 Å larger than tritycene, making it the largest rotational site in amphidynamic crystals to date. Single-crystal X-ray structure analysis revealed that bulky NHC ligands allowed the formation of crystal structures with rotatable rotators. Variable-temperature solid-state ^2H NMR measurements evaluated the molecular motion in crystals **6**

and 7, showing clear spectral changes corresponding to triptycene's threefold rotational motion in crystal 6 and similar spectral changes for pentiptycene's molecular motion in crystal 7.

Chapter 2: different fold-mode of helical polymer and emission



Chapter 3: tuning the rotational barrier



Chapter 4 : largest rotator

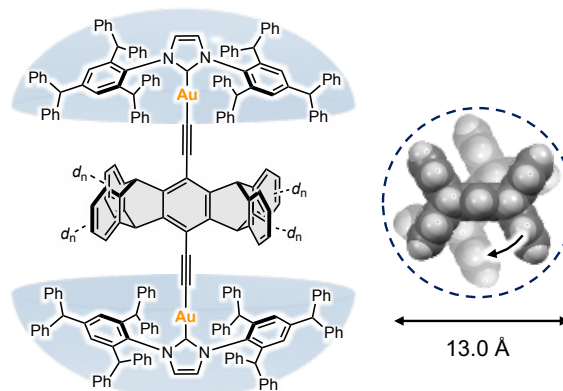


Figure 1-9. Overview of my Ph.D. studies.

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Chapter 2.

Tuning Fold-Mode Formation of Crystalline Cu(I) Helical Coordination Polymers and the Solid-State Emission Using Shape of the Counter Anions

2.1 Introduction

Helical polymer structure is a basic motif often found in nature^{1,2,3}, and it can be a key structure for implementing various functions in polymeric materials in both solution and solid state.^{4,5,6} Their structures can be controlled by their molecular structures as well as environmental factors around the helical polymers.^{4,5,6} An interesting property of natural helical materials is that the helical structure can be drastically changed by external factors. For example, DNA chains in cells can build several helical structures known as A-, B-, and Z-DNA, which have distinct helicity or degree of coiling corresponding to different enzymatic properties.⁷ However, in general, rational control of the structure of helical polymeric materials in artificial systems remains a challenge.

One-dimensional (1D) cationic coordination polymers constructed by infinitely coordinated metal complexes have been a promising scaffold to provide various helical shapes in solid-state through the structural flexibility.^{8,9,10} In particular, the included counter anions can modulate the structural factors of helicity in the solid-state.¹⁰ As a pioneering example, Puddephatt *et al.* reported the first structural characterization of a cationic Au(I) helical coordination polymer with a heterotactic architecture, and that the tacticity of the polymer was altered through a simple change in the included anions in the crystals.¹¹ Mak and co-workers *et al.* reported that the pitch length of a series of Ag(I) helical coordination polymers in the solid state can be modulated by changing the size of counter anions.¹² Although there are several examples of solid-state coordination polymers in which the helical structures depend on the anion moiety, it is still challenging to accomplish the solid-state functional properties, such as photo-luminescence, by altering the helical structure.^{13,14} Design of solid state emissions of molecular crystals have been approached by the molecular conformation or arrangement control via polymorphism as well as using metal-metal or ion-ion interactions.^{15,16,17} I envisioned that the combination between the emission properties of Cu(I) complexes, which are highly affected by the coordination geometry^{18,19}, and the structural modulation of helical coordination polymers would provide a novel strategy to design solid-state emission.

In this study, I investigated a formation of various fold-mode of cationic Cu(I) coordination polymers using the structural features of counter anions, which can determine the coordination geometry, following alteration of the solid-state emission. The Cu(I) coordination polymers were synthesized with *N*-heterocyclic carbene (NHC), pyrazine ligands, and octahedral anions (SbF₆ and PF₆) or tetrahedral anions BF₄ (Figure 2-1b). Interestingly, the coordination polymers formed a 4-fold helical column with a square in the vertical direction from the axis in red-emissive crystals when the octahedral anions (SbF₆

or PF_6) were included. However, a 3-fold helical columnar structure with a triangular planar on the vertical axis was constructed with the tetrahedral anion BF_4 (Figure 2-1c-d). The observed packing geometries near the counter anions suggest that the steric features of the interaction sites, such as octahedral or tetrahedral, can determine the folding mode of the coordination polymers in the solid-state. Consequently, the red emission near 580 nm by the 4-fold helical structure in the crystal was red-shifted to approximately 687 nm by forming the 3-fold helical structure. The coordination environment of the 3-fold mode produced densely packed pyrazines near the Cu(I) atom rather than in the 4-fold helical column, which may expand the p-conjugated domain, inducing a red-shifted emission in the crystals (Figure 2-1e). To the best of my knowledge, this is the first example of a luminescent solid-state helical coordination polymer in which the emission properties are correlated to the fold-mode determined by the shape of counter anions.

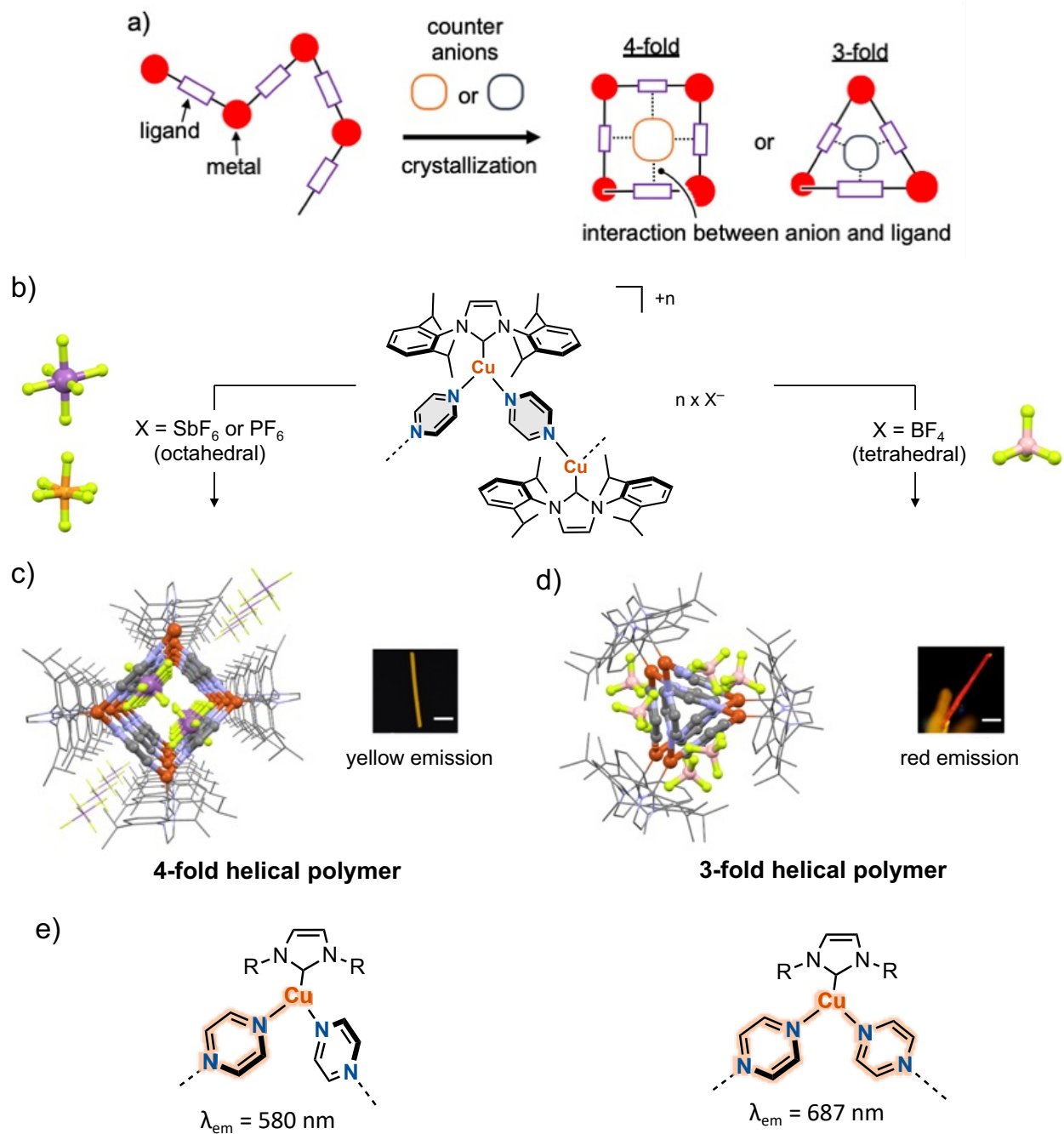
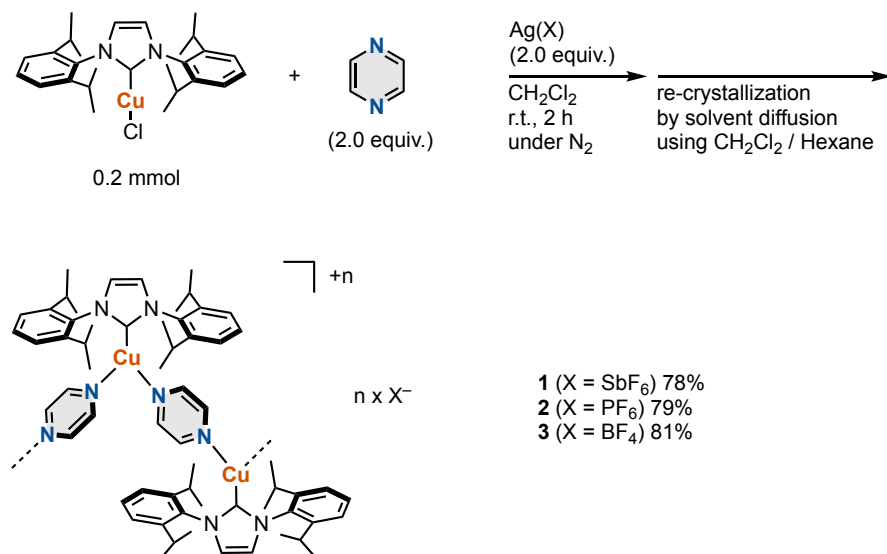


Figure 2-1. a) Representation of the fold-mode control of a coordination polymer using a distinct shape of counter anions. b) Prepared cationic NHC Cu(I) coordination polymers containing pyrazine and IPr-NHC ligands with three different counter anions (SbF_6 , PF_6 , and BF_4). Three-dimensional representations of the c) 4-folding helical columnar structure observed in crystals **1** and **2** and d) 3-folding helical column observed in crystal **3**. e) Schematic representation of the expected conjugation environment between 4-fold and 3-fold helical structures in the solid state, corresponding to the emission shift.

2.2 Result and Discussion

Synthesis and Preparations. Cationic NHC Cu(I) coordination polymers **1**, **2**, and **3** were obtained as crystalline solids through anion exchange in a CH₂Cl₂ solution from pyrazine, chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]Cu(I) [IPrCu(I)Cl], and three different Ag(I) salts (counter anions = SbF₆, PF₆, and BF₄), as shown in Scheme 1. Crystallization was performed through solvent diffusion using the CH₂Cl₂ solution of each compound with layered hexane, yielding needle-shaped yellow crystals. The crystals **1**, **2**, and **3** emitted orange or red light under ultraviolet (UV) light at ambient temperature. The crystalline samples were dissolved in CD₂Cl₂ solution and characterized through ¹H and ¹³C NMR spectroscopies.²⁰ Furthermore, characterization of the samples in the solid-state was conducted using thermogravimetric analysis (TGA) and single-crystal X-ray diffraction (XRD), indicating that CH₂Cl₂ solvents were included in all crystals (see Experimental Section, Figure 2-9).

Scheme 2-1. Synthesis of cationic NHC Cu(I)-coordination polymers.



Single-crystal XRD of **1, **2**, and **3**.** Single-crystal XRDs of the crystals **1**, **2**, and **3** revealed that the cationic NHC Cu(I) complexes formed an infinitely coordinated polymer in the solid state, as shown in Figures 2-2–2-4. In all the crystals, two pyrazines and the IPr-NHC ligand were coordinated to Cu(I) to form a trigonal-planar complex, and the pyrazines were linked to the Cu(I). The Cu(I) complexes **1** and **2** were crystallized in the space group *P2*₁/*c*, while the Cu(I) complex **3** was formed in the chiral space

group $P3_1$. Interestingly, the fold-mode of the coordination Cu(I) polymers depended on the shape of the included counter anions.

In the case of crystal **1** containing SbF_6 as the counter anion with an octahedral structure, a 4-folded helical columnar coordination polymer was observed, as shown in Figure 2-2. The coordination polymers were packed into the $P2_1/n$ space group (Table 2-1). The Cu–C and Cu–N bond lengths of the Cu(I) complex **1** are 1.943 and 2.031 Å, respectively (Figure 2-2a). Two pyrazines were coordinated to Cu(I) at a binding angle of 101° (Figure 2-2a). Indeed, with a non-overlapped arrangement of pyrazines, the torsion angles between pyrazines and the NHC ring were 33.8° and 35.2° (Figure 2-2b). The angles between the Cu trigonal coordination plane and the pyrazine planes were 55° and 69° , indicating that the pyrazine planes were not close to co-planar in the Cu coordination geometry (Figure 2-10e). The bulky NHC groups were packed outside the column, and infinitely coordinated Cu(I) and pyrazines were folded with the included SbF_6 anions (Figures 2-2c–d). I observed that the fluorine atoms of octahedral SbF_6 interacted at the square site with hydrogen atoms of four pyrazines [(I) to (IV)] in the coordination polymer, and the corresponding F–H distances were in the range of 2.248–2.659 Å (Figures 2-2c and 2-10a). Additionally, the angle of C–H–F were arranged in ca. 115° – 168° , as shown in Figure 2-10f. This suggests that the octahedral shape of the SbF_6 anion can assist the formation of H–F interactions between the anions and pyrazines in square and vertical sites, inducing the 4-folding mode of the helical structure. This packing was infinitely arranged, which constructed a 4-fold columnar structure with 12.537 Å of helical pitch between Cu(I)-a and Cu(I)-b including four pyrazines (Figures 2-2d, e and 2-10b–d). The columnar structure in Figure 2-2d shows *P*-helicity and is surrounded by *M*-helical columns in the crystal (Figure 2-10d). The inclusion of CH_2Cl_2 solvent molecules was observed between the intercolumnar arrangements (Figure 2-10d).

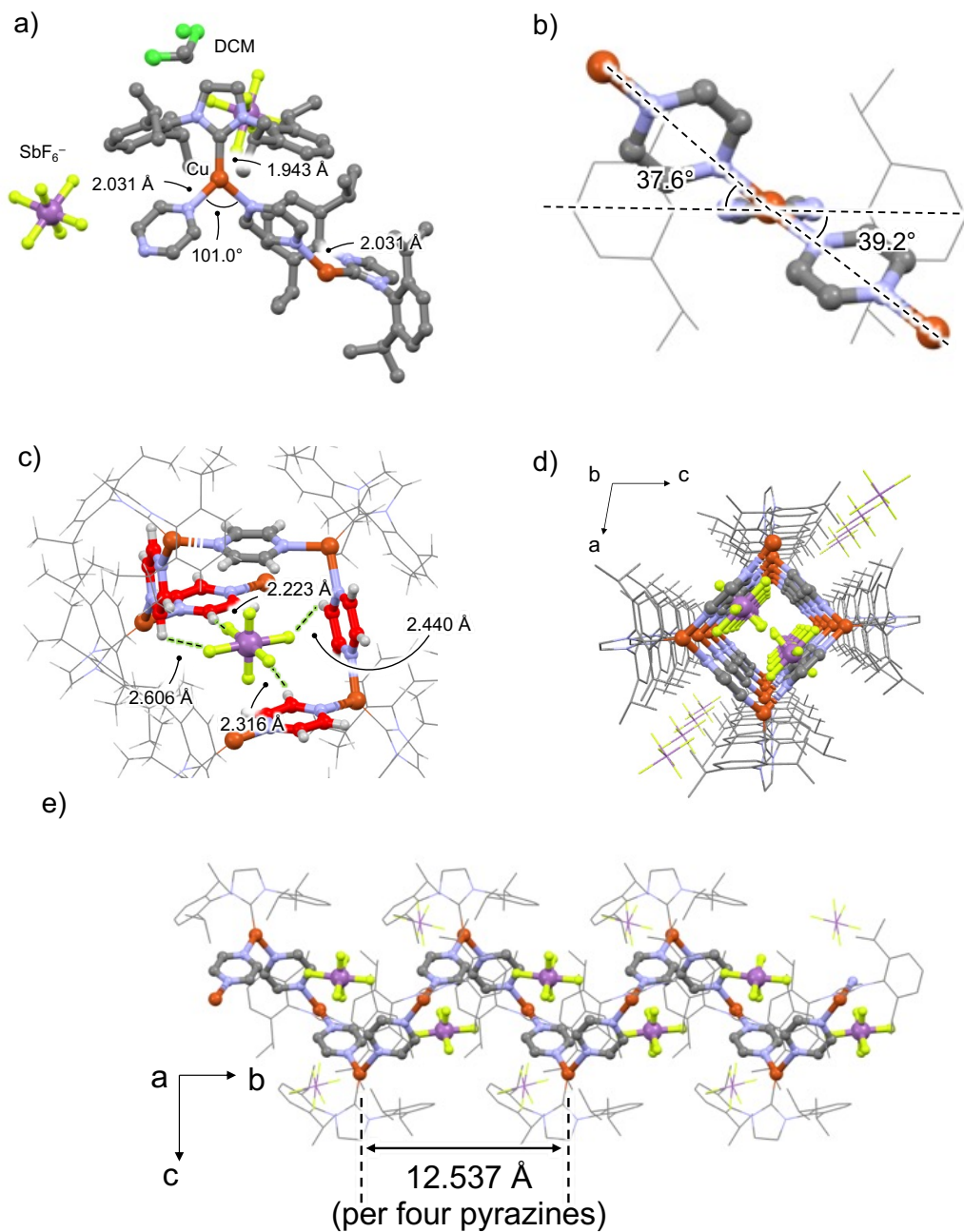


Figure 2-2. Crystal structure of the cationic NHC Cu(I) coordination polymer **1** containing SbF₆. a), b) Coordination geometry near Cu(I) atoms. c) Observed H-F interactions between pyrazines and SbF₆. d) Axial and e) side views of *P*-helicity of the 4-fold helical columnar structure of **1**.

Crystal **2**, which included octahedral PF₆ as the counter anion, also formed a 4-folded helical columnar structure in the $P2_1/n$ space group, similar to crystal **1** (Figure 2-3 and Table 2-1). As described in Figure 2-3a, the distances of the coordination bonds between Cu and the NHC ring or pyrazines were 1.907 Å and 2.014–2.022 Å, respectively. The two pyrazines were trigonally coordinated with torsional angles of 98.1° and 36.6°–41.4° between pyrazines and the NHC plane (Figure 2-3b). Moreover, the pyrazine planes were tilted in 76.2° and 61.6° from the trigonal coordination plane of Cu(I), indicating that the pyrazine planes were also not close to co-planar in the Cu(I) coordination geometry as observed in crystal **1** (Figure 2-11e). As observed in crystal **1**, the fluorine atoms of octahedral PF₆ were close to the hydrogen atoms of four pyrazines [(I) to (IV)] in the coordination polymer, and their corresponding distances ranged from 2.430 Å to 2.679 Å (Figure 2-3c and 2-11). In addition, we observed that the angle of C–H–F ranged in ca. 100°–156° (Figure 2-11f). This 4-folded structure was infinitely elongated in a helical columnar structure with 12.372 Å of helical pitch measured between Cu(I)-a and Cu(I)-b containing four pyrazines (Figure 2-3e and 2-11d). The helical pitch in crystal **2** is shorter than that of crystal **1**, which may be caused by the relatively smaller size of PF₆[−] anion than that of SbF₆[−]. The helical column described in Figure 2-3d exhibits *P*-helicity, and the *M*-helical columns are nearly packed as illustrated in Figure 2-11d. CH₂Cl₂ molecules were included in the intercolumnar packing environment (Figure 2-11d).

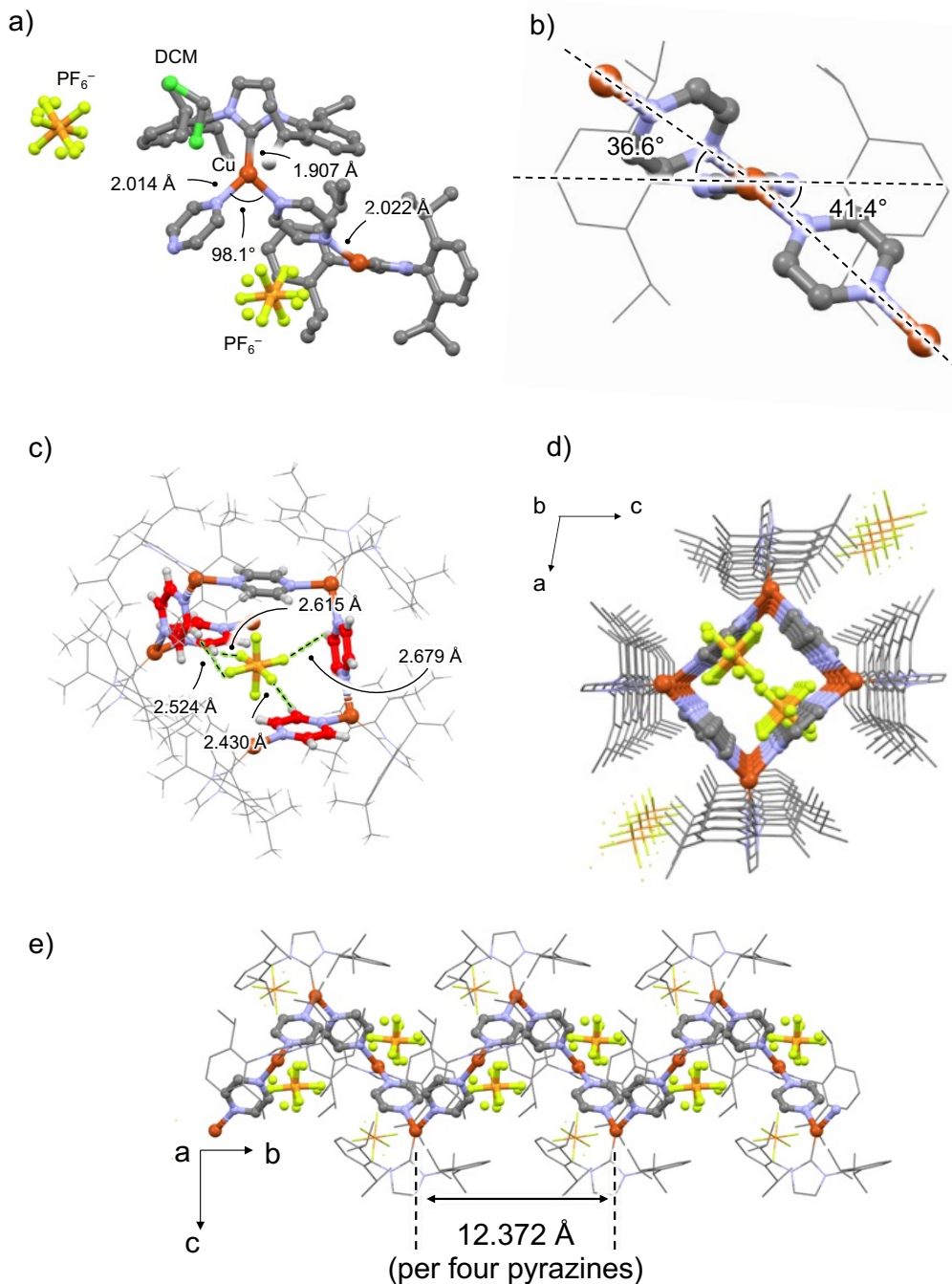


Figure 2-3. Crystal structure of the cationic NHC Cu(I) coordination polymer 2 containing PF_6^- . a) and b) Coordination geometry near the Cu(I) atoms. c) Observed H-F interactions between pyrazines and PF_6^- . d) Axial and e) side views of *P*-helicity of the 4-fold helical columnar structure of 2.

Interestingly, crystal 3 containing BF_4^- anions with a tetrahedral structure formed a coordination polymer with a helical 3-fold mode packed in the chiral $P3_1$ space group, which is distinct from the fold

mode and space group of crystals **1** and **2** (Figure 2-4 and Table 2-1). Two pyrazines and the NHC ligand were trigonally coordinated to Cu(I), and the distance and coordinated angle between the nitrogen atoms of pyrazines and the Cu(I) atom were 2.079 Å and 99.1°, respectively. Furthermore, the distance between the carbon atom at the 2-position of the NHC ring and Cu(I) was 1.930 Å (Figure 2-4a). The torsion angles between Cu(I) and the two pyrazines were 0.7° and 2.8°, which are smaller than those observed in crystals **1** and **2** (Figure 2-4b). Furthermore, I observed that crystal **3** formed the angle between the Cu(I) trigonal coordination plane and the pyrazine planes as 34.3° and 50.3°, indicating that the pyrazine planes were clearly closer to co-planar with the Cu(I) trigonal coordination plane than those in crystals **1** and **2** (Figure 2-12d). The tetrahedral BF₄ anions formed the H–F interactions with protons in pyrazines [(I) to (III)] and the isopropyl moiety of the NHC ligand with the corresponding distances of 2.517–2.953 Å. The observed C–H–F angles ranged in ca. 127° to 169° (Figure 2-12e). Moreover, the 3-fold coordination pattern was elongated and formed a trigonal shape (Figures 2-4c–d and 2-12). Indeed, the helical pitch per four pyrazines between Cu(I)-a and Cu(I)-b was 19.594 Å, which is longer than those of the 4-fold helical structures in crystals **1** and **2** (Figure 2-4e and 2-12). The observed helical column in crystal **3** showed *M*-helicity, and no counter-helical structure was confirmed in the crystal structure (Figure 2-12c).

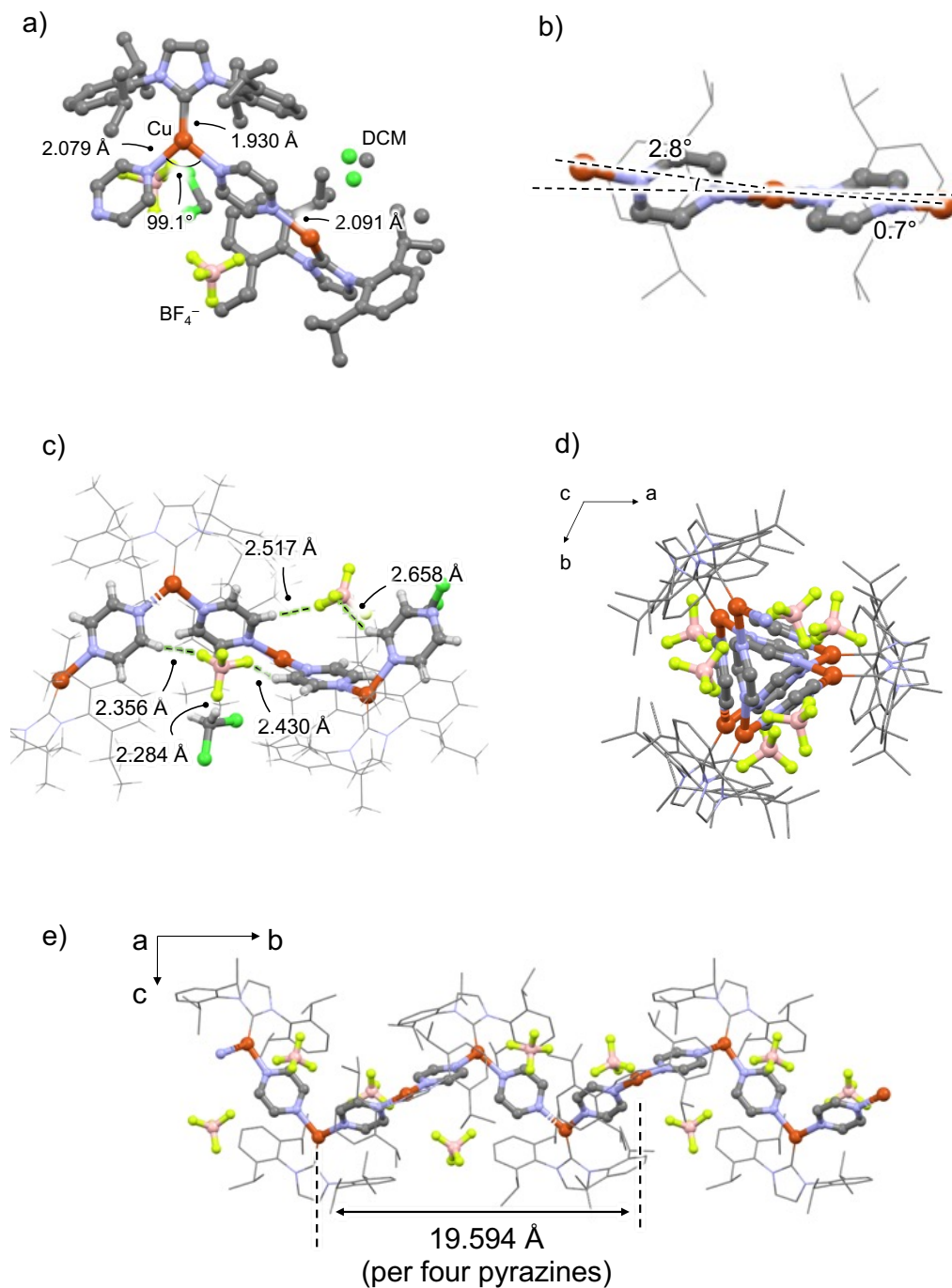


Figure 2-4. Crystal structure of the cationic NHC Cu(I) coordination polymer 3 containing BF_4 . a) and b) Coordination geometry near the Cu(I) atom. c) Observed H-F interactions between hydrogen atoms in pyrazines and the NHC ligand and fluorine atoms in BF_4^{-1} . d) Axial and e) side views of *M*-helicity the 3-fold helical columnar structure.

I investigated the relationship between the shape of the counter anions and the observed helical structures. In the case of crystals **1** and **2**, the octahedrally distributed fluorine atoms of the SbF_6 or PF_6 anions gathered four pyrazines in square-like positions through H–F interactions, resulting in 4-folded helical structures (left in Figure 2-5). On the other hand, the tetrahedrally positioned fluorine atoms of the two BF_4 anions contributed to the formation of a triangle-like helical arrangement of three pyrazines through H–F interactions and the occupation space, resulting in a 3-folded helical columnar structure (right in Figure 2-5). In general, it is difficult to design a helical structure of a coordination polymer in the solid-state due to unpredictable packing environment. However, the observed geometries of the cationic NHC Cu(I) coordination polymers **1–3** can suggest a promising motif to design the helical fold-mode in crystal.

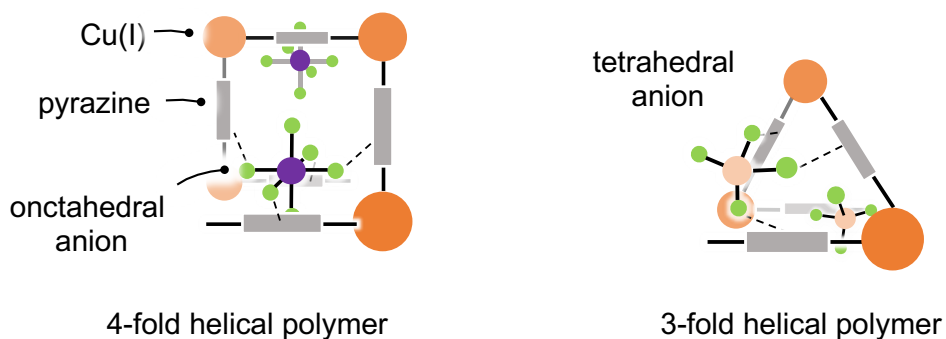


Figure 2-5. Illustrations showing the observed folding modes of the cationic NHC Cu(I) coordination polymers **1** to **3** in crystals, the interactions between the counter anions and pyrazines, and geometrical shape of the anions.

Solid-state emission properties of crystals 1, 2, and 3. Cu(I) coordination polymers have been broadly developed based on the ability of Cu(I) to form linear or trigonal coordination with arylene ligands.^{17,18} The solid-state emissions of Cu(I) complexes are generally engaged in the metal-to-ligand charge-transfer (MLCT) excitation process, which is highly correlated with the coordination geometry. Thus, designing a coordination environment for 1D-coordination polymers containing Cu(I) is a promising method to modulate solid-state emission. As shown in Figures 2-6a–b, crystal **3** with a 3-fold helical structure exhibited a clear red-shifted emission under UV light at room temperature compared to crystals **1** and **2**, forming a 4-fold helical column. No emission of crystals **1–3** in the CH_2Cl_2 solution

was observed, while relatively high quantum yields (F) of approximately 1.0–2.9% were measured in the crystalline samples, suggesting that the emissions of the crystals were determined by their aggregated structures (Figures S2-13–15 and Table 2-2).^{21,22,23,24} Crystals **1** and **2** showed a broad emission with maximum intensity ($I_{em,max.}$) at 573 and 586 nm, respectively, under 365 nm irradiation (Figure 2-6b). Interestingly, the emission of crystal **3** has the $I_{em,max.}$ at 687 nm, which is longer than those of crystals **1** and **2** (Figure 2-6b). The excitation spectra of crystals **1** and **2** monitored for each $I_{em,max.}$ were very similar broad bands with $I_{ex,max.}$ of the maximum excitation at 365 nm (Figure 2-6c). However, the excitation spectrum of crystal **3** clearly shows a larger excitation intensity at 400–470 nm than those of crystals **1** and **2** (Figure 2-6c). The emission decay and emission lifetimes ($t_{av.}$) for crystals **1** and **2** were similar, that is, 5.4 and 5.6 μ s, respectively. This indicates that both crystals exhibit similar phosphorescence (Table 2-2 and Figure 2-16). However, the relatively shorter emission lifetime of crystal **3** was detected as $t_{av.} = 4.6 \mu$ s, suggesting that the red-shifted emission should be yielded from different structural or electronic environments (Table 2-2 and Figure 2-16).

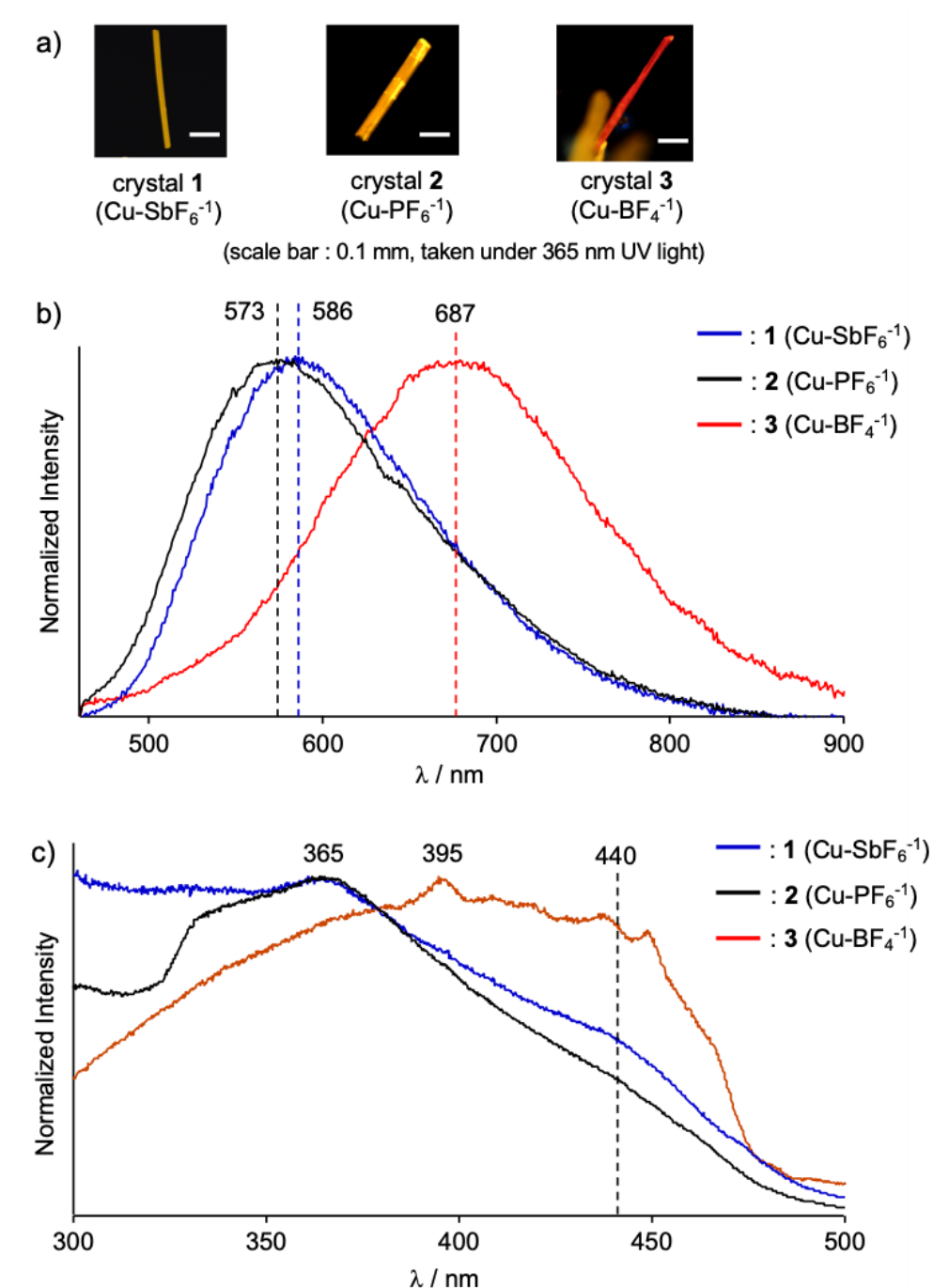


Figure 2-6. a) Photographs of crystal 1, 2, and 3 taken under UV light. b) Emission spectra of crystals 1, 2, and 3 measured by 365 nm of excitation (represented by blue, black, and red solid lines, respectively). c) Excitation spectra of crystals 1–3 monitored at each $I_{em,max}$.

Based on the observed emission properties and crystal structures of the cationic NHC Cu(I) coordination polymers **1–3**, I assumed that the red-shifted emission of crystal **3** correlated with tightly packed pyrazines near Cu(I) through the 3-fold helical structure. The 4-fold helical structure of crystals **1** and **2** constructed a non-overlapped pyrazine arrangement, as shown in Figures 2-2c and 2-3c. On the other hand, the 3-fold helical structures of crystal **3** formed closely packed pyrazines in the column, inducing a coplanar-like structure of the p planes with central coordination of Cu(I). I expected that the expand electronic conjugation along pyrazines and Cu(I) via the co-planar like geometry, inducing a narrow HOMO–LUMO gap that determines the emission band (Figure 2-7). This hypothesis was documented with time-dependent (TD) DFT calculations using the geometries containing two NHC Cu(I) moiety and three pyrazines taken from the single-crystal XRD structures of **1**, **2**, and **3** as the input for the calculations (Figure 2-17). The calculated UV/vis absorption spectra showed qualitatively good agreement with the measured excitation spectra (Figure 2-17), and the involved molecular orbitals were identified as transitions from HOMO or HOMO-1 to LUMO or LUMO+1 (Figures 2-8 and 2-17–2-20). The HOMO-1 of crystal **3**, which has the co-planar-like geometry close to the trigonal coordination of Cu(I) atom mainly consisted of the orbitals across the three pyrazines with two Cu(I) as delocalized distribution. In contrast, the HOMO-1 in crystal **1** is localized near the Cu(I) atom and one pyrazine ring, and one NHC ring (Figure 2-8). This suggested that the co-planar-like geometry between Cu(I) atom and the coordinated pyrazines induce the delocalization of the molecular orbitals involved in the excitation process.

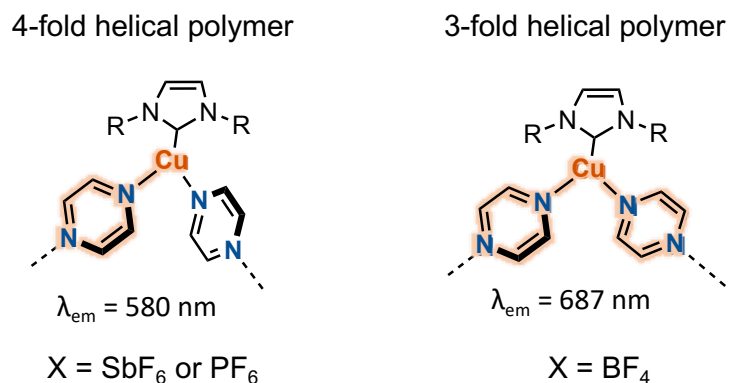


Figure 2-7. Schematic representation of the expected relationship between the coordination geometries built by 4-fold or 3-fold helical structures and the electronic conjugation shown in red.

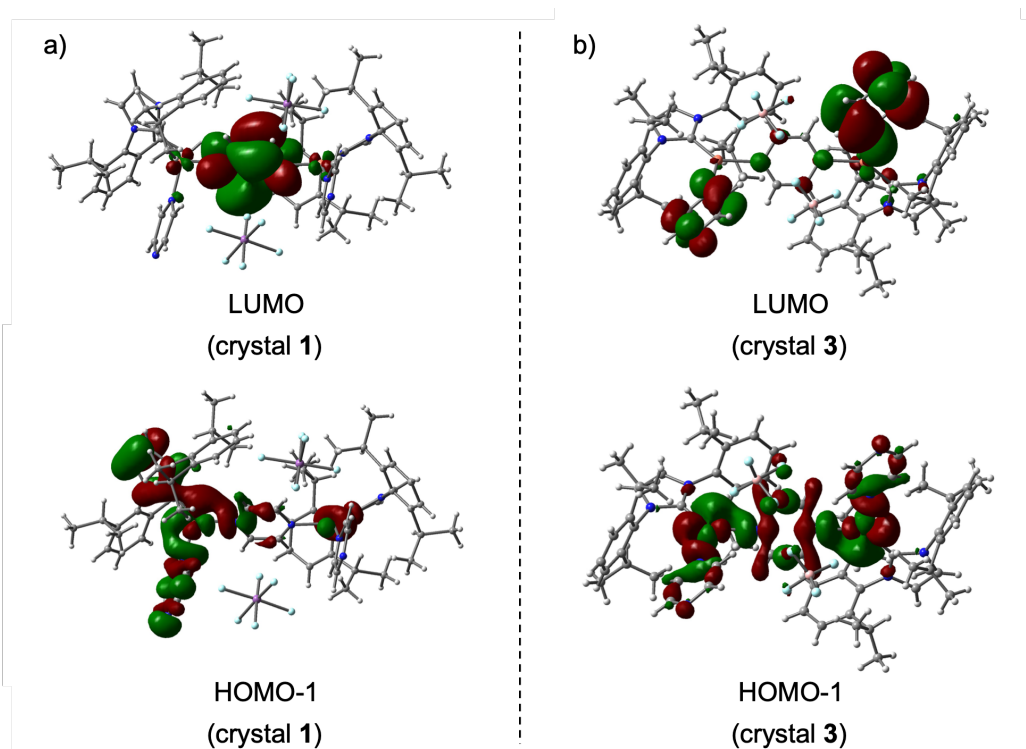


Figure 2-8. Selected orbitals dominantly involved in the singlet transitions of the NHC Cu(I) complex a) **1** (4-fold) and b) **3** (3-fold).

2.3 Summary

Herein, I describe a novel helical structure modification of cationic NHC Cu(I) coordination polymers in crystals by using the structural features of the counter anions, which also induce clear alternation of solid-state emission. The Cu(I) coordination polymers formed a 4-fold helical column in crystals using octahedral anions (SbF_6 or PF_6), while a 3-fold helical columnar structure was formed using the tetrahedral anion BF_4 . Crystals with a 4-fold helical structure exhibited red emission near 580 nm under UV light. Furthermore, a red-shifted emission near 687 nm was observed when the helical structure was altered to the 3-fold mode through using a different shape of the counter anion. I expected that the red-shifted emission would be induced by the expanded electronic conjugation through densely packed pyrazines near the Cu(I) atom in the 3-folded coordination structure rather than those in the 4-fold helical column. These results reveal that a fold-mode design of 1D-coordination polymers in crystals can be demonstrated by exploiting the structural features of the counter anions. Especially, shape of the counter anion structure as well as geometry of the interaction site can be a motif to design fold-mode of the coordination polymers, even the rational design of packing structure in solid-state is generally difficult. Moreover, fine tuning of the solid-state emission can also be developed by utilizing the coordination geometry design method via fold-mode control in the crystals.

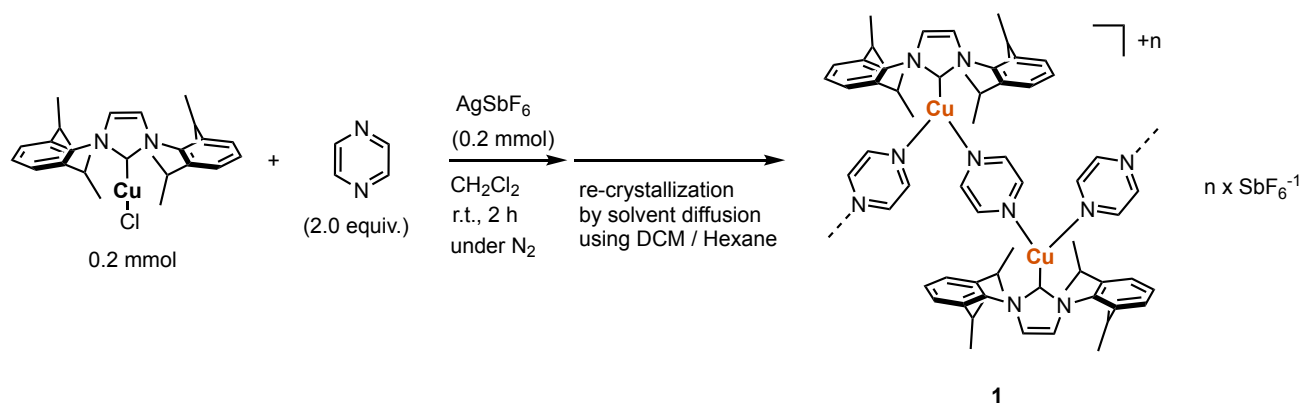
2.4 Experimental Section

General

All commercially available reagents, including chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]Cu(I), and solvents are reagent grade and were used without further purification unless otherwise noted. Solvents for the synthesis were purchased from commercial suppliers, degassed by three freeze-pump-thaw cycles, and further dried over molecular sieves (4 Å). NMR spectra were recorded on a JEOL JNM-ECX400P or JNM-ECS400 (^1H : 400 MHz; ^{13}C : 99.5 MHz) using tetramethylsilane and CD_2Cl_2 as internal standards, respectively. Emission spectra were recorded on a Hitachi F-7000 spectrometer. Absorption spectra were recorded on the basis of synchronous fluorescence spectroscopy using a Hitachi F-7000 spectrometer equipped with an integrating sphere. The emission quantum yields of the solid samples were recorded on a Hamamatsu Quantaurus-QY spectrometer with an integrating sphere. Emission lifetime measurements were recorded on a Hamamatsu Quantaurus-Tau spectrometer. Fluorescence microscopic spectra were recorded on a Photonic Hamamatsu PMA-12 Multichannel Analyzer. Photographs were obtained using Olympus BX51 or SZX7 microscopes with Olympus DP72, Nikon D5100 digital cameras. Thermal gravimetric analysis profiles were recorded on Bruker TG-DTA2010SAT. The raw data files were plotted on Igor Pro Version 6.37.

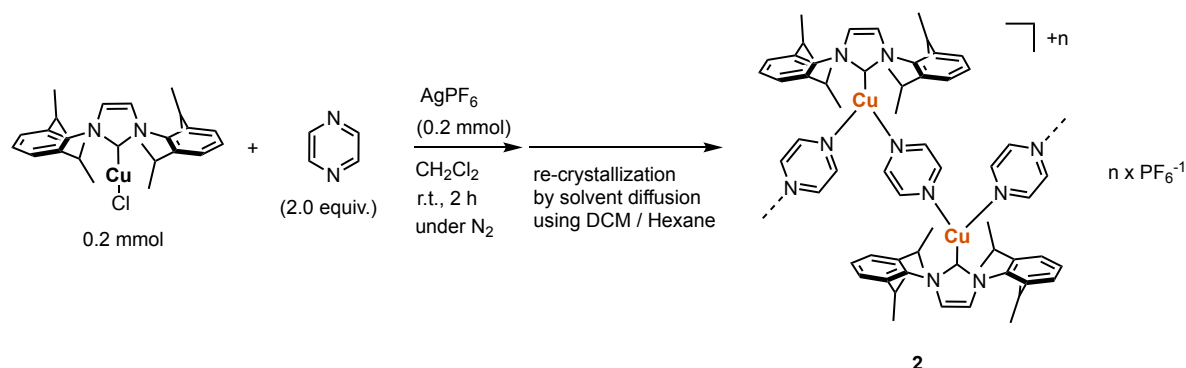
Synthesis

Synthesis of the NHC Cu(I) complex **1** (counter anion: SbF₆⁻)



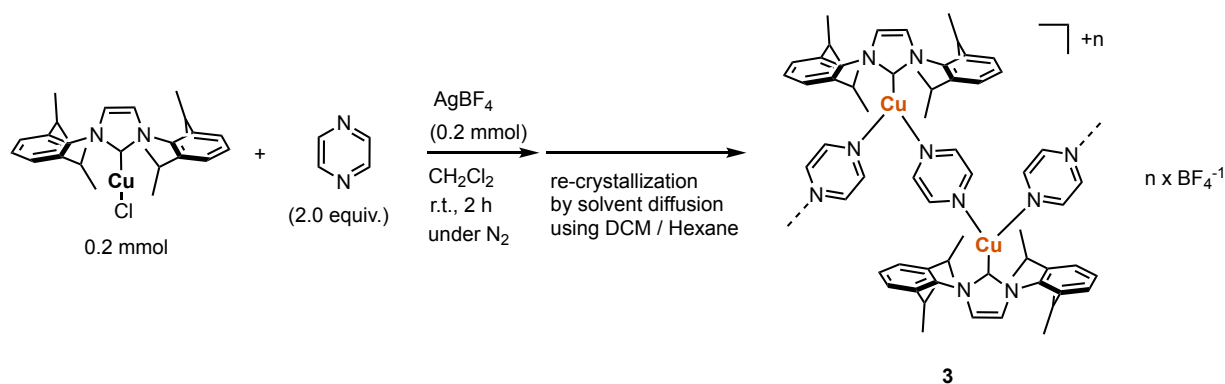
A powder of chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]Cu(I) (0.095 g, 0.20 mmol) and pyrazine (0.032 g, 0.40 mmol) was placed in an oven-dried 20 ml of one-neck vial. The flask was connected to a vacuum/nitrogen manifold through a rubber tube. It was evacuated and then backfilled with nitrogen. Dry CH₂Cl₂ (5.0 ml) was then added to the flask under a nitrogen atmosphere. The reagents contained CH₂Cl₂ solution was added AgSbF₆, and the reaction was performed at room temperature for 2 h. The suspended CH₂Cl₂ solution was followed by separating the liquid organic layer using a centrifuge. The organic layers were collected, and the solvent was removed *in vacuo*. Further purification by recrystallization using CH₂Cl₂/Hexane gave analytically pure yellow crystals of **1** with red emission under UV light (0.110 g of needle shape crystals). The crystalline sample was not well soluble in chloroform, thus, CD₂Cl₂ was used for dissolving the crystal for measurements of the ¹H and ¹³C NMR spectra in solution phase. ¹H NMR (400 MHz, CD₂Cl₂, δ): 1.16 (d, *J* = 6.8 Hz, 12H), 1.26 (d, *J* = 7.2 Hz, 12H), 2.55 (septet, *J* = 6.9 Hz, 4H), 5.32 (s, CH₂Cl₂), 7.36 (s, 2H), 7.39 (d, *J* = 8.4 Hz, 4H), 7.61 (t, *J* = 8.0 Hz, 2H), 7.87 (s, 4H). ¹³C NMR (125 MHz, CD₂Cl₂, δ): 23.8 (CH₃), 25.1 (CH₃), 29.1 (CH), 124.4 (CH), 124.9 (CH), 131.2 (CH), 135.7 (C), 145.3 (CH), 146.1 (C), 179.5 (C).

Synthesis of the NHC Cu(I) complex **2** (counter anion: PF₆⁻)



The NHC Cu(I) coordination polymer **2** was prepared from chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]Cu(I) (0.095 g, 0.20 mmol), pyrazine (0.032 g, 0.15 mmol), and Ag(PF₆) (0.051 g, 0.20 mmol) according to the procedure similar to that described for the preparation of **1** (0.118 g, yellow needle shape crystal). The crystalline sample was not well soluble in chloroform, thus, CD₂Cl₂ was used for dissolving the crystal for measurements of the ¹H and ¹³C NMR spectra in solution phase. ¹H NMR (400 MHz, CD₂Cl₂, δ): 1.04 (d, *J* = 7.2 Hz, 12H), 1.26 (d, *J* = 6.8 Hz, 12H), 2.56 (septet, *J* = 6.9 Hz, 4H), 5.33 (s, CH₂Cl₂), 7.34 (s, 2H), 7.35 (s, 4H), 7.41 (d, *J* = 8.0 Hz, 4H), 7.65 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CD₂Cl₂, δ): 23.7 (CH₃), 25.1 (CH₃), 29.0 (CH), 124.4 (CH), 124.9 (CH), 131.2 (CH), 135.2 (C), 145.4 (CH), 146.1 (C), 179.6 (C).

Synthesis of the NHC Cu(I) complex **3** (counter anion: BF₄⁻)



The NHC Cu(I) coordination polymer **3** was prepared from chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]Cu(I) (0.095 g, 0.20 mmol), pyrazine (0.011 g, 0.15 mmol), and AgBF₄ (0.040 g, 0.20 mmol) according to the procedure similar to that described for the preparation of **1** (0.091 g, yellow needle shape crystal). The crystalline sample was not well soluble in chloroform, thus, CD₂Cl₂ was used for dissolving the crystal for measurements of the ¹H and ¹³C NMR spectra in solution

phase. ^1H NMR (400 MHz, CD_2Cl_2 , δ): 1.04 (d, $J = 6.4$ Hz, 12H), 1.25 (d, $J = 7.2$ Hz, 12H), 2.55 (septet, $J = 6.9$ Hz, 4H), 5.32 (s, CH_2Cl_2), 7.33 (s, 6H), 7.42 (d, $J = 8.0$ Hz, 4H), 7.69 (t, $J = 7.8$ Hz, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2 , δ): 23.8 (CH_3), 25.0 (CH_3), 29.0 (CH), 124.3 (CH), 124.9 (CH), 131.2 (CH), 135.3 (C), 145.7 (CH), 146.3 (C), 180.1 (C).

Thermogravimetric Analysis (TGA) of Crystals 1, 2 and 3

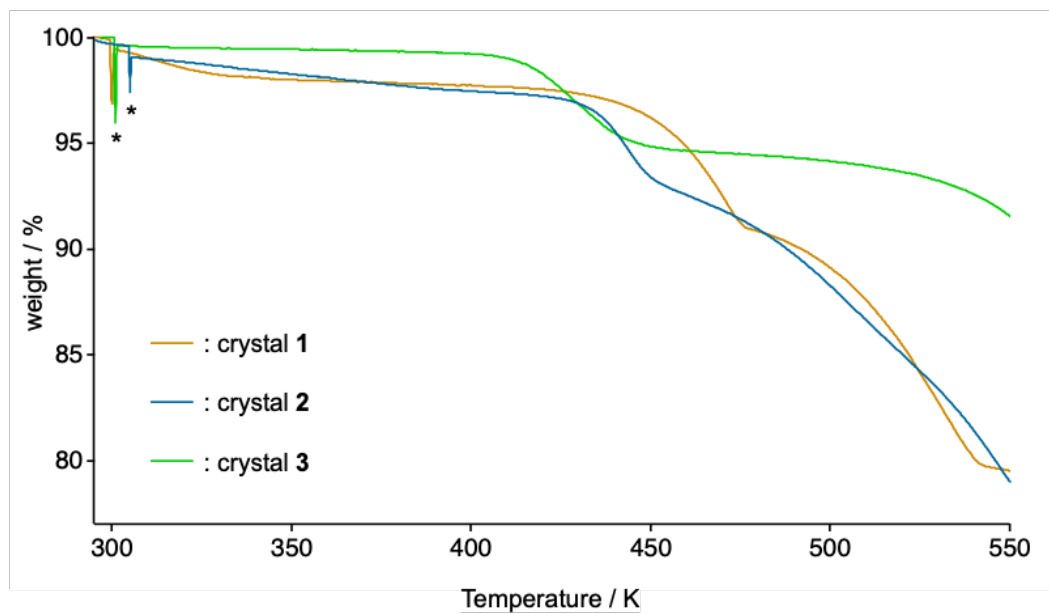


Figure 2-9. TGA profile of the crystal **1** (brown line), **2** (blue line), and **3** (green line). The heating rate is 5 °C/min. Weight decreasing of all crystalline samples were observed from ca. 305 K. *Peaks may be recorded by suddenly occurred release of the included CH_2Cl_2 molecules in the crystals.

Data for Single-Crystal X-Ray Structural Analyses

Single-crystal X-ray structural analyses were carried out on a Rigaku XtaLAB PRO MM007 diffractometer using graphite monochromated Cu-K α radiation. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the Olex2 crystallographic software package except for refinement, which was performed using SHELXL-2013²⁴.

Table 2-1. Summary of X-ray crystallographic data of the crystal **1**, **2**, and **3**.

compound	Crystal 1	Crystal 2	Crystal 3
CCDC Number	2103728	2103721	2103729
Empirical Formula	C _{62.75} H _{82.5} Cl _{1.5} Cu ₂ F ₁₂ N ₈ Sb ₂	C ₆₃ H ₈₂ Cl ₂ Cu ₂ F ₁₂ N ₈ P ₂	C _{31.63} H _{41.25} BCl _{1.25} CuF ₄ N ₄
Formula Weight	1600.62	1439.28	672.10
Crystal System	monoclinic	monoclinic	trigonal
Crystal Size / mm	0.03×0.50×0.03	0.06×0.61×0.08	0.02×0.55×0.03
<i>a</i> / Å	18.2333(7)	18.29400(10)	14.22200(10)
<i>b</i> / Å	12.5385(7)	12.37150(10)	14.22200(10)
<i>c</i> / Å	32.323(3)	31.3965(2)	28.3708(2)
α / °	90	90	90
β / °	96.369(5)	95.1050(10)	90
γ / °	90	90	120
<i>V</i> / Å ³	7344.0(7)	7077.60(8)	4969.62(8)
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 3 ₁
<i>Z</i> value	4	4	6
<i>D</i> _{calc} / g cm ⁻³	1.448	1.351	1.347
Temperature / K	153	153	153
2 θ _{max} / °	151.464	150.394	150.23
μ (Cu K α) / mm ⁻¹	7.536	2.501	2.847
No. of Reflections	Total: 47383 Unique: 14594 <i>R</i> _{int} = 0.2082	Total: 53514 Unique: 14068 <i>R</i> _{int} = 0.0304	Total: 17912 Unique: 8529 <i>R</i> _{int} = 0.0352
<i>R</i> ₁ ^a	0.2051	0.0652	0.0317
<i>wR</i> ₂ ^b	0.4584	0.1860	0.0796
GOF ^c	1.426	1.039	1.024
Max./Mini. peak <i>I</i> ^d / Å ³	3.39 e ⁻ /−1.36 e ⁻	3.21 e ⁻ /−1.67 e ⁻	0.59 e ⁻ /−0.26 e ⁻
Flack Parameter	-	-	−0.001(18)

^a: $I > 2.00\sigma(I)$. ^b: All reflections. ^c: Goodness of Fit Indicator. ^d: in Final Diff. Map.

Note: Large *R*₁, *wR*₂, and GOF value for crystal **1** due to the low crystallinity. Large peak (3.39 e⁻ for crystal **1** and 3.21 e⁻ for crystal **2**) come from the solvent which couldn't be assigned.

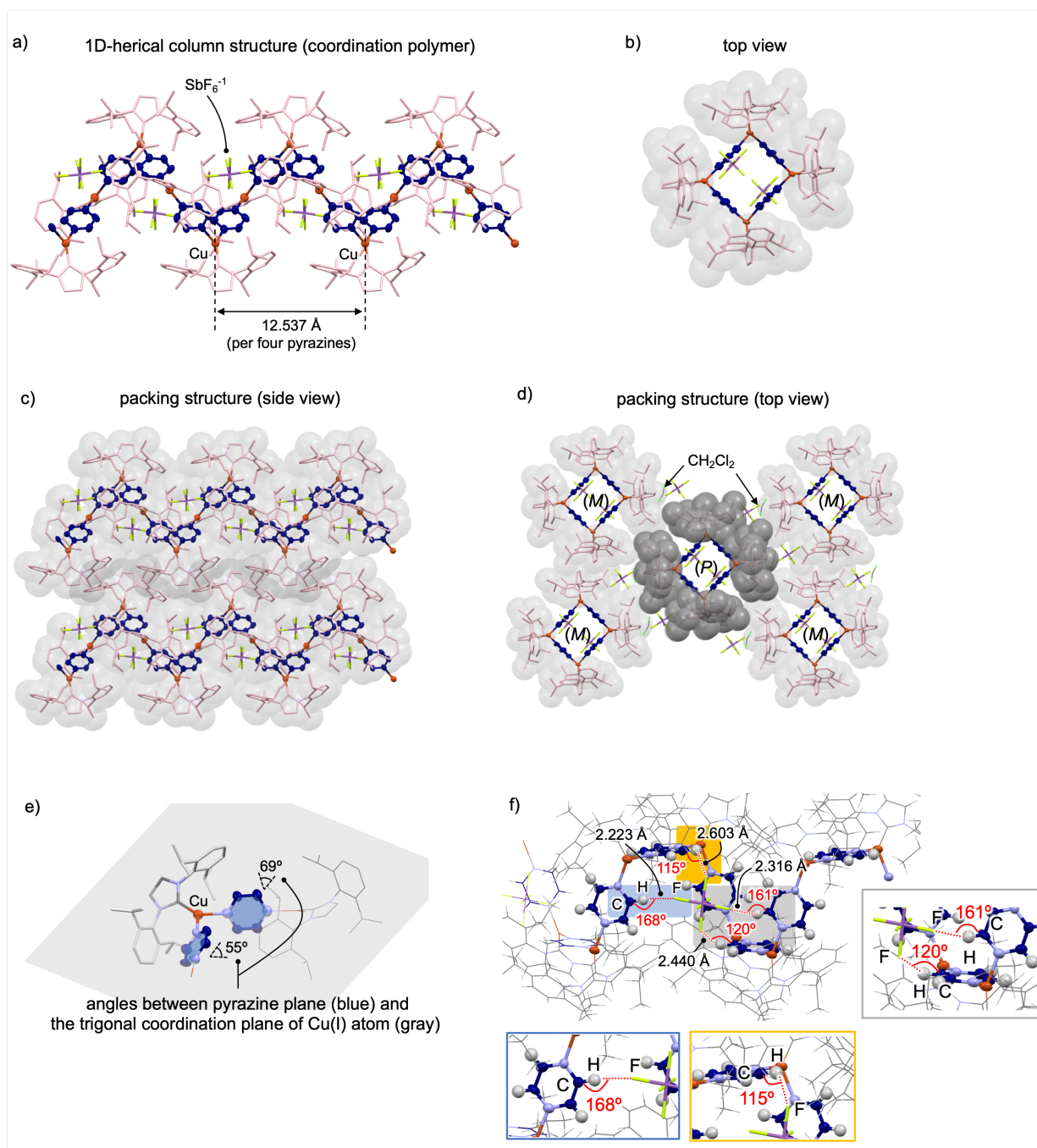


Figure 2-10. Molecular packing structure of crystal **1** at 123 K. H atoms are omitted for clarity. a) 1D-helical structure and b) the view from helical axis. c) Inter-columnar packing structure and d) the view from helical axis. e) Illustration of the angles between trigonal coordination plane of Cu(I) and pyrazine plane. f) Distance between F of SbF₆⁻ and H of pyrazine with angle of the C–H–F.

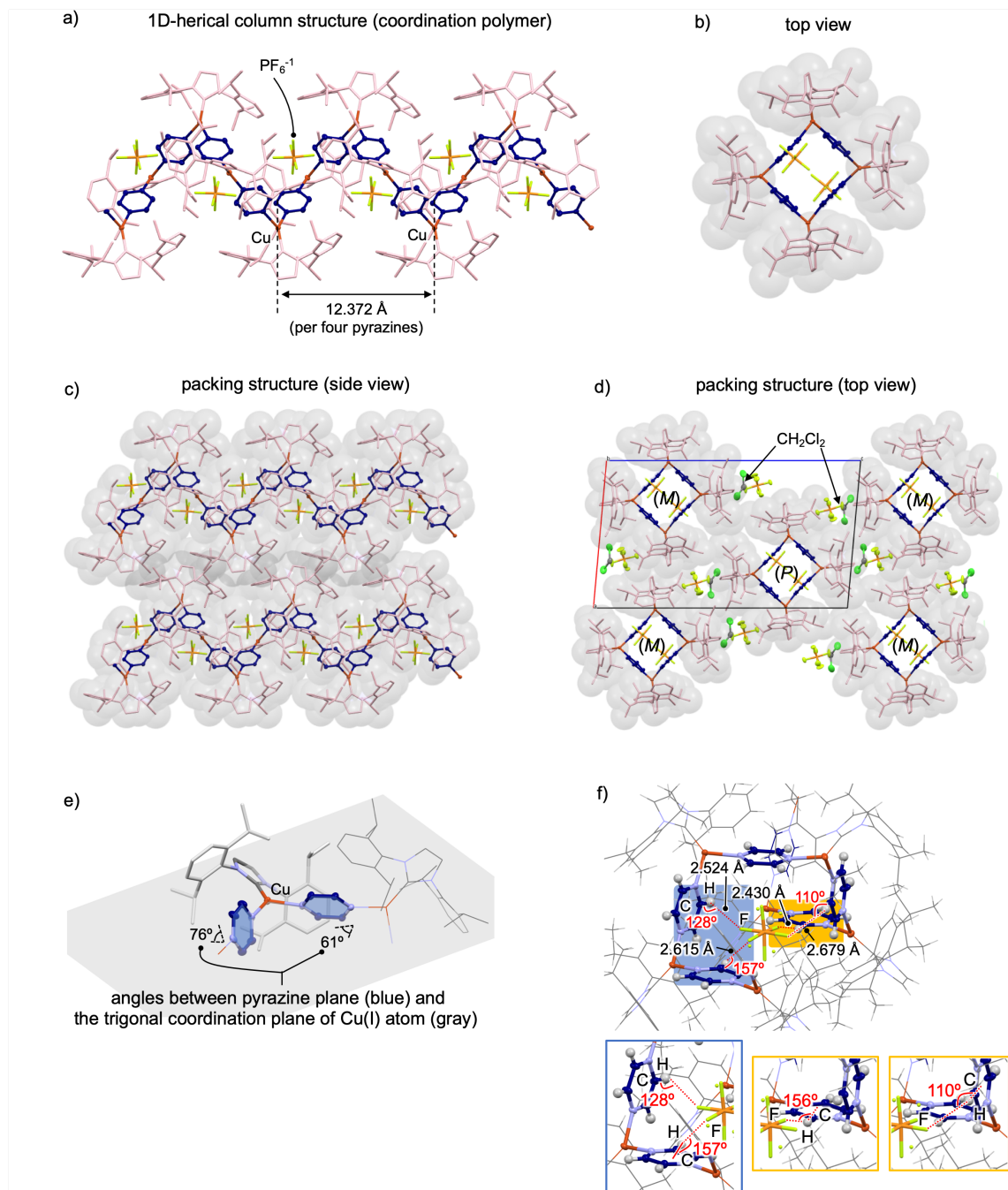


Figure 2-11. Molecular packing structure of crystal **2** at 123 K. H atoms are omitted for clarity. a) 1D-helical structure and b) the view from helical axis. c) Inter-columnar packing structure and d) the view from helical axis. e) Illustration of the angles between trigonal coordination plane of Cu(I) and pyrazine plane. f) Distance between F of PF_6^- and H of pyrazine with angle of the C-H-F.

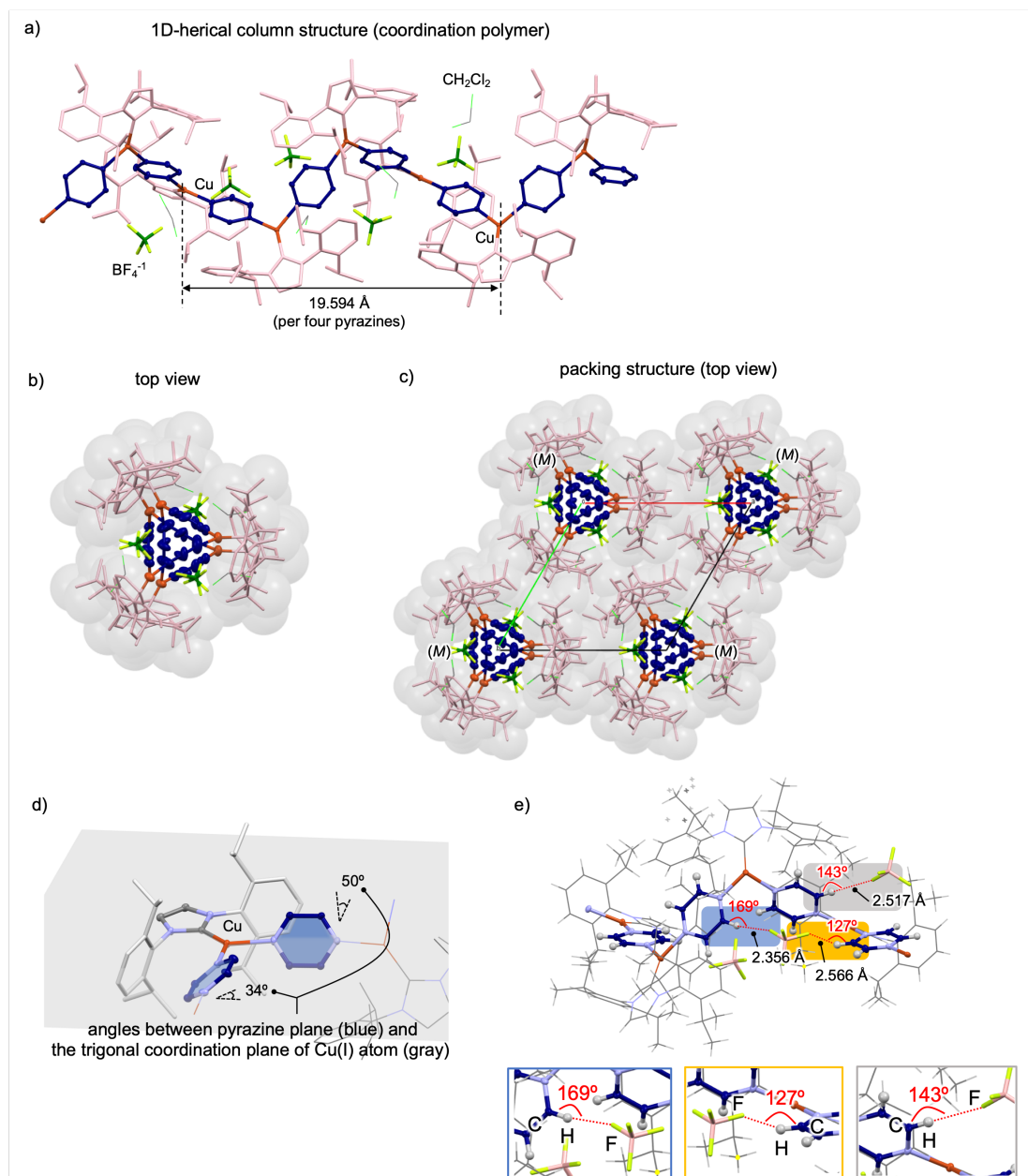


Figure 2-12. Molecular packing structure of crystal **3** at 123 K. H atoms are omitted for clarity. a) 1D-helical structure and b) the view from helical axis. c) Inter-columnar packing structure. d) Illustration of the angles between trigonal coordination plane of Cu(I) and pyrazine plane. e) Distance between F of BF₄⁻ and H of pyrazine with angle of the C–H–F.

Optical Properties of Cu Complexes 1, 2, and 3 in Solution

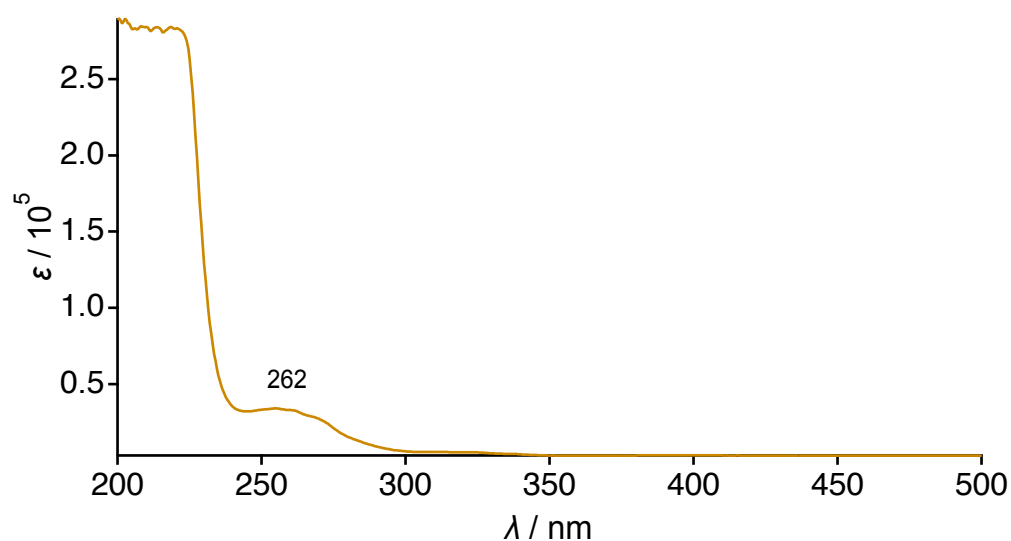


Figure 2-13. UV/vis of Cu(I) complex **1** in CH₂Cl₂ ($c = 1.9 \times 10^{-4}$ M) at room temperature. The solution of **1** in CH₂Cl₂ exhibited no emission under UV light.

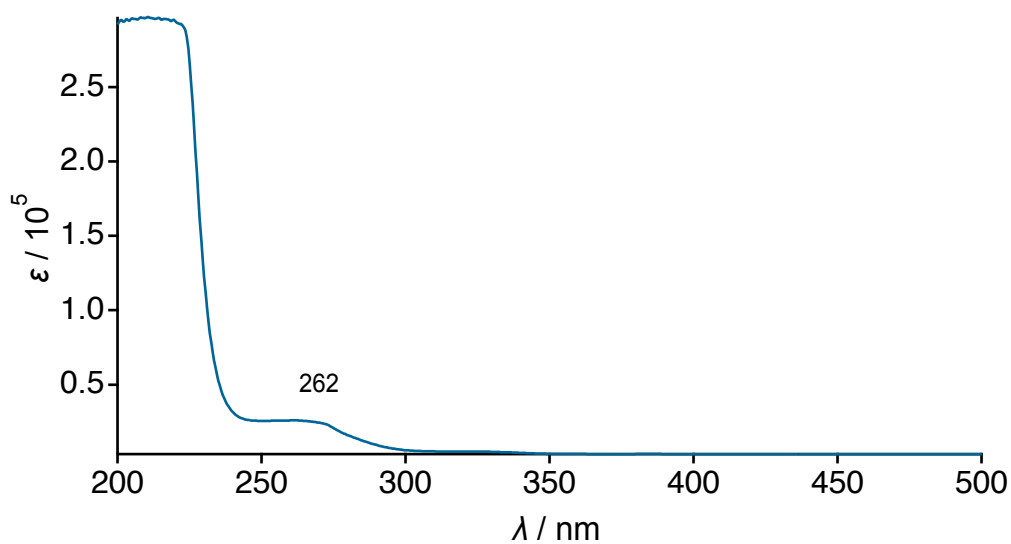


Figure 2-14. UV/vis of Cu(I) complex **2** in CH₂Cl₂ ($c = 2.8 \times 10^{-4}$ M) at room temperature. The solution of **2** in CH₂Cl₂ exhibited no emission under UV light.

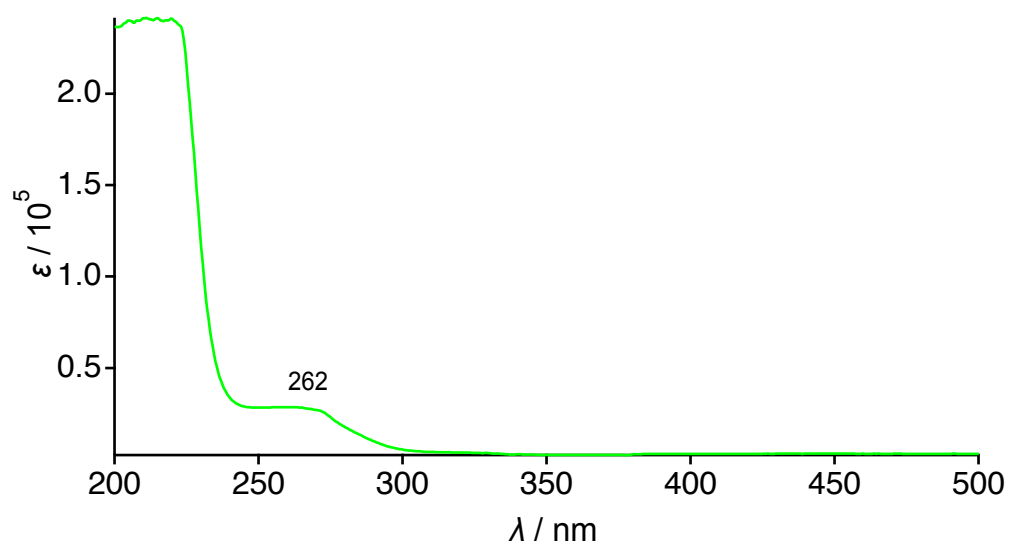


Figure 2-15. UV/vis of Cu(I) complex **3** in CH_2Cl_2 ($c = 1.7 \times 10^{-4}$ M) at room temperature. The solution of **3** in CH_2Cl_2 exhibited no emission under UV light.

Photophysical Properties of Crystal 1, 2, and 3

For emission decay traces of crystals **1**, **2**, and **3**, I used 370 nm as the excitation wavelength and detected kinetic traces at the maximum emission wavelength of each crystal (586 nm, 573 nm, 687 nm, respectively). The emission decays were measured until 10^3 counts. The obtained emission decays were fitted by using a second-order exponential decay function.

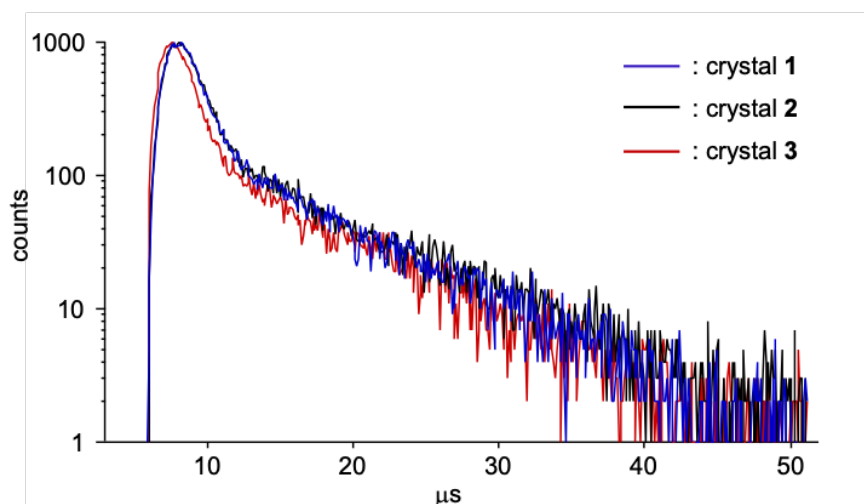


Figure 2-16. Emission decay profiles of the crystal **1**, **2**, and **3** measured at room temperatures (described as blue, black, and red bold lines, respectively). The emission decays were monitored at 586 nm, 573 nm, and 687 nm, respectively, under 370 nm of excitation.

Table 2-2. Emission lifetimes fitted from the emission decays and quantum yield of crystals **1** and **2**

Sample	$\tau_{av} / \mu s^{a,b}$	$\tau_1 / \mu s^a$ (A / -)	$\tau_2 / \mu s^a$ (A / -)	CHI	Φ^c
crystal 1	5.42	1.17 (0.44)	8.72 (0.56)	1.26	0.014
crystal 2	5.61	1.29 (0.46)	9.33 (0.54)	1.22	0.029
crystal 3	4.56	1.29 (0.57)	8.84 (0.43)	1.44	0.010

^a: $\lambda_{ex} = 370$ nm, $\lambda_{em} = 586$ nm for crystal **1**, $\lambda_{em} = 573$ nm for crystal **2** and $\lambda_{em} = 687$ nm for crystal **3**. ^b: $\tau_{av} = \sum \tau_n A_n$.

^c: $\lambda_{ex} = 365$ nm for crystal **1** and **2**, $\lambda_{ex} = 395$ nm for crystal **3**.

TD-DFT Calculations

All calculations were performed using the Gaussian 16 (revision C.01 and E.01) program package²⁵. The singlet state TD-DFT calculations of the NHC Cu(I) coordination polymers in the crystal **1**, **2** and **3** were performed with the goal of understanding relationship between the fold modes and their emission properties. In the calculations, the B3LYP functional and the SDD basis set with an effective core potential for metals and the 6-31G* for the other atoms were used. The geometries containing two NHC Cu(I) moiety and three pyrazines were taken from the single-crystal structures of **1** to **3** with the counter anions. The position of the heavy atoms were fixed and only the positions of H atoms were optimized using the DFT calculations under B3LYP/6-31G* before TD-DFT calculations. The simulated UV/vis absorption spectra and the excitation spectra from the experiments exhibited a similar tendency on the traces (Figure 2-17).

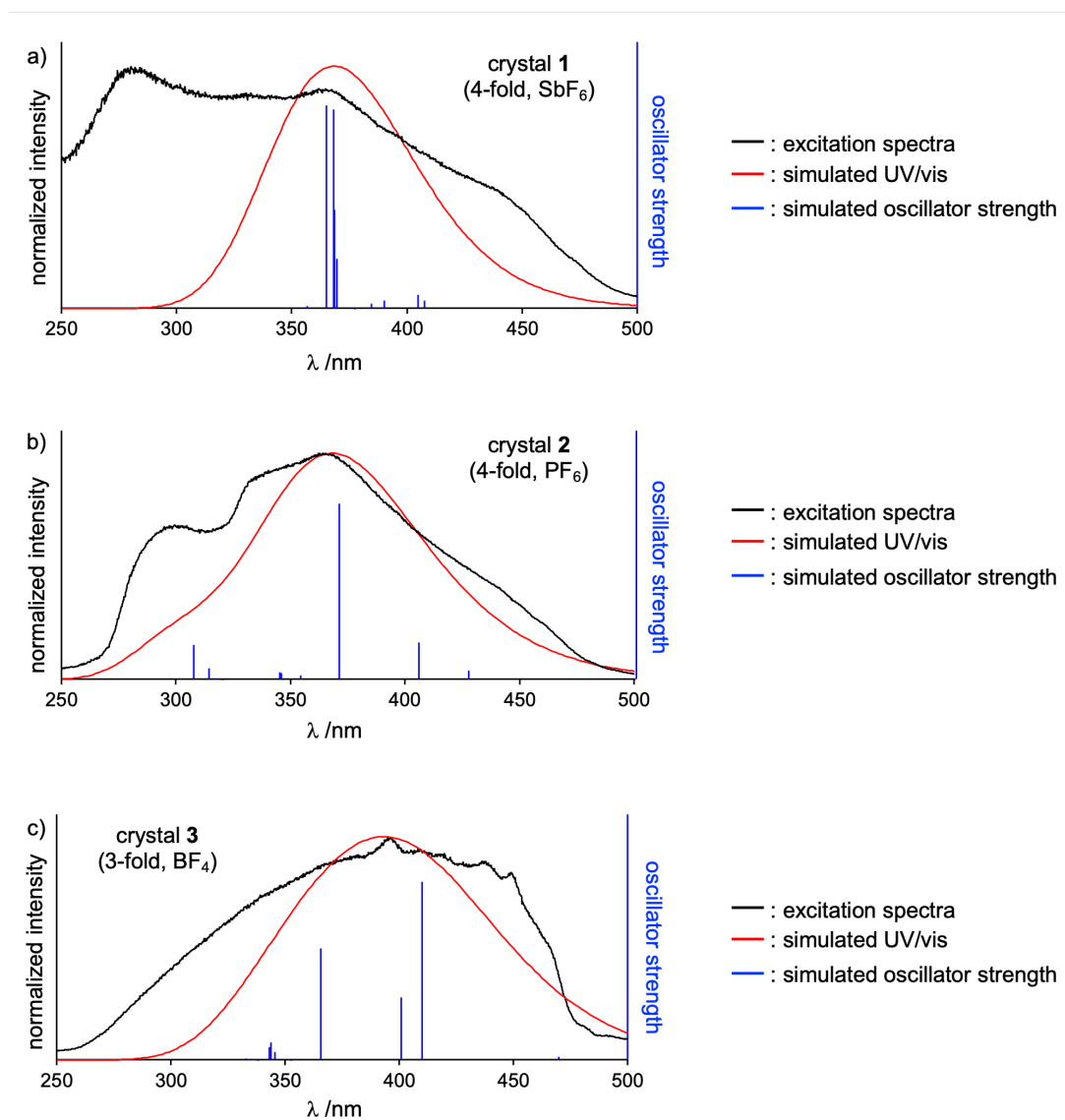
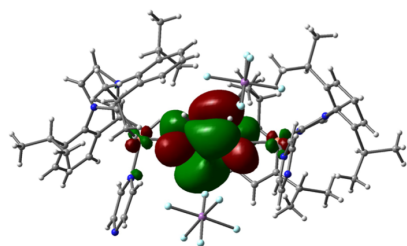
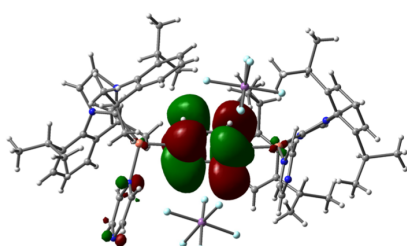


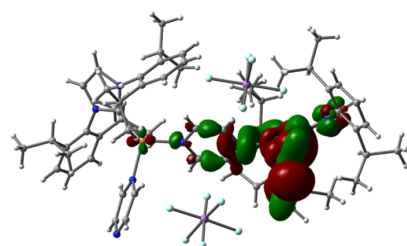
Figure 2-17. Comparison of experimental and theoretical studies on emission properties of the crystal a) **1**, b) **2** and c) **3**. Excitation spectra of the crystal **1**, **2** and **3** (black solid-line) observed at the emission peak top. Simulated UV/vis absorption spectra of the NHC Cu(I) complex **1**, **2** and **3** in the crystals (red solid-line, respectively) and oscillator strengths (blue sticks) based on the singlet state TD-DFT calculations of the geometries derived from the single crystalline structures of **1**, **2** and **3** measured at (B3LYP/6-31G* for C, H, N, F and SDD for Cu).



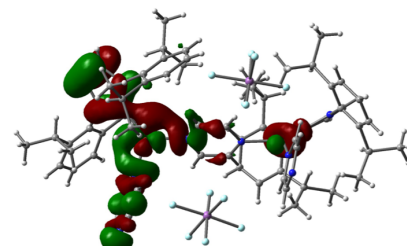
LUMO



LUMO+1

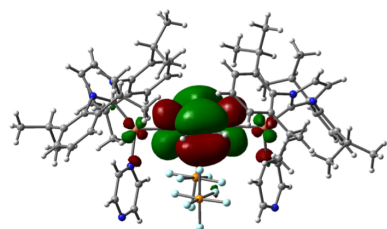


HOMO

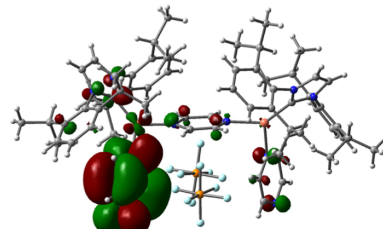


HOMO-1

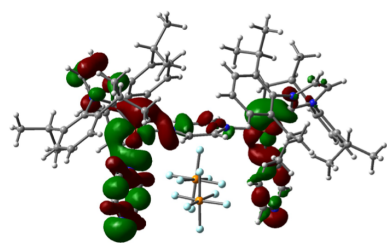
Figure 2-18. Selected orbitals involved in singlet transitions of the Cu(I) complex **1**.



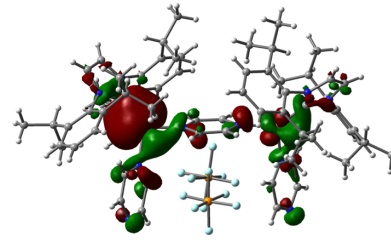
LUMO



LUMO+1



HOMO



HOMO-1

Figure 2-19. Selected orbitals involved in singlet transitions of the Cu(I) complex **2**.

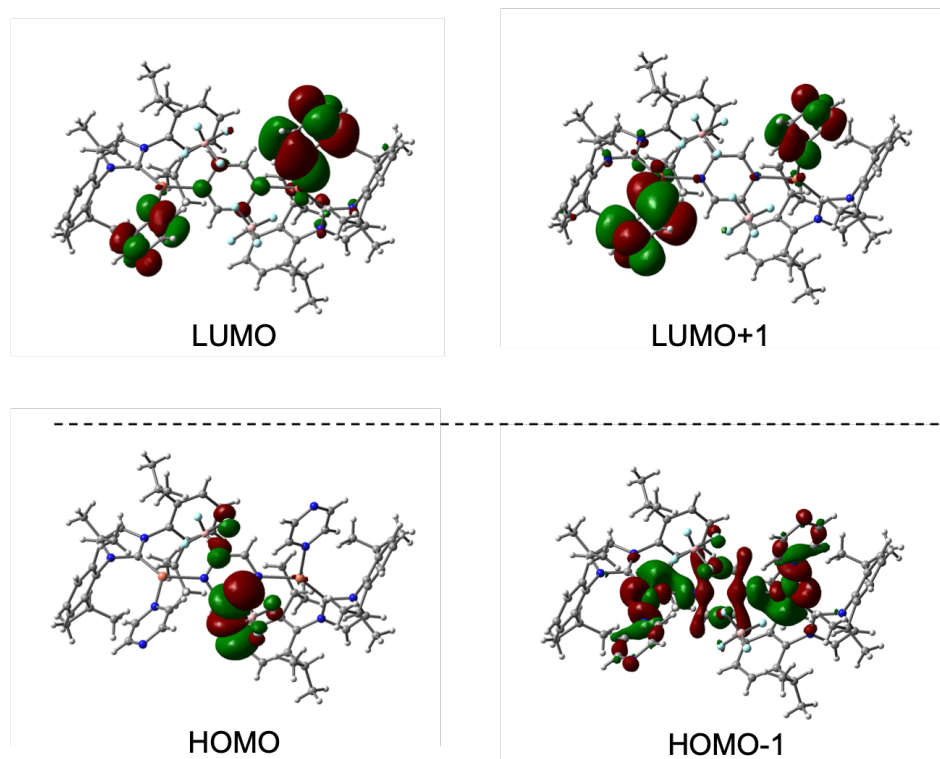


Figure 2-20. Selected orbitals involved in singlet transitions of the Cu(I) complex **3**.

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Chapter 3.

Crystalline Molecular Rotors via NHC Metal Complexes: Control of the Molecular Rotation and Emission Property

3.1 Introduction

Molecules in crystals are generally packed in highly dense close-packing environments and show limited atomic and molecular motion. However, design elements that generate sufficient volume near axially linked molecular rotators allows for large angular displacements, even in the solid phase (Figure 3-1a). With highly ordered structures and fast rotatory dynamics precisely defined at the molecular and macroscopic scales, it has been suggested that such "*amphidynamic crystals*"¹⁻⁵ are a promising platform for the development of smart materials and molecular machines.² In these systems, solid-state functions arise from molecular rotations and reorientations that cause anisotropic changes in most physical properties. Examples reported include materials that present useful gas adsorption/desorption^{3,5}, semiconducting behavior⁶, tunable optics⁷⁻⁸, and mechanically responsive properties^{9-11,14}, among several others^{4,12}. In a recent example, it was reported that a series of luminescent amphidynamic crystals where the intensity of their solid-state phosphorescence is correlated to time-dependent changes in conjugation that result from the rotational motion of the aromatic luminophores that are part of Au(I)-containing complexes¹³⁻¹⁴. Crystalline molecular rotors capable of controlling physical properties by altering the molecular rotation represent a critical development in solid-state functional materials, as well as a promising strategy to transduce molecular-level functions to the macroscopic scale. However, the construction new structural motifs to control rotary motions in solid-state remains a significant challenge.

Gyroscope-like molecular rotors^{1,2,7,15,16}, dumbbell-shaped molecules^{1,2}, and porous materials such as metal-organic frameworks (MOFs)^{3,5,12,17-21} have been employed as general platforms of amphidynamic crystals. Molecular gyroscopes possessing a functional rotator connected to an enclosing stator by triple bonds serving as the rotation axle, were first proposed by Garcia-Garibay *et al.* for constructing crystalline molecular rotors.^{1,2} This was followed by the development of bridged trityl-based molecular gyroscopes¹⁵ by the same group, metal complexes with bridgehead diphosphine cages¹⁶ by Gladysz *et al.*, and phenylene rotors shielded by bridging silyl cages⁷ by Setaka *et al.* (Figure 3-1b). All these examples were shown to have rotational motion limited by intra-molecular steric effects with the enclosing stators.^{1,2} Unfortunately, structural optimization in these examples has been limited by the inherent difficulties in the synthesis of their multi-bridged macrocyclic structures. Efficient access to a wide range of amphidynamic crystals was shown to be possible by taking advantage of dumbbell-shaped structures with open topologies, as shown by the Garcia-Garibay group (Figure 3-1c)^{1,2}. In this particular design, trityl stators create a convex shape around the central rotator that prevents intra-molecular steric interactions, but inter-molecular steric shielding has been shown to be largely unpredictable².

In contrast to gyroscope-like or dumbbell-shaped close-packed molecular rotors, highly porous metal organic frameworks (MOFs) can be built with molecular rotors that have minimal steric hindrance^{3,5}. In the case of arylene dicarboxylates used both as building blocks and molecular rotators in zinc-oxide and paddle wheel MOF structures, electronic barriers to rotation are the result of changes in conjugation between the central phenylene rotator and the carboxylate groups that are coordinated to the metal center. For example, a 1,4-phenylene-dicarboxylate rotator in MOF-5 showed relatively slow two-fold rotational motion due to a high electronic barrier ($E_a = 11.3 \pm 2$ kcal/mol), despite having a very low packing density and no steric hindrance in solid-state (Figure 3-1d)¹⁷. By contrast, non-aromatic dicarboxylates acting as molecular rotators in the same MOF architectures have insignificant rotational electronic ($E_a < 0.2$ kcal/mol), which result in the fastest molecular rotations ($\sim 10^{10}$ Hz) reported thus far in the crystalline phase, as recently demonstrated by Garcia-Garibay *et al.*²¹ and by Sozzani *et al.*²²

Searching for a new structural entry for the development of molecular rotation in the solid-state I envisioned a semi-enclosed, encapsulating bimetallic complex rotor with a concave-shaped bulky N-heterocyclic carbene (NHC) stator, and an aromatic rotator co-axially coordinated to transition metals (Cu or Au) along the rotational axis (Figure 3-1e). The bulky concave-shaped NHC ligands have been used to design organometallic catalysts due to their shielding effects that protect the metal-center during reactions while also providing them with steric interactions that control the stereochemistry of products^{23,24}. I reasoned that the shielding feature of the bulky NHC groups should shield the rotator in a manner that is similar to that of the enclosed rotators of molecules gyroscopes. At the same time, the metal-centered axle should be able to modulate the rotary motion by altering the steric hindrance and electronic interactions between the central rotator, the variable metal center, and the carbene carbon. Under these conditions, it should be possible to tune the length of the axle by altering the metal atoms as they have different sizes, while π -back donation from their filled d orbitals to the π^* orbitals of the ligands can also be influenced by the torsional angles of the ligands^{25,26}. Considering the high accessibility and structural diversity of the NHC ligands, as well as the simplicity of complex formation with various transition metals, I hypothesize that this NHC-based design will afford a promising new platform for the construction of tunable amphidynamic crystals (Figure 3-1e).

To explore this concept, I prepared two novel Cu(I) and Au(I) binuclear complexes bridged by deuterated pyrazine, as a rotator and internal ligand, with two 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr-NHC) groups at the two ends (Figure 3-1e). The concave-shaped IPr-NHC ligands constitute the enclosing stator while the pyrazine ring with π -accepting ability from the d orbitals of

either Cu(I) or Au(I) metals plays the role of the central rotator. Red and blue luminescent crystals of NHC Cu(I) rotor **4** and Au(I) rotor **5**, respectively, were obtained in good yields, and were shown to have the expected structures by single-crystal X-ray diffraction (XRD). Variable temperature solid-state ^2H NMR confirmed that the two crystals are amphidynamic with 2-fold rotational motion. Arrhenius plots built with rotational frequencies obtained by line shape analysis revealed activation energies (E_a) of 12.3 kcal/mol and 8.4 kcal/mol for crystals of Cu(I) rotor **4** and Au(I) rotor **5**, respectively. DFT calculations revealed that the lower rotational barrier in the case of the Au(I) rotor **5** is the result of a smaller intra-molecular steric repulsion between the bulky NHC ligand and pyrazine rotator that correlates with the elongation of the axle, and a larger stabilization of the transition state by greater π -back donation from the metal to the rotator due to the increased overlap between the d and π^* orbitals.

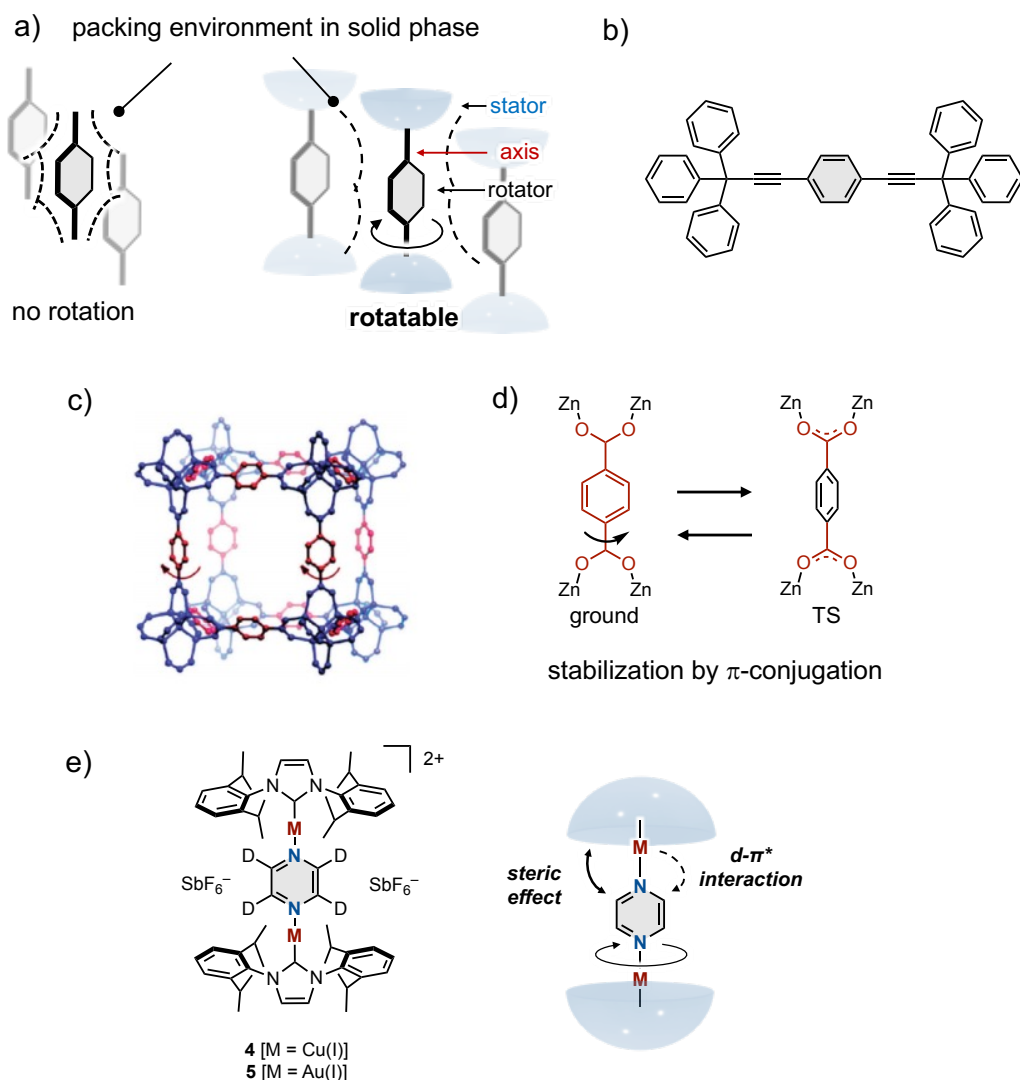


Figure 3-1. Crystalline molecular rotors built with a concave-shaped NHC group and the implantation of metals to rotation-axis. **a**, Molecular rotation and packing environment in the solid phase. **b**, Dumbbell shape molecular rotors possessing trityl-based stator. **d**, MOF-5 with phenyl groups acting as rotators and linkers with high rotational barriers due to the loss of π -conjugation at the transition state. **e**, Representation of the newly designed concave-shaped NHC cationic, luminescent molecular rotors **4** and **5** with Cu(I) or Au(I) metals implanted along the rotational-axis.

3.2 Results and Discussion

Synthesis and Characterization.

Cationic Cu(I) and Au(I) molecular rotors with NHC ligands (**4** and **5**) were obtained as crystalline solids in 73% and 68% of yield (Figure 3-2a and 2b), respectively, by anion exchange from deuterated pyrazine, chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]Cu(I) [IPrCu(I)Cl] or chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]Au(I) [IPrAu(I)Cl], and AgSbF₆ (Figure 3-2a and b). Crystallizations were performed by solvent diffusion from DCM solutions of **4** or **5** into layered hexane. Crystals **4** and **5** were shown to emit red and blue luminescence, respectively, under UV light ($\lambda=365$ nm) at ambient temperature as shown in Figures 3-2a and 2b. Solvent inclusion was not observed by either single crystal XRD, or by thermogravimetric analysis (TGA) (Figures 3-2d–g and 3-6). Crystalline samples were characterized in solution by ¹H and ¹³C NMR spectroscopy, and in the solid-state by elemental analysis, TGA, and single-crystal X-ray diffraction (XRD) (see Experimental Section).

Single Crystal X-Ray Diffraction of **4** and **5**.

Single crystal XRD measurements confirmed the expected encapsulating structure of the NHC Cu(I) rotor complex **4**. The NHC Cu(I) complex **5** crystallized in the monoclinic space group *P2₁/c* with four molecules per unit cell (*Z*=4) (Table 3-2). Several key structural parameters are described in Figure 3-2c. The concave shaped IPr-NHC ligand having a cone angle of ca. 164°, as evaluated by the Tolman cone angle definition, was coordinated to the Cu(I) atom with distance of 1.873(2) Å (*l_{M-NHC}*) (Figure 3-2c and d)²³. The pyrazine rotator was coordinated to the two Cu(I) metals with the same length of 1.896(2) Å from either pyrazine nitrogen of to the Cu(I) center (*l_{M-Py}*). The NHC carbene carbon, the Cu(I) atoms, and the pyrazine rotator were co-linearly arranged, as though the transition metal had been implanted into the rotational axis with a total length (*l_{M-NHC}* + *l_{M-Py}*) of 3.769 Å. The dihedral angle θ between the NHC plane and the pyrazine ring was 15.5°, showing that the rotator was slightly rotated from the plane of the NHC (Figure 3-2d). The SbF₆ anions were positioned between the diisopropylbenzene substituents of the alpha and beta side of NHC ligands in a molecule with having a distance of 2.505 Å from the closest proton of the isopropyl moiety of the NHC ligand to the fluorine atom of the SbF₆ anion. Additionally, the anions have a distance of 2.917 Å from the closest fluorine atom of the anion to the pyrazine plane, which are relatively far-away from the bridging pyrazine rotator comparing to that of mononuclear Cu(I) cationic complex bearing the NHC moiety and pyridine as ligands²⁷. The observed geometries of anions near the Cu(I) complex **4** indicated that access of the anions to the central rotator

was obstructed by the bulkiness of the NHC ligands, which provided local volume for motion of the rotator to occur (Figure 3-2c and 3-7).

Crystal structure of the NHC Au(I) rotor complex **5** was also obtained by single crystal XRD, and the structure was very similar with that of crystal **4** (Figures 3-2d and 3-8). The Au(I) complex **4** was packed in the space group $P2_1/c$, and structure of the metal complex with packing manner of the SbF_6 anions were homologous to that of the Cu(I) complex **4** (Figures 3-2d, 3-8, and Table 3-2). Geometry parameters $l_{\text{M-NHC}}$, $l_{\text{M-Py}}$, and θ of the Au(I) complex **5** showed differences from those of the Cu(I) complex **4**. The $l_{\text{M-NHC}}$ and $l_{\text{M-Py}}$ of the Au(I) complex **5** were 1.95(2) Å and 2.04(1) Å, respectively, indicating that the length of rotational-axis ($l_{\text{M-NHC}} + l_{\text{M-Py}}$) was ca. 0.2 Å longer than that of the Cu(I) complex **4**, reasoned by the larger van der waals radius of Au than Cu atom. A larger dihedral angle θ was observed for the Au(I) complex **5** (20.7°) than that of the Cu complex **4** (15.5°, Figure 3-2c,d and Table 3-1).

Single-crystal XRD measurements between 195 K to 350 K, with four intermediate points at 250, 275, 300, and 325 K (Figure 3-9–10 and Table 3-2), revealed no significant structural changes and, similarly, differential scanning calorimetry (DSC) profiles in the range 195–350 K showed no significant peaks indicating that the crystals **4** and **5** have no thermally triggered phase transitions (Figure 3-12).

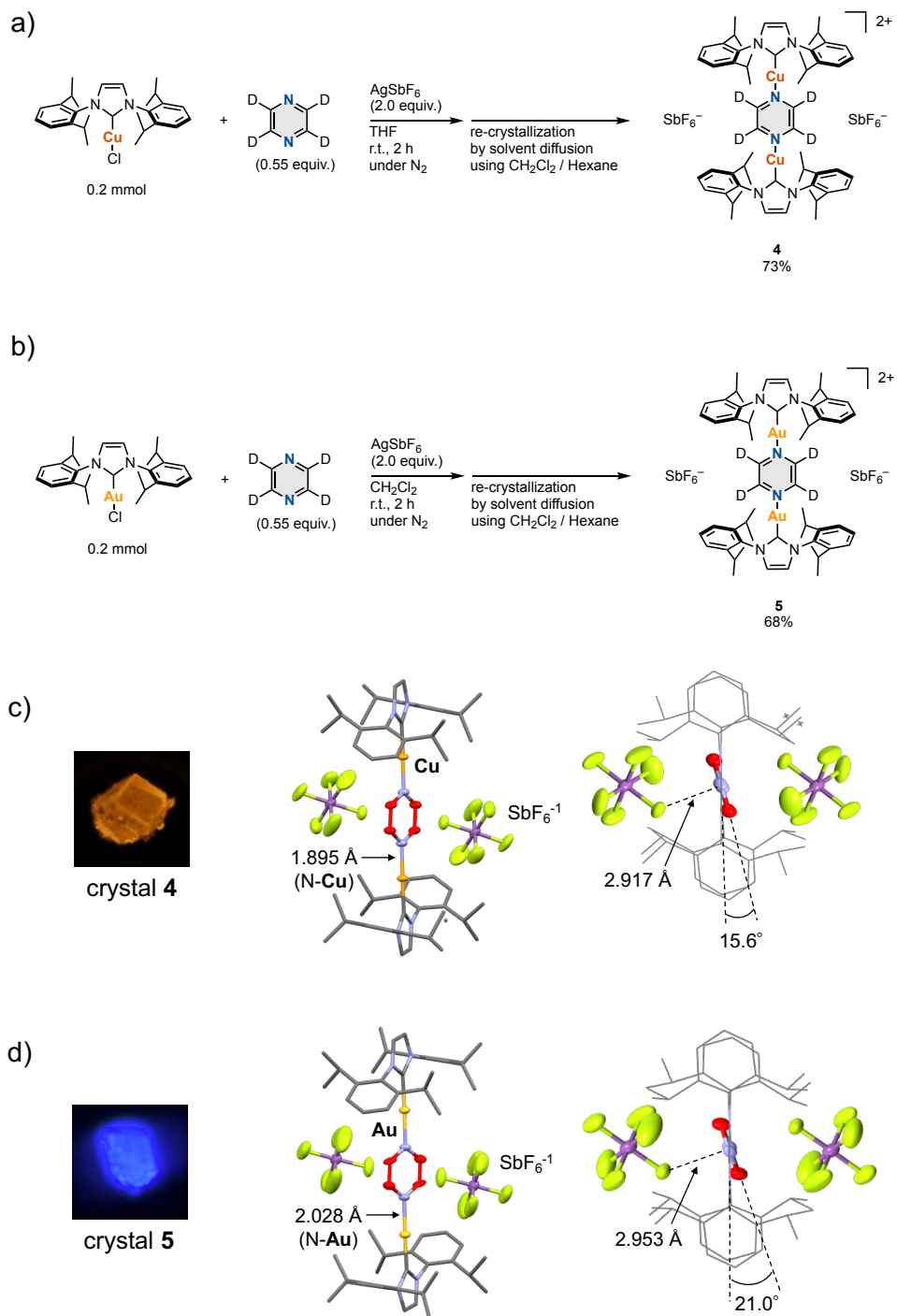


Figure 3-2. Synthesis and crystal structures of 4 and 5. a Synthesis of the NHC cationic rotors Cu(I) 4 and, b Au(I) rotor 5. Crystal structures of c, 4 and d, 5 with the NHC ligands shown in stick bar and pyrazine rotator highlighted in red.

Table 3-1. Key solid-state structural parameters of the NHC rotor 4 and 5

samples	$l_{\text{M-Py}} / \text{\AA}$	$l_{\text{M-NHC}} / \text{\AA}$	$\theta / ^\circ$
4 at 275 K	1.896(2)	1.873(2)	15.5
4 at 350 K	1.895(2)	1.871(2)	15.1
5 at 275 K	2.04(1)	1.95(2)	20.7
5 at 350 K	2.04(1)	1.96(1)	20.5

Characterization of Rotational Dynamics by Variable Temperature Solid-State ^2H NMR

In order to investigate the rotational dynamics of the pyrazine- d_4 rotator in crystals of NHC complex **4** and **5**, I carried out variable temperature solid-state (SS) ^2H NMR spin-echo measurements that were followed by line shape simulations. It has been established that the method is ideally suited to determine the dynamics of deuterium-enriched moieties with site-exchange rates in the dynamic range of ca. 10^4 - 10^7 s^{-1} ²⁵. Figures 3-3a and b show the experimentally obtained spectra (solid black lines) measured in the temperature range between 340 K and 275 K. Simulated SS ^2H NMR spectra (dashed red lines) were obtained using a quadrupolar coupling constant (QCC) of 180 kHz, a cone angle of 60° formed between the rotational 1,4-axis and C-D bond vector, and Brownian jumps of 180° , in agreement with the crystal structures (Figure 3-3c)²⁸.

The calculated line shapes provided a reasonable match with the experimental spectra with the Cu(I) complex **4** experiencing dynamics in the intermediate exchange regime, as given by a simulated rotational frequency of 2.80 MHz. Further measurements at 325, 315, 300 K were simulated with rotational exchange frequencies (k_{rot}) of ca. 1.20, 0.70, and 0.20 MHz, respectively (Figure 3-3a). By contrast, the spectra of Au(I) complex **5** measured at 325, 300, 290, and 275 K were simulated with k_{rot} values of 13.5, 5.00, 3.00, and 1.25 MHz, which are clearly greater than those of the Cu(I) complex **4**. Notably, the Arrhenius plots constructed from the k_{rot} of **4** and **5** presented a significant difference in the corresponding activation energy ($E_{\text{a-Cu}}$ and $E_{\text{a-Au}}$). As shown in Figure 3-3d, the Cu(I) complex **4** showed an $E_{\text{a-Cu}} = 12.3 \text{ kcal/mol}$ and a pre-experimental factors $A = 2.2 \times 10^{14} \text{ s}^{-1}$. In contrast, results from the Au(I) rotor **5** revealed $E_{\text{a-Au}} = 8.4 \text{ kcal/mol}$ and $A = 6.6 \times 10^{12} \text{ s}^{-1}$. We note that the line shapes of both complexes measured above 275 K were reasonably characterized by a simple 180° site exchange model approaching the fast exchange regime.

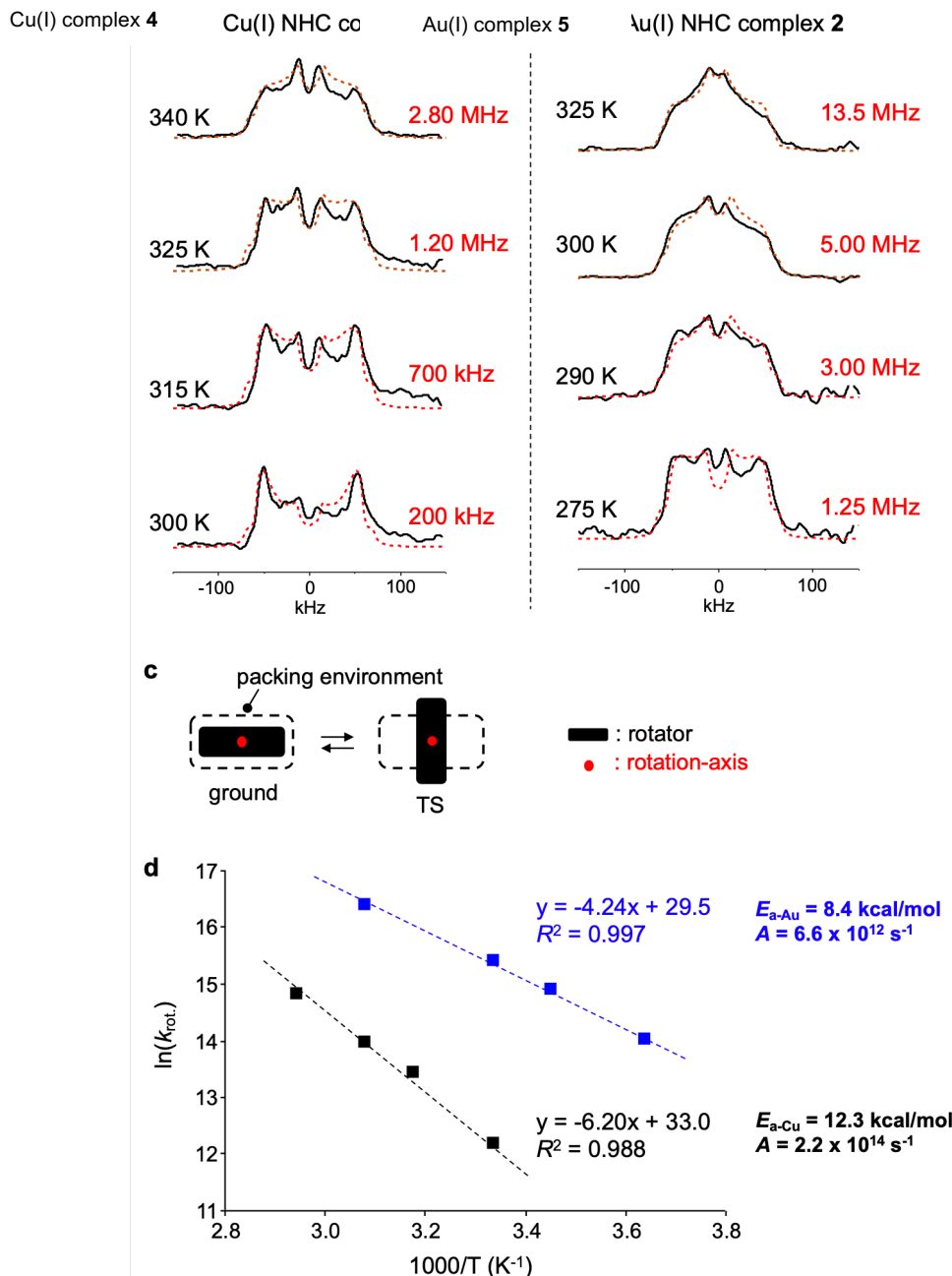


Figure 3-3. Variable temperature (VT) solid-state (SS) NMR studies of crystals 4 and 5. Experimental SS ^2H NMR spectra of **a**, the Cu(I) rotor **4** and **b**, the Au(I) rotor **5** represented in black solid line and the simulated spectra illustrated in red dashed line. **c**, Representation of the ground and transition states of 2-fold rotation in solid-state. **d**, Arrhenius plot with evaluated energy barrier (E_a) and pre-exponential factor (A) of pyrazine rotator dynamics in crystal **4** and **5** described in black and blue, respectively.

Investigation into the Origin of Energy Difference in Activation Barriers between Rotor 4 and 5

In order to understand the rotational dynamics of NHC Cu(I) rotor **4** and Au(I) rotor **5**, we carried out DFT calculations using Intramolecular Symmetry-Adapted Perturbation Theory (I-SAPT)²⁹ and Natural Bond Orbital (NBO) analysis^{30,31} to gain insights, respectively, into their steric and electronic effects. I considered that steric repulsion between the rotator and the NHC ligand should increase the energy of the rotational transition state while π -back donation from the filled d orbitals of the metal to the π^* orbitals of the rotator should stabilize it. I hypothesized that Au(I) rotor **5** would experience a weaker steric effect and a stronger π -back donation than those of Cu(I) rotor **4** because of the longer length of the rotational axis and the relatively large size of d orbitals of the Au(I) atom.

To obtain geometries and energy values for the rotational ground and transition states (TS) I took the initial geometries of both NHC bimetal cationic complexes from the crystal structures, followed by optimizing the positions of H atoms by fixing the geometries of heavy atoms using DFT calculation with B3LYP/6-31G level³². To avoid complication on the calculations and further analysis, the counter anions were omitted. The geometry-optimized ground states were calculated using ω B97XD/6-31G(d) for organic atoms and LanL2DZ for metals with all but the carbons and hydrogen atoms of the pyrazine rotator fixed in order to simulate the rigidity of the local rotator environment³². The TS for the 2-fold rotation of rotors **4** and **5** were obtained by the Locally Updated Planes (LUP) method, one of the conventional path optimization calculations using the GRRM17 program³³⁻³⁵. The atoms on the NHC ligands and metals were fixed, and the calculation for the TS set at the same level as that used for the ground state.

The calculated ground state geometries of rotors **4** and **5** were analogous to those obtained from the single crystal XRD, and the calculated energy barriers qualitatively matched the tendency observed from the ²H-SS-NMR analyses. The optimized ground-state geometries of the two rotors showed that the pyrazine rings were slightly tilted from the NHC planes with dihedral angles θ of ca. 6.0–7.0°, which were ca. 10 ° smaller than those observed in the crystal structures (Figures 3-4a and b and 3-14–15). Transition state calculations indicated that the pyrazine rotators are orthogonal to the planes of the NHC (θ = ca. 90°), with the greatest steric congestion occurring between the isopropyl groups on the ligands and the rotator (Figures 3-4a and b). The calculated energy barriers for the rotations were 10.2 kcal/mol

for the Cu(I) rotor **4** ($\Delta E_{\text{cal.-Cu}}$) and 6.0 kcal/mol for the Au(I) rotor **5** ($\Delta E_{\text{cal.-Au}}$), respectively. The ca. 4.0 kcal/mol of higher energy barrier of the Cu(I) rotor **4** is consistent with the experimental activation energies determined by SS-NMR studies, although the calculated values are ca. 2.0 kcal/mol lower (Figures 3-4a and b). We propose that the difference between the SS ^2H NMR experiments and calculations may originate from steric interactions with the SbF_6 anions, which were omitted in the calculations.

As seen in the crystal structures, changing the metal from Cu to Au increased the length of rotation-axis by ca. 0.2 Å, which is expected to cause a smaller steric effect in the case of Au (I) rotor **5**. Steric effects quantitatively evaluated by the I-SAPT analysis method using the TS geometries (Figure 3-4c and 3-18) indicated that calculated repulsive interactions in Cu(I) rotor **4** and Au(I) rotor **5** were 4.2 kcal/mol and 2.6 kcal/mol, respectively (Figure 3-4c and Table 3-3).

As shown by the NBO analysis of the transition states for both rotors in Figure 3-4d, the stabilization via the π -back donation from d orbitals of the metals to a π^* orbital of the pyrazine rotator gives energy values of -5.2 kcal/mol for Cu(I) rotor **4** and -7.2 kcal/mol for Au(I) rotor **5**. Calculations indicated that the Au(I) rotor **5** has a larger d orbital as well as more d and π^* overlap than those of the Cu(I) rotor **4**. These results suggest that stabilization via π -back donation in the TS can be one of the major factors for determining the rotational barriers, and the magnitude can be enhanced by changing metals on the rotation-axis from Cu to Au. To evaluate the electronic stabilization on the TS geometry in a different way, we investigated the ground and transition states for the rotation of a model rotor complexes with less steric hinderance by introducing methyl groups instead of bulky 2,6-diisopropylphenyl groups on the NHC rings (Figure 3-19). Notably, the orthogonal conformation between pyrazine and NHC ring goes from being the rotational transition state geometry in the bulky NHC rotors **4** and **5**, to become the ground state in the non-sterically encumbered models of both Cu(I) and Au(I) rotors. NBO analysis of these geometries indicated that the Au(I) rotor has 2.8 kcal/mol larger stabilization energy via the π -back donation than the Cu(I) rotor. This difference in the electronic stabilization effect for model complexes of Cu(I) and Au(I) have the same trend as those observed in the actual bulky complexes (Figure 3-20). The d orbitals interactions with the NHC ligands were ca. 8–16 kcal/mol stronger than those of between the metals and the pyrazine, as evaluated by further NBO analysis of both the actual and modeled rotors. Based on these results, we interpret that the ca. 4.0 kcal/mol lower rotational barrier of the Au(I) rotors is the result of ca. 1.6 kcal/mol of the weaker steric repulsive interactions and ca. 2.0 kcal/mol of the stronger stabilization on the TS by the π -back donation.

These analyses suggest that my design strategy based on the encapsulating NHC metal complexes does make it possible to modulate the stabilization effect from the π -back donation from the metals to the rotator. Unfortunately, a simple numerical analysis of the calculated rotation barriers ($\Delta E_{\text{cal.-Cu}}$ and $\Delta E_{\text{cal.-Au}}$) cannot not be obtained from the energies of derived from steric (I-SAPT) and π -back donating interactions (NBO) because of the different calculation methods as well unaccounted lattice contributions (Figure 3-21 for details).

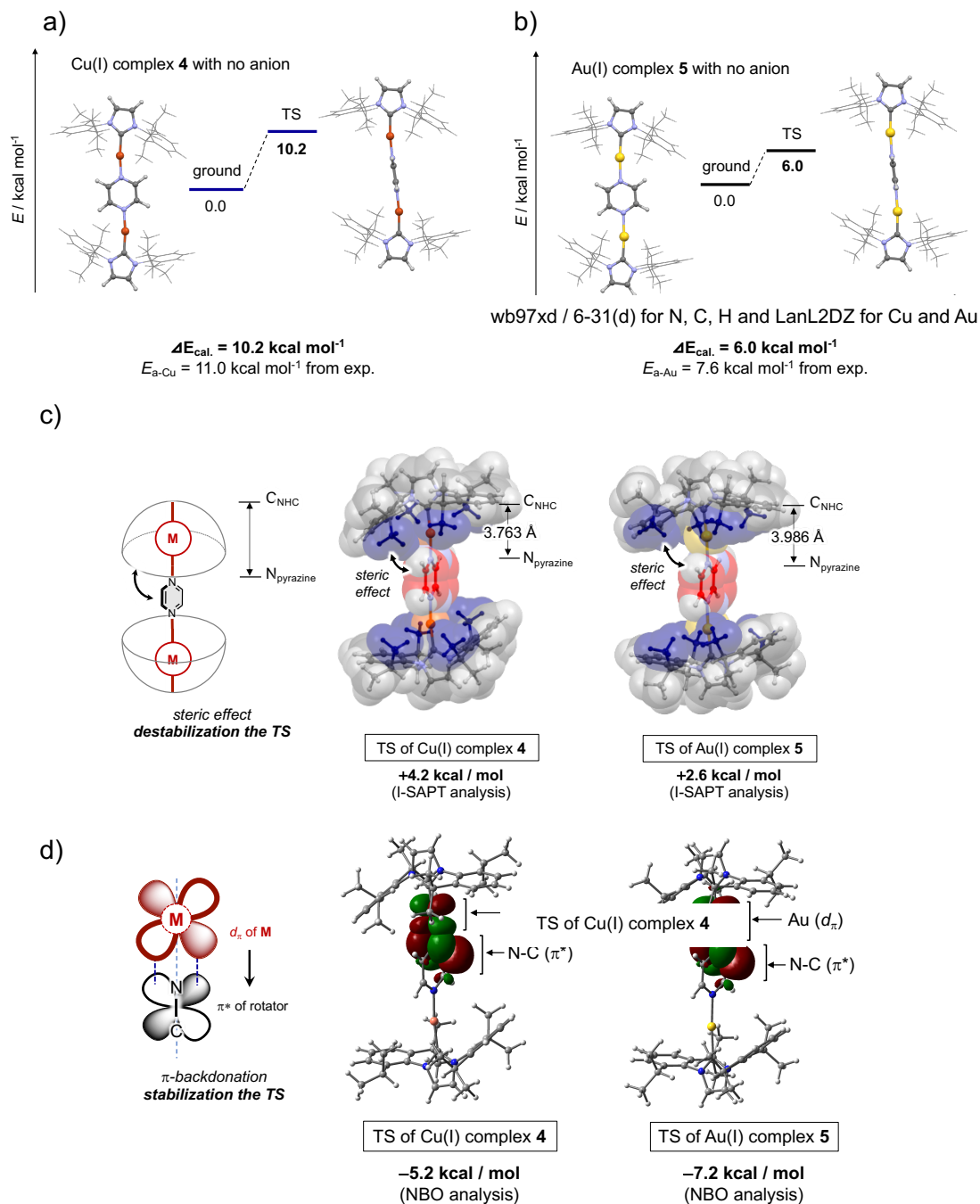


Figure 3-4. DFT calculations with NBO and SAPT analysis of rotor 4 and 5. Calculated energy diagrams and the obtained structural geometries of ground state and TS of **a**, Cu(I) rotor **4** and **b**, Au(I) rotor **5**. **c**, Evaluated steric repulsive interactions on TS for rotor **4** (left) and **5** (right) using DFT-SAPT analysis and the TS geometries illustrated in space-filling. **d**, Estimated electronic interaction via π -back donation from d_π of metals to π^* of pyrazine for rotor **4** (left) and **5** (right).

Solid-State Emission Properties of Rotor **4** and **5**.

As shown in Figures 3-5a–b, crystals of Cu(I) rotor **4** and Au(I) rotor **5** exhibited significantly different emission, red and blue, respectively, under irradiation with UV light ($\lambda_{\text{ex}} = 365$ nm) at room temperature. The emissions of **4** and **5** in CH_2Cl_2 solutions were very weak as compared to those in the solid-state. Relatively high quantum yields (Φ) as 0.14 for crystal **4** and 0.12 for crystal **5** suggest that their emission properties are determined by their aggregated structures (Table 3-4 and Figure 3-22–24)³⁶. Crystals of Cu(I) rotor **4** showed a broad emission with maximum intensity ($\lambda_{\text{em.max}}$) at 600 nm, and broad excitation band with a peak ($\lambda_{\text{ex.max}}$) at 380 nm (Figure 3-5a). On the other hand, crystal **5** exhibited the blue-shifted excitation and emission spectra with shorter $\lambda_{\text{ex.max}}$ at 345 nm and $\lambda_{\text{em.max}}$ at 420 nm (Figure 3-5b). This trend was also documented with time-dependent (TD) DFT calculations using the single-crystal XRD structures of **4** and **5** at room temperature as the input for the calculations (Figure 3-25). The calculated excitations exhibit qualitatively good agreement with the measured $\lambda_{\text{ex.max}}$ of the excitation spectra (Figure 3-25), and the contributed molecular orbitals were identified as transitions from HOMO and HOMO-6 to LUMO (Figures 3-5e–f and Tables 3-5–6). The LUMOs of both rotors mainly consisted of orbitals on the pyrazine and partial Cu or Au metal participations, as shown in Figures 3-5e and f. The HOMO and HOMO-6 of Cu(I) rotor **4** were distributed over the pyrazine and imidazole planes with Cu(I) atoms on the rotation-axis. In contrast, those orbitals in Au(I) rotor **5** were majorly localized on the NHC ligands and Au(I) atoms where orbitals in the pyrazine moiety were scarcely contributed (Figures 3-5e–f and Tables 3-5–6). These results of the TD-DFT calculation studies indicated that photoexcitation states of both crystalline rotors can be characterized as ligand-to-ligand with metal charge transfer involvement. The more largely delocalized HOMO and HOMO-6 of Cu(I) rotor **4** as compared to that of the Au(I) rotor **5** might explain the red shifted excitation and emission bands in the former.

Crystals of Au(I) rotor **5** exhibited a significant and reversible emission enhancement by lowering temperature from 295 K to 153 K (Figure 3-5d). An emission lifetime ($\tau_{\text{av.}}$) of 0.87 μs measured at room temperature (Table 3-4 and Figure 3-24) indicates the involvement of triplet states in the emission process. I noted that the rotational dynamics of pyrazine rotator clearly turned in slower during this cooling and the phosphorescence occurs near the range of the time scale for the rotations (ca. 0.3 μs for the Au(I) rotor **5** at the room temperature). The previous luminescent Au(I)-aryl complexes with amphidynamic properties, the arylene rotations have induced large rate of emission quenching because the altered geometry of chromophore by the rotation induces change in the excited and ground electronic states^{13,14}.

I interpreted that the observed emission enhancement of Au(I) rotor **5** by the cooling may also correlate with the suppression of molecular rotation, as expected for the molecular rotation-induced emission quenching in solid-state^{13,14,37}.

Emission enhancement of crystal **4** by the lowering temperature was also observed (Figure 3-5c), and the emission decay measured at room temperature was fitted with having 3.06 μs of τ_{av} . The μs scale of emission decay was near the pyrazine rotation time scale (ca. 5.0 μs for the Cu(I) rotor **4**), indicating that conformational change via the rotation might increase the rate of nonradiative pathway as observed in the Au(I) rotor **5**. We noted that crystal **4** showed ca. 15 nm red-shifted emission by cooling the sample while no emission shift was observed in crystal **5** at the similar cooling process. The red-shifted phosphorescence emission of Cu(I) rotor **4** observed at the low temperature conditions might participate in thermally activated delayed fluorescence (TADF) at the room temperature, which was suggested by the narrow energy gap between the emission bands at the lower and higher temperatures with μs time scale of the emission lifetime³⁸.

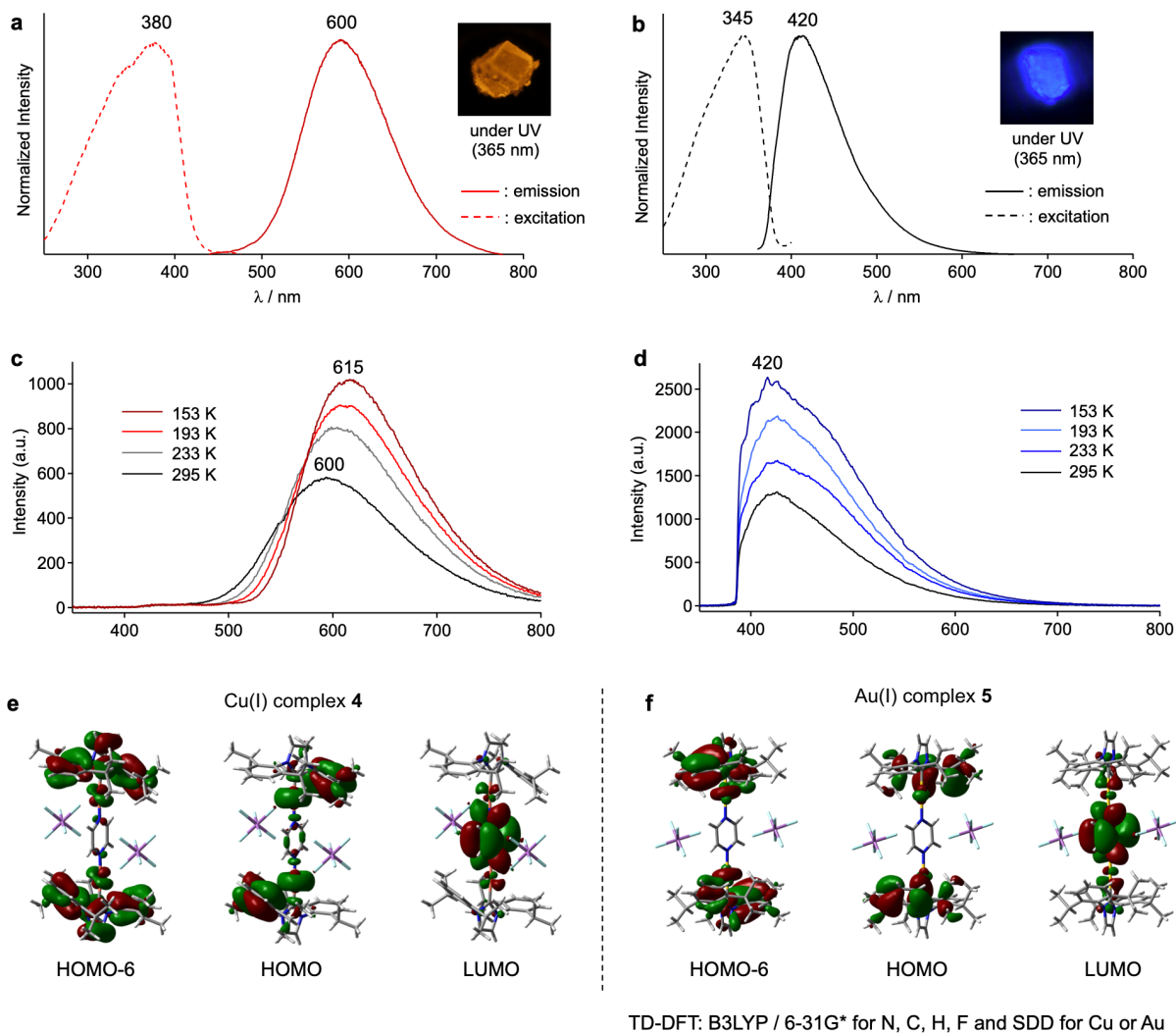


Figure 3-5. Emission and excitation spectra of crystals 4 and 5 as a function of temperature. Emission and excitation spectra of the crystal **a**, **4** and **c**, **5**. Emission spectra of crystal **b**, **4** and **d**, **5** under UV (365 nm) irradiation as a function of temperature ranging 153-295K. Frontier molecular orbitals obtained by TD-DFT calculation of the Cu(I) rotor **e**, **4** and the Au(I) rotor **f**, **5** in crystals.

3.3 Summary

I described here a novel platform of crystalline molecular rotors by utilizing the concave-shield of NHC groups with implanted transition metals (Cu or Au) on the rotation-axis. The crystalline rotors were constructed from bulky *N*-heterocyclic carbene (NHC) ligand as an encapsulating stator, deuterated pyrazine as the rotator having π -accepting ability, and Cu(I) or Au(I) metals as a center of the axle. The designed encapsulating NHC rotors are easier to synthesize compared to previously reported enclosed gyroscopic rotors, and scarcely depended on the crystal structures, which are crucial features for an encapsulating, dumbbell type design. The rotational barriers were reasonably modulated by changing the metals on the axle, which routed from steric repulsive interactions near the rotator and electronic interaction on the TS via π -back donation from the metal to the rotator. DFT calculations revealed that altering the metals from Cu to Au results in both the elongation of rotation-axis, reducing the steric hinderance, and the largely overlapped $d-\pi^*$ orbitals yielding stronger π -back donation, which lower energy barrier. The difference in electronic delocalization between the Cu(I) and Au(I) rotors yielded distinct emission colors in solid-state. Both crystalline rotors exhibited emission lifetimes on the μ s time scale, which could be quenched by the molecular rotations occurring near the time scale. A broad library of NHC ligands including bulky structures have already been developed with aim at controlling steric and electronic effects near the metal-center space. Thus, many NHC metal complex-based molecular rotors can be developed to demonstrate a similarly broad range of rotational dynamics and fine-control of rotational barriers in solid-state. These results reveal a general way to use these abundant ligands as functional stators and the metal-ligand coordination bonds as an adjustable rotation-axis for amphidynamic crystals. This platform will enable the further study on these exotic materials, which have both high structural integrity and high mobility of the molecular components, and greatly enhance the development of new functional materials based on the molecular dynamics change in the static crystalline solid.

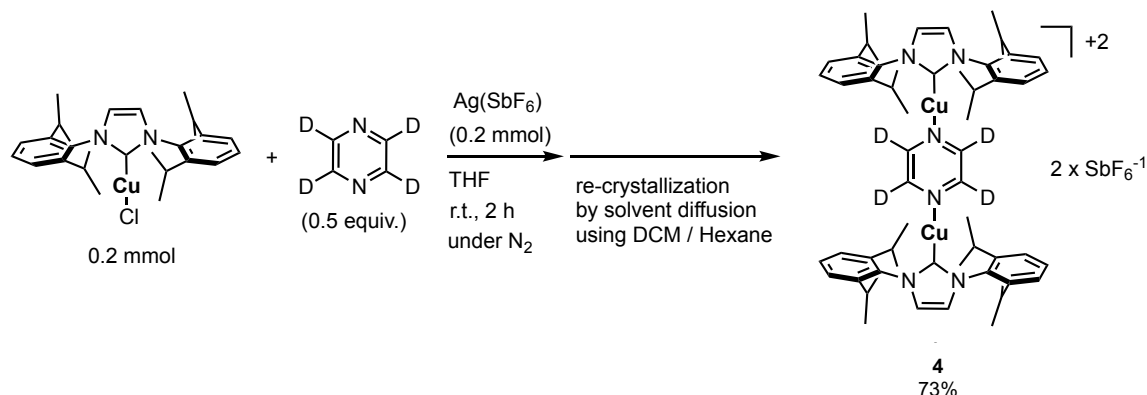
3.4 Experimental Sections

General

All commercially available reagents and solvents are reagent grade and were used without further purification unless otherwise noted. Solvents for the synthesis were purchased from commercial suppliers, degassed by three freeze-pump-thaw cycles and further dried over molecular sieves (4 Å). NMR spectra were recorded on a JEOL JNM-ECX400P, JNM-ECS400 (^1H : 400 MHz; ^{13}C : 99.5 MHz) or a Bruker AVANCE III 500 MHz spectrometer (^1H : 500 MHz; ^{13}C : 125 MHz) using tetramethylsilane and CDCl_3 as internal standards, respectively. Solid-state NMR spectra were acquired on a Bruker AVANCE III HD 600 MHz (^2H : 92.10 MHz). Emission spectra were recorded on a Hitachi F-7000 spectrometer. Absorption spectra were recorded on the basis of synchronous fluorescence spectroscopy using a Hitachi F-7000 spectrometer equipped with an integrating sphere. The emission quantum yields of the solid samples were recorded on a Hamamatsu Quantaurus-QY spectrometer with an integrating sphere. Emission lifetime measurements were recorded on a Hamamatsu Quantaurus-Tau spectrometer. Fluorescence microscopic spectra were recorded on a Photonic Hamamatsu PMA-12 Multichannel Analyzer. Elemental analyses were recorded at the Global Facility Center at Hokkaido University. Photographs were obtained using Olympus BX51 or SZX7 microscopes with Olympus DP72, Nikon D5100 digital cameras. Thermal gravimetric analysis profiles were recorded on Bruker TG-DTA2010SAT. Differential Scanning Calorimetry (DSC) profiles were measured on DSC Q2000 V24.11. The raw data files were plotted on Igor Pro Version 6.37.

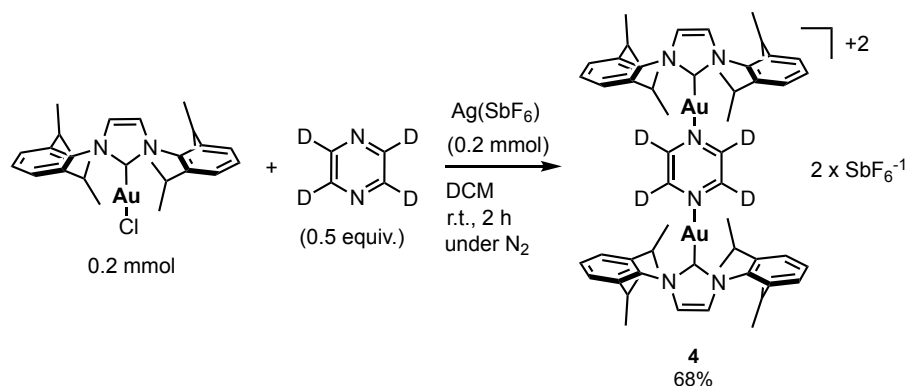
Synthesis

Synthesis of the NHC Cu(I) rotor **4**



A powder of chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]Cu(I) (0.095 g, 0.2 mmol) and deuterated pyrazine (0.009 g, 0.1 mmol) was placed in an oven-dried 19 ml of one-neck vial. The flask was connected to vacuum/nitrogen manifold through a rubber tube. It was evacuated and then backfilled with nitrogen. This process was repeated three times. Dry THF (5.0 ml) was then added to the flask under nitrogen atmosphere. The reagents contained THF solution was added AgSbF₆ and the reaction was performed under room temperature for 2 h. The suspended THF solution was followed by separating the liquid organic layer using centrifuge. The organic layers were collected, and the solvent was removed *in vacuo*. Further purification by recrystallization using CH₂Cl₂/Hexane gave analytically pure light-yellowish crystals of **4** with red emission under UV light (0.224 g, 0. mmol, 73 %). ¹H NMR (400 MHz, CD₂Cl₂, δ): 7.54-7.58 (t, *J* = 8.02, 4H), 7.37 (s, 4H), 7.32-7.34 (d, *J* = 8.7, 8H), 2.47-2.51 (h, *J* = 6.99, 8H), 1.22-1.23 (d, *J* = 6.88 Hz, 24H), 1.17-1.19 (d, *J* = 7.32 Hz, 24H). ¹³C NMR (125 MHz, CD₂Cl₂, δ): 24.0, 25.1, 29.1, 124.8, 125.0, 131.5, 134.3, 146.1, 176.7. Anal. Calcd. for C₅₈H₇₂D₄Cu₂N₆Sb₂F₁₂: C, 47.65; H, 5.65; N, 5.75; Found: C, 47.90; H, 5.27; N, 5.46.

Synthesis of the NHC Au(I) rotor **5**



The NHC Au(I) rotor **5** was prepared from chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]Au(I), deuterated pyrazine, and AgSbF₆ (0.040 g, 0.20 mmol) according to the procedure similar to that described for the preparation of **5** (0.175g, 0.14 mmol, 68%, white solid). ¹H NMR (400 MHz, CD₂Cl₂, δ): 7.53-7.57 (t, *J* = 8.02, 4H), 7.37 (s, 4H), 7.33-7.35 (d, *J* = 8.24, 8H), 2.41-2.48 (h, *J* = 6.78, 8H), 1.25-1.27 (d, *J* = 6.88 Hz, 24H), 1.21-1.23 (d, *J* = 6.88 Hz, 24H). ¹³C NMR (125 MHz, CD₂Cl₂, δ): 24.1, 24.8, 29.3, 125.0, 125.3, 131.8, 133.2, 146.0, 177.0. Calcd. for C₅₈H₇₂D₄Au₂N₆Sb₂F₁₂: C, 40.30; H, 4.78; N, 4.86; Found: C, 39.59; H, 4.26; N, 4.36.

Thermogravimetric Analysis (TGA) of Crystals 4 and 5

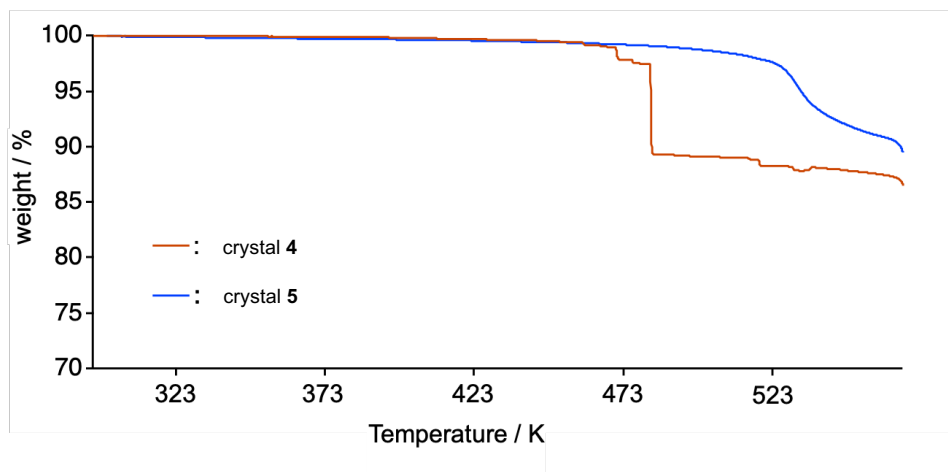


Figure 3-6. TGA profiles of the crystal 4 (orange line) and 5 (blue line). The heating rate is 5 °C/min. There was no significant decrease of weight of the samples until decomposition at approximately 470 K.

Data for Single-Crystal X-Ray Structural Analyses

Single-crystal X-ray structural analyses were carried out on a Rigaku XtaLAB PRO MM007 diffractometer using graphite monochromated Mo-K α radiation. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the Olex2 crystallographic software package except for refinement, which was performed using SHELXL-2013.³

Table 3-2 Summary of X-ray crystallographic data of the crystal **4** and **5**.

compound	4 at 195 K	4 at 250 K	4 at 275 K
CCDC Number	1868948	1868944	1868942
Empirical Formula	C ₂₉ H ₃₈ CuF ₆ N ₃ Sb	C ₂₉ H ₃₈ CuF ₆ N ₃ Sb	C ₂₉ H ₃₈ CuF ₆ N ₃ Sb
Formula Weight	727.91	727.91	727.91
Crystal System	monoclinic	monoclinic	monoclinic
Crystal Size / mm	0.35×0.33×0.32	0.34×0.33×0.33	0.34×0.34×0.33
<i>a</i> / Å	11.88340(10)	11.94546(10)	11.97178(11)
<i>b</i> / Å	14.12370(10)	14.15596(14)	14.16779(13)
<i>c</i> / Å	19.6903(2)	19.78395(17)	19.82944(17)
<i>α</i> / °	90	90	90
<i>β</i> / °	106.2540(10)	106.3123(9)	106.3401(9)
<i>γ</i> / °	90	90	90
<i>V</i> / Å ³	3172.68(5)	3210.78(5)	3227.49(5)
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i> value	4	4	4
<i>D</i> _{calc} / g cm ⁻³	1.524	1.506	1.498
Temperature / K	195	250	275
2 θ _{max} / °	152.836	152.808	152.874
μ (Mo K α) / cm ⁻¹	80.83	79.87	79.45
No. of Reflections	Total: 22528 Unique: 6432 <i>R</i> _{int} = 0.0309	Total: 23240 Unique: 6454 <i>R</i> _{int} = 0.0308	Total: 24498 Unique: 6504 <i>R</i> _{int} = 0.0333
<i>R</i> ₁ ^a	0.0347	0.0326	0.0403
<i>wR</i> ₂ ^b	0.1142	0.0909	0.1150
GOF ^c	0.949	1.055	1.082
Max./Mini. peak <i>I</i> ^d / Å ³	0.45 e ⁻ /–1.33 e ⁻	0.46 e ⁻ /–0.91 e ⁻	0.79 e ⁻ /–0.76 e ⁻
compound	4 at 300 K	4 at 325 K	4 at 350 K
CCDC Number	1869943	1868949	1868946
Empirical Formula	C ₂₉ H ₃₈ CuF ₆ N ₃ Sb	C ₂₉ H ₃₈ CuF ₆ N ₃ Sb	C ₂₉ H ₃₈ CuF ₆ N ₃ Sb
Formula Weight	727.91	727.91	727.91
Crystal System	monoclinic	monoclinic	monoclinic
Crystal Size / mm	0.36×0.35×0.35	0.38×0.37×0.37	0.38×0.38×0.36
<i>a</i> / Å	12.00159(11)	12.03480(10)	12.06050(10)
<i>b</i> / Å	14.18178(15)	14.20220(10)	14.2164(2)
<i>c</i> / Å	19.87407(19)	19.9261(2)	19.9658(2)
<i>α</i> / °	90	90	90
<i>β</i> / °	106.3277(10)	106.3150(10)	106.3220(10)
<i>γ</i> / °	90	90	90
<i>V</i> / Å ³	3246.22(6)	3268.64(5)	3285.31(6)
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i> value	4	4	4
<i>D</i> _{calc} / g cm ⁻³	1.489	1.479	1.472
Temperature / K	300	325	350
2 θ _{max} / °	152.836	152.418	145.48
μ (Mo K α) / cm ⁻¹	79.00	78.45	78.06
No. of Reflections	Total: 22875 Unique: 6489 <i>R</i> _{int} = 0.0343	Total: 25148 Unique: 6572 <i>R</i> _{int} = 0.0301	Total: 20046 Unique: 6238 <i>R</i> _{int} = 0.0273
<i>R</i> ₁ ^a	0.0416	0.0370	0.0381
<i>wR</i> ₂ ^b	0.1221	0.1125	0.1371
GOF ^c	1.085	0.969	1.089
Max./Mini. peak <i>I</i> ^d / Å ³	0.79 e ⁻ /–0.81 e ⁻	0.32 e ⁻ /–0.98 e ⁻	0.30 e ⁻ /–1.09 e ⁻

^a: $I > 2.00\sigma(I)$. ^b: All reflections. ^c: Goodness of Fit Indicator. ^d: in Final Diff. Map.

compound	5 at 195 K	5 at 250 K	5 at 275 K
CCDC Number	1868938	1868935	1868934
Empirical Formula	C ₂₉ H ₃₈ AuF ₆ N ₃ Sb	C ₂₉ H ₃₈ AuF ₆ N ₃ Sb	C ₂₉ H ₃₈ AuF ₆ N ₃ Sb
Formula Weight	861.34	861.34	861.34
Crystal System	monoclinic	monoclinic	monoclinic
Crystal Size / mm	0.61×0.55×0.45	0.71×0.6×0.5	0.71×0.61×0.52
<i>a</i> / Å	11.9022(11)	11.9762(8)	12.0155(7)
<i>b</i> / Å	14.2196(13)	14.2322(10)	14.2691(8)
<i>c</i> / Å	19.937(2)	20.0321(11)	20.0602(9)
α / °	90	90	90
β / °	105.281(10)	105.388(6)	105.462(5)
γ / °	90	90	90
<i>V</i> / Å ³	3254.9(6)	3292.0(4)	3314.9(3)
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i> value	4	4	4
<i>D</i> _{calc} / g cm ⁻³	1.758	1.738	1.726
Temperature / K	195	250	275
2 θ _{max} / °	173.602	153.254	151.772
μ (Mo K α) / cm ⁻¹	154.28	152.54	151.49
No. of Reflections	Total: 16273 Unique: 5973 <i>R</i> _{int} = 0.0564	Total: 16505 Unique: 6086 <i>R</i> _{int} = 0.0557	Total: 16771 Unique: 6082 <i>R</i> _{int} = 0.0567
<i>R</i> ₁ ^a	0.1188	0.1088	0.1120
<i>wR</i> ₂ ^b	0.3549	0.3052	0.3406
GOF ^c	1.089	1.132	1.094
Max./Mini. peak <i>I</i> ^d / Å ³	3.39 e ⁻ /–2.27 e ⁻	2.36 e ⁻ /–2.02 e ⁻	2.25 e ⁻ /–2.02 e ⁻
compound	5 at 295 K	5 at 325 K	5 at 350 K
CCDC Number	1868933	1868941	1868939
Empirical Formula	C ₂₉ H ₃₈ AuF ₆ N ₃ Sb	C ₂₉ H ₃₈ AuF ₆ N ₃ Sb	C ₂₉ H ₃₈ AuF ₆ N ₃ Sb
Formula Weight	861.34	861.34	861.34
Crystal System	monoclinic	monoclinic	monoclinic
Crystal Size / mm	0.75×0.65×0.55	0.78×0.67×0.55	0.79×0.69×0.59
<i>a</i> / Å	12.0137(10)	12.0977(14)	12.1313(15)
<i>b</i> / Å	14.2628(11)	14.3105(14)	14.3728(18)
<i>c</i> / Å	20.0865(12)	20.1580(17)	20.2040(17)
α / °	90	90	90
β / °	105.393(8)	105.261(10)	105.513(11)
γ / °	90	90	90
<i>V</i> / Å ³	3318.3(4)	3366.8(6)	3394.4(7)
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i> value	4	4	4
<i>D</i> _{calc} / g cm ⁻³	1.724	1.699	1.685
Temperature / K	295	325	350
2 θ _{max} / °	173.992	145.872	146.354
μ (Mo K α) / cm ⁻¹	151.33	149.15	147.93
No. of Reflections	Total: 16313 Unique: 6156 <i>R</i> _{int} = 0.0583	Total: 14563 Unique: 6099 <i>R</i> _{int} = 0.0650	Total: 18214 Unique: 6311 <i>R</i> _{int} = 0.0566
<i>R</i> ₁ ^a	0.1154	0.1494	0.1290
<i>wR</i> ₂ ^b	0.3475	0.4533	0.4130
GOF ^c	1.064	1.761	1.520
Max./Mini. peak <i>I</i> ^d / Å ³	2.27 e ⁻ /–1.91 e ⁻	6.56 e ⁻ /–2.18 e ⁻	5.15 e ⁻ /–1.89 e ⁻

^a: $I > 2.00\sigma(I)$. ^b: All reflections. ^c: Goodness of Fit Indicator. ^d: in Final Diff. Map.

Note: Large *R*₁, *wR*₂, GOF, and electron density for crystal **5** come from the effect of Au atoms.

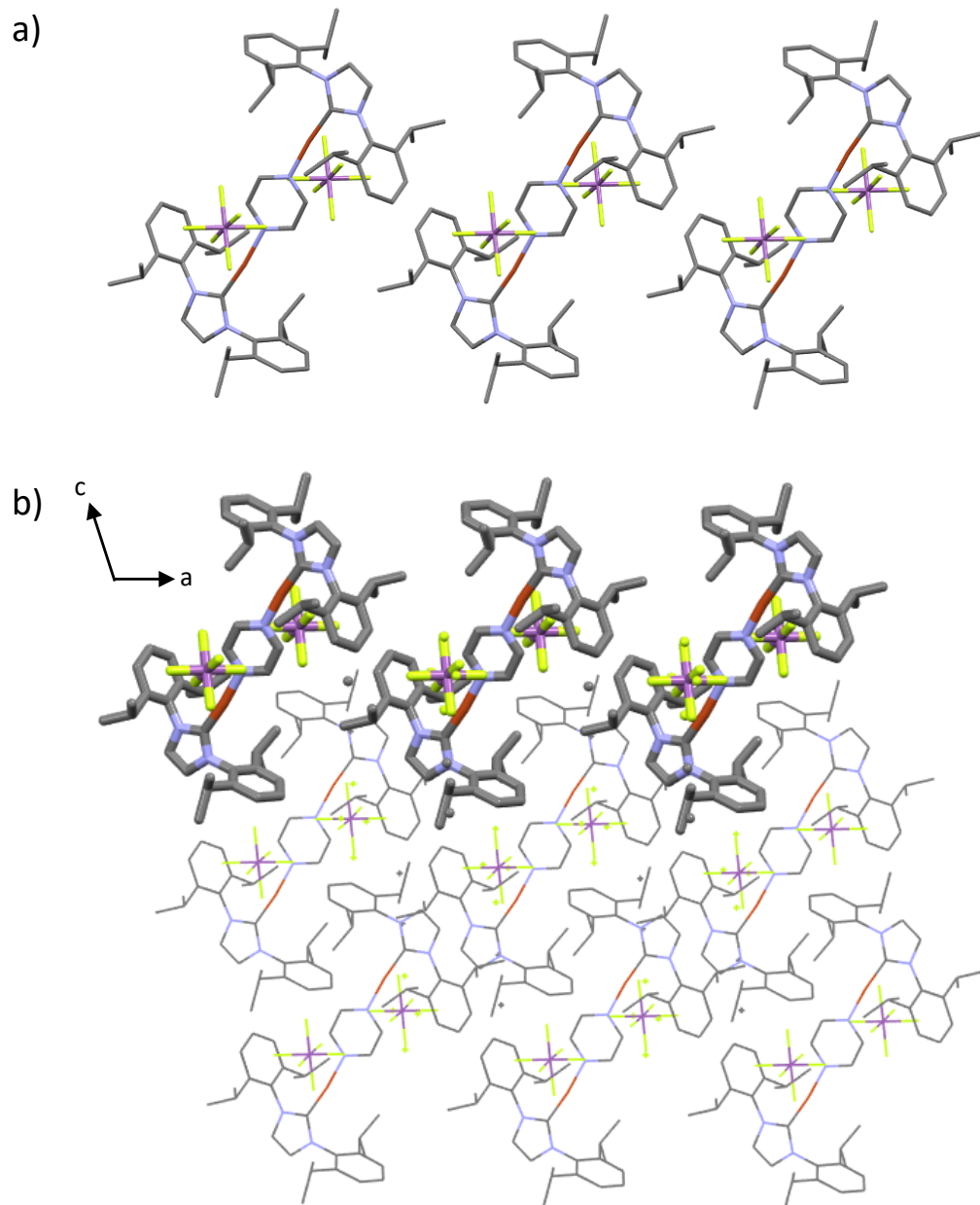


Figure 3-7. Single-crystal structure of **4** at 195 K. H atoms are omitted for clarity in a), b).

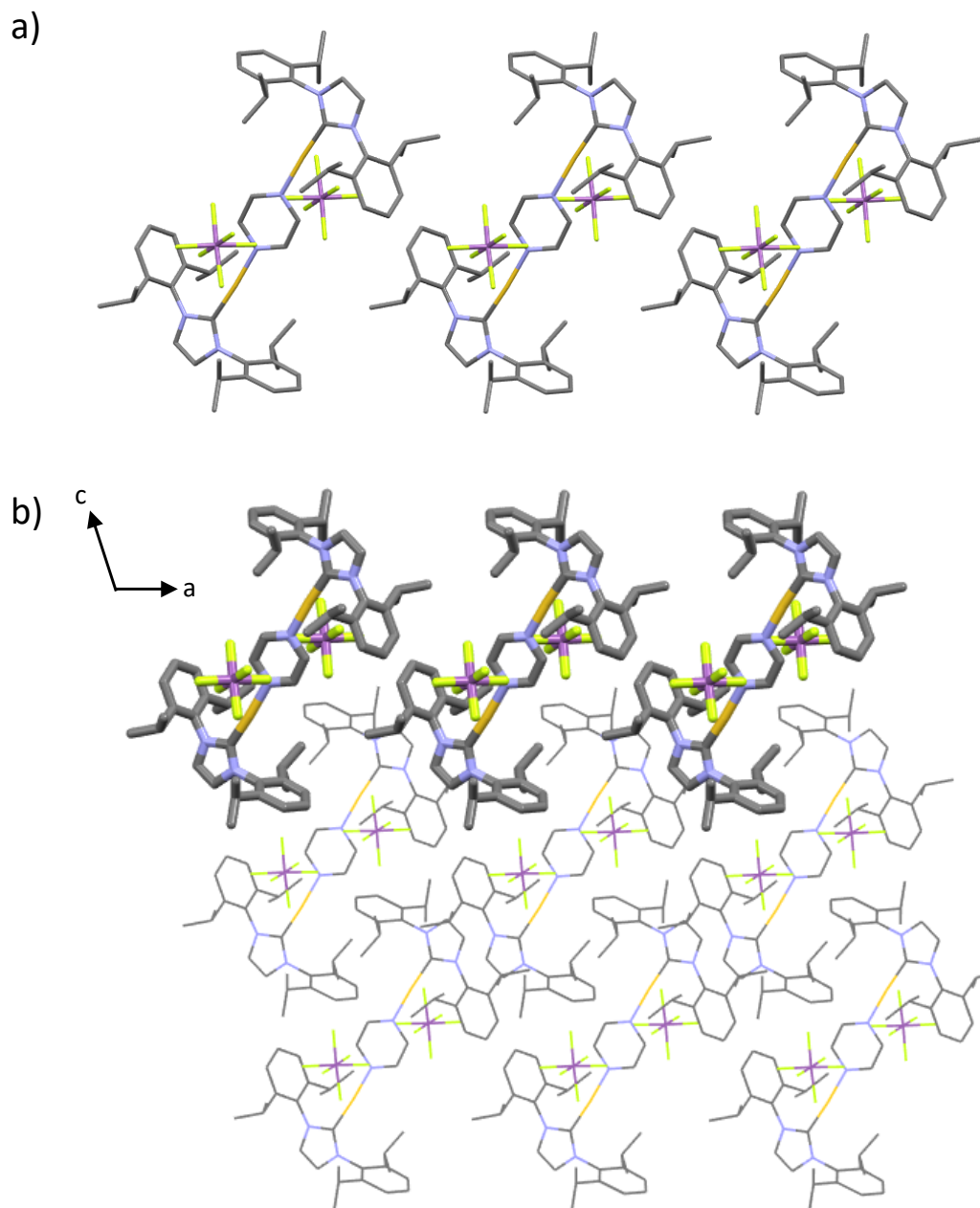


Figure 3-8. Single-crystal structure of **5** at 195 K. H atoms are omitted for clarity in a, b).

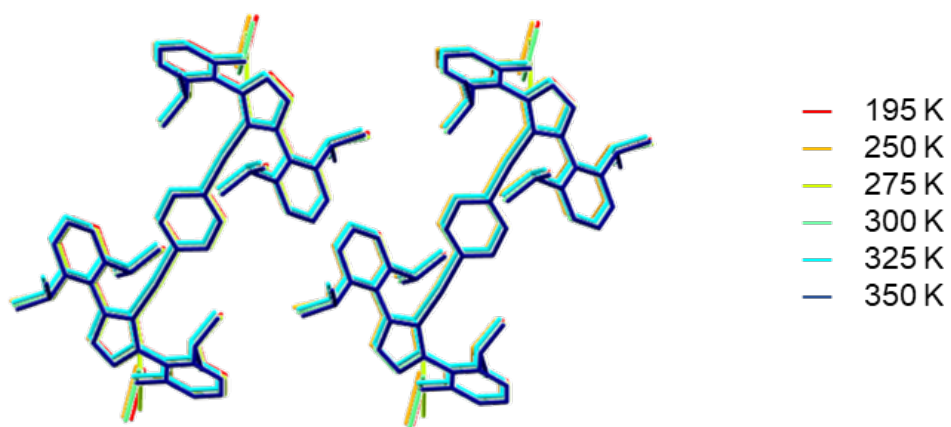


Figure 3-9. Superimposition of the crystal **4** obtained at 195 K to 350 K.

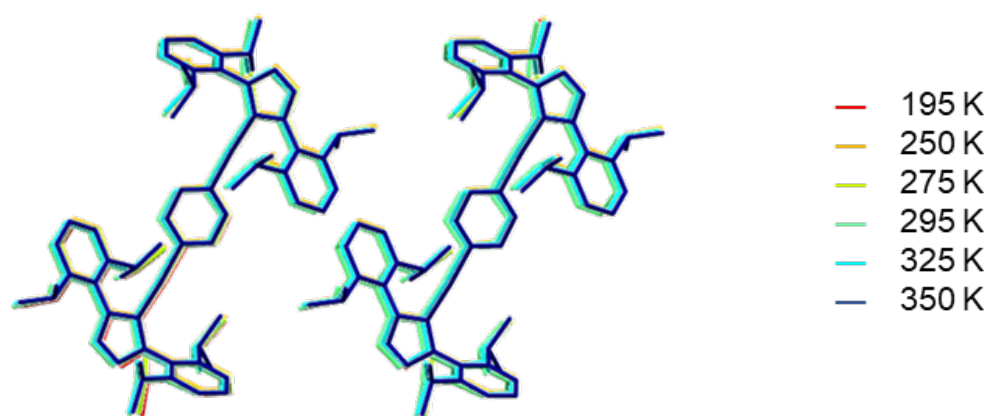


Figure 3-10. Superimposition of the crystal **5** obtained at 195 K to 350 K.

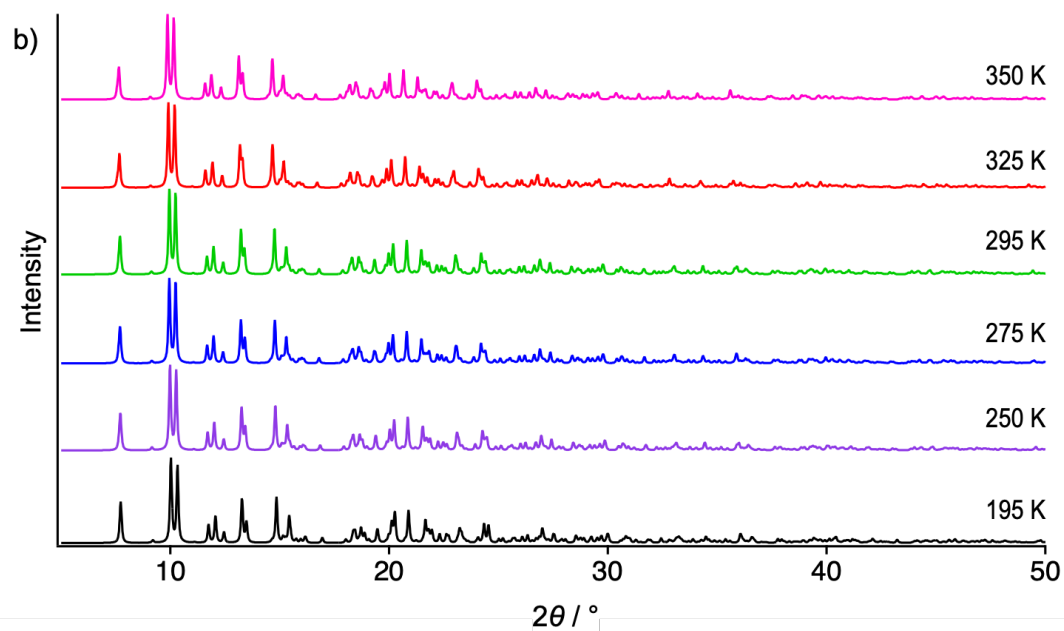
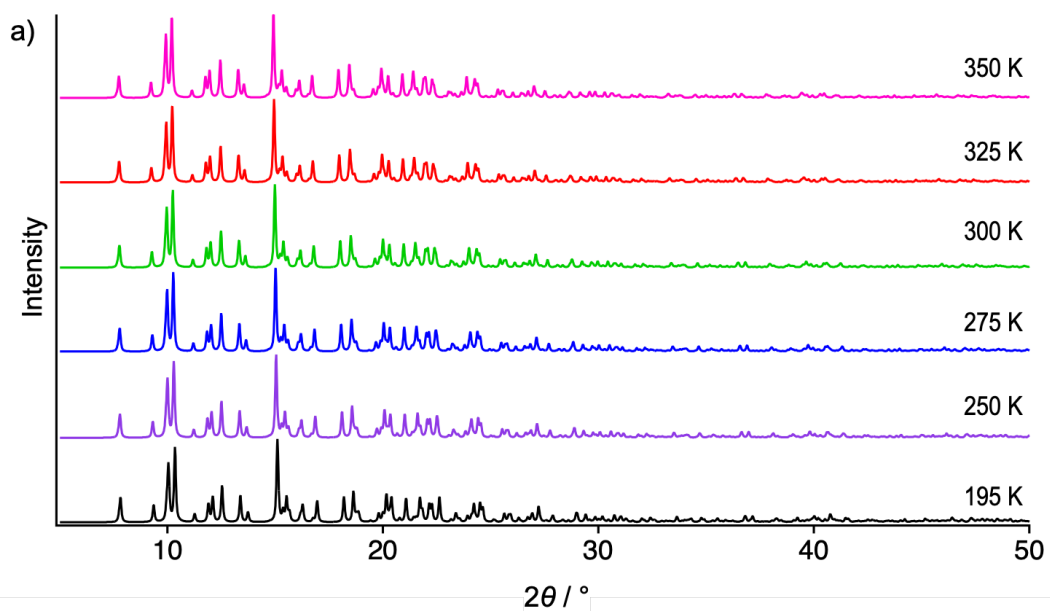


Figure 3-11. Simulated PXRD patterns derived from the VT-single crystal structures of a) **4** and b) **5** taken between 195 K and 350 K.

Differential Scanning Calorimetry (DSC) of Crystals 4 and 5

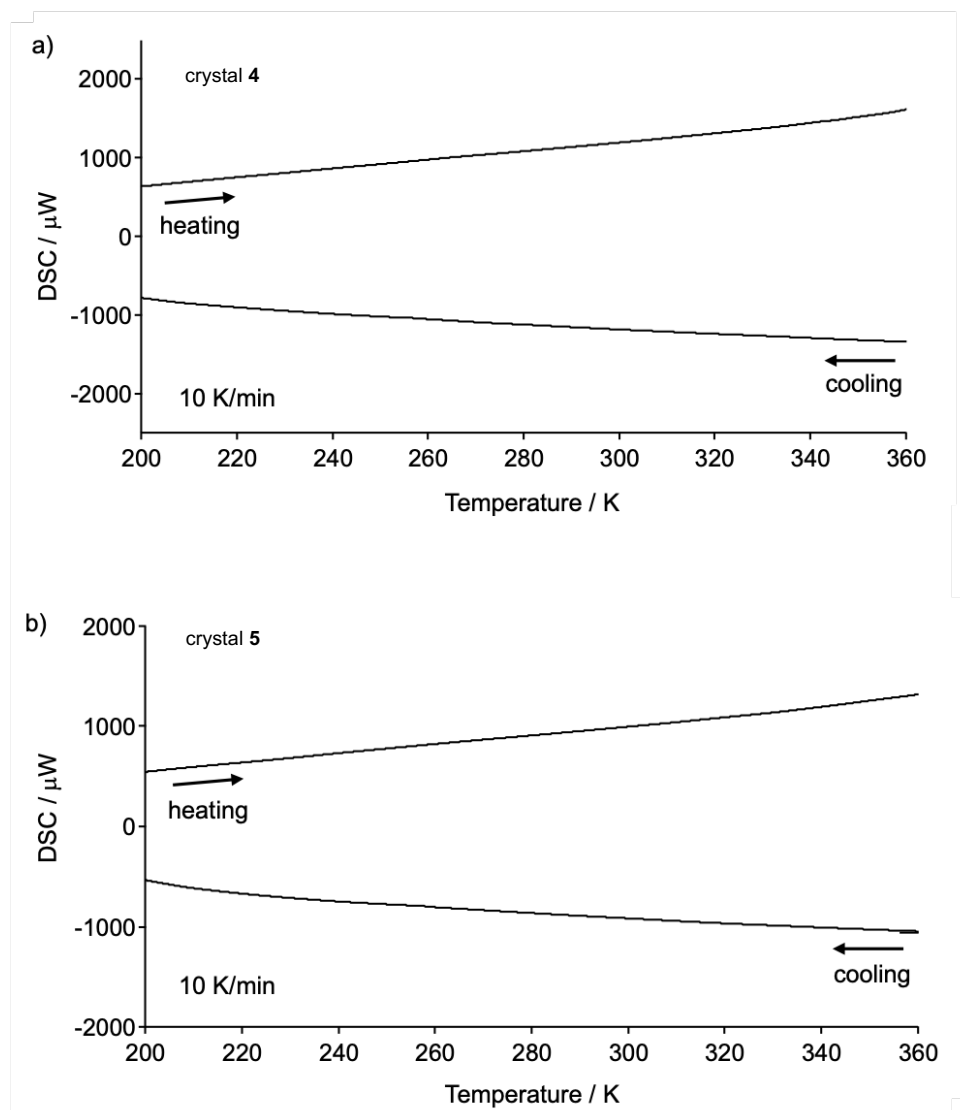


Figure 3-12. DSC profiles of a) the crystal 4 and b) 5. Heating and cooling rates were 10 K/min. (Temperature range: 200 K – 360 K)

Solid-State NMR Studies of Crystals 4 and 5

Solid-state ^2H NMR Spin-echo Experiments

The solid-state ^2H NMR (SS ^2H NMR) spin-echo experiments in this work were performed on a Bruker AV600 instrument at 92.1 MHz (deuterium resonance frequency) with a 5 mm wideline probe and 90-degree pulse of 2.9 μs . To suppress the undesired artifacts, a quadrupolar-echo sequence with phase recycling was used. An echo delay of 50 μs was used after the refocusing delay of 46 μs , and the recycle delay between pulses was 30s. About 250 mg of sample was placed in a short borosilicate glass NMR tube for each experiment. 512 scans or more were used to acquire each spectrum. All spectra in this work were obtained using a line broadening of 5.0 kHz in data processing.

Simulation of the Experimental Spectra

All simulation was performed utilizing the online program offered by professor H. W. Spiess.⁴ The spectra obtained for crystals **4** and **5** were identified to be the result of simple 2-fold rotation.

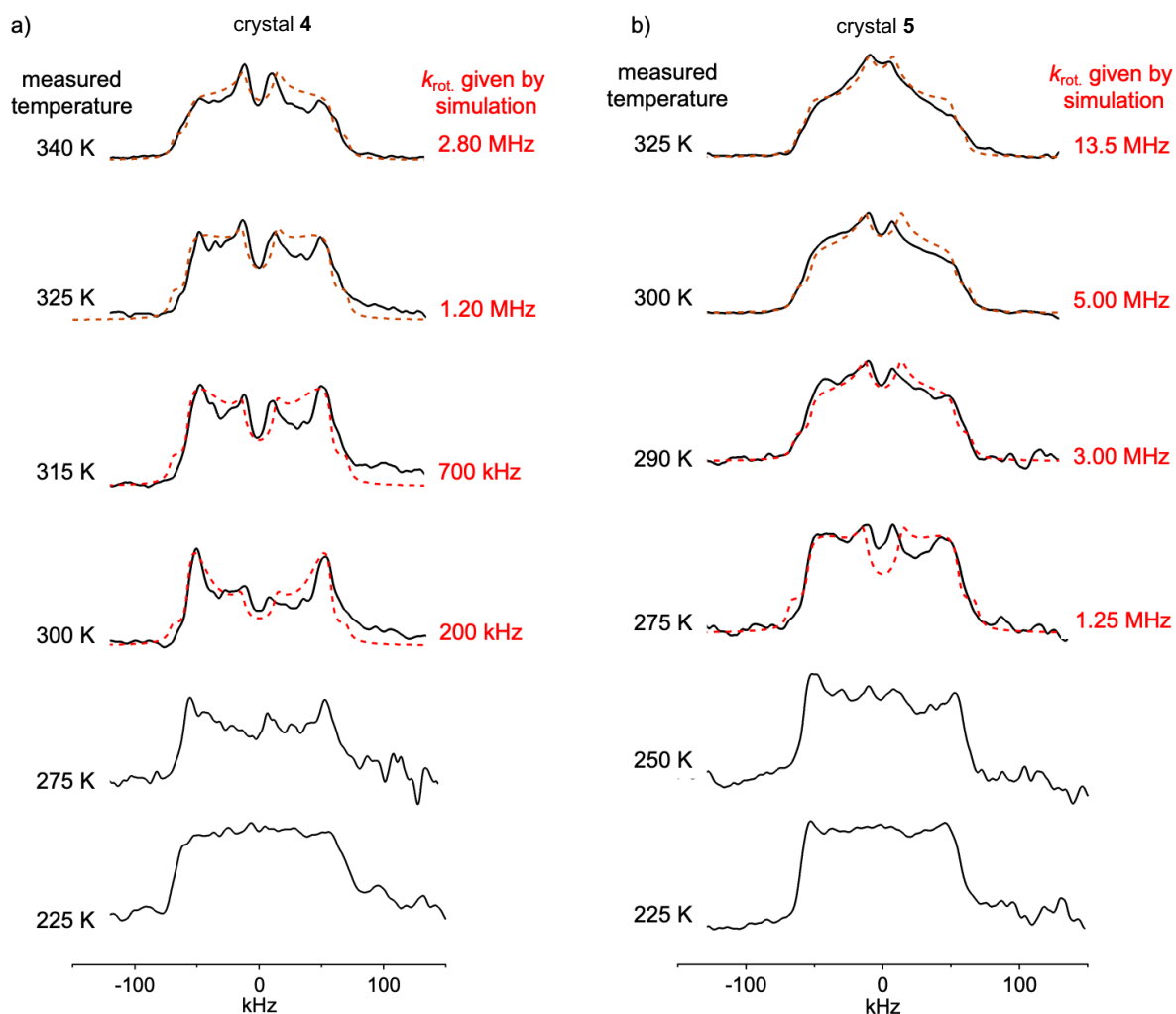


Figure 3-13. Variable temperature (VT) solid-state ^2H NMR spectra of the crystal a) 4 and b) 5 obtained from the experiment (black solid line) and the simulation with rotation frequency k_{rot} . (red dashed line).

DFT Calculation Study for Molecular Rotation

Details of DFT calculations for the ground state and TS with NBO analysis

All geometry optimizations and thermal energy correction calculations (frequency analyses) using density functional theory (DFT) were performed with Gaussian 16 programs. The initial geometries of both NHC cationic metal complexes were taken from the crystal structures, followed by optimizing the positions of H atoms with fixing the geometries of heavy atoms using DFT calculation with B3LYP/6-31G level. The ground states were obtained by geometry optimization using wB97XD/6-31G(d) for organic atoms and LanL2DZ for metals with fixing whole atoms without pyrazine rotator to represent the origins of crystal packing environment. Under the fixation of whole atoms without pyrazine rotator, the geometries of transition states (TS) for the 2-fold rotation of rotor **4** and **5** were obtained by the Locally Updated Planes (LUP) method which is one of conventional path optimization calculations using the GRRM17 program. Natural bond orbital (NBO) analysis of the obtained TS structures of **4** and **5** have been performed by using wB97XD/6-31G(d) for organic atoms and LanL2DZ for metals on NBO 7.0 programs.

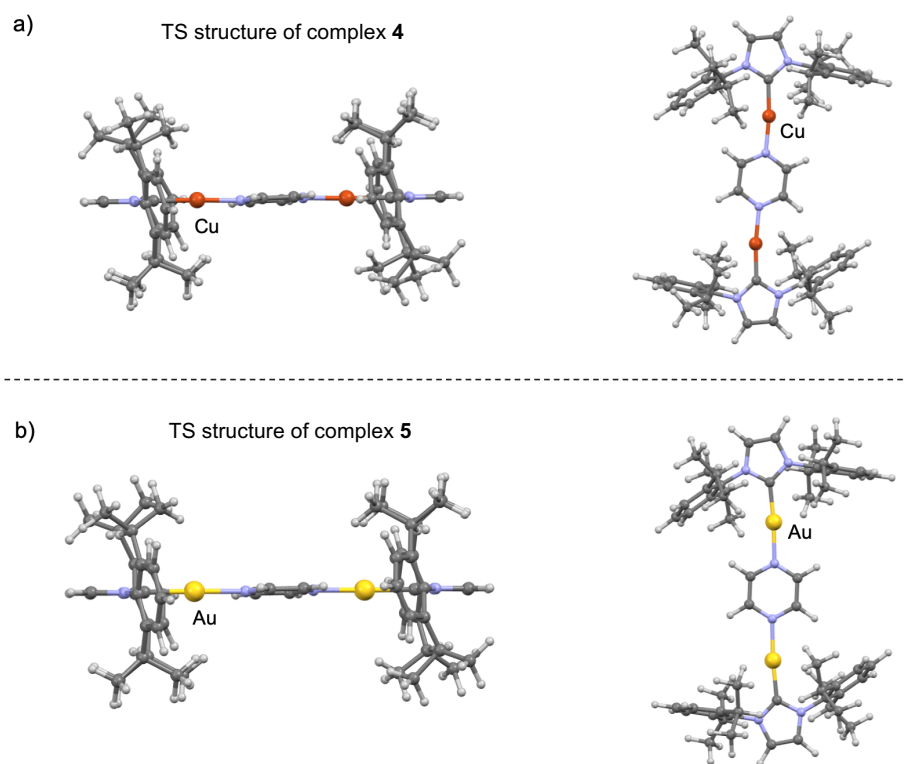


Figure 3-14. Geometries of the ground state of a) **4** and b) **5** obtained from the calculations.

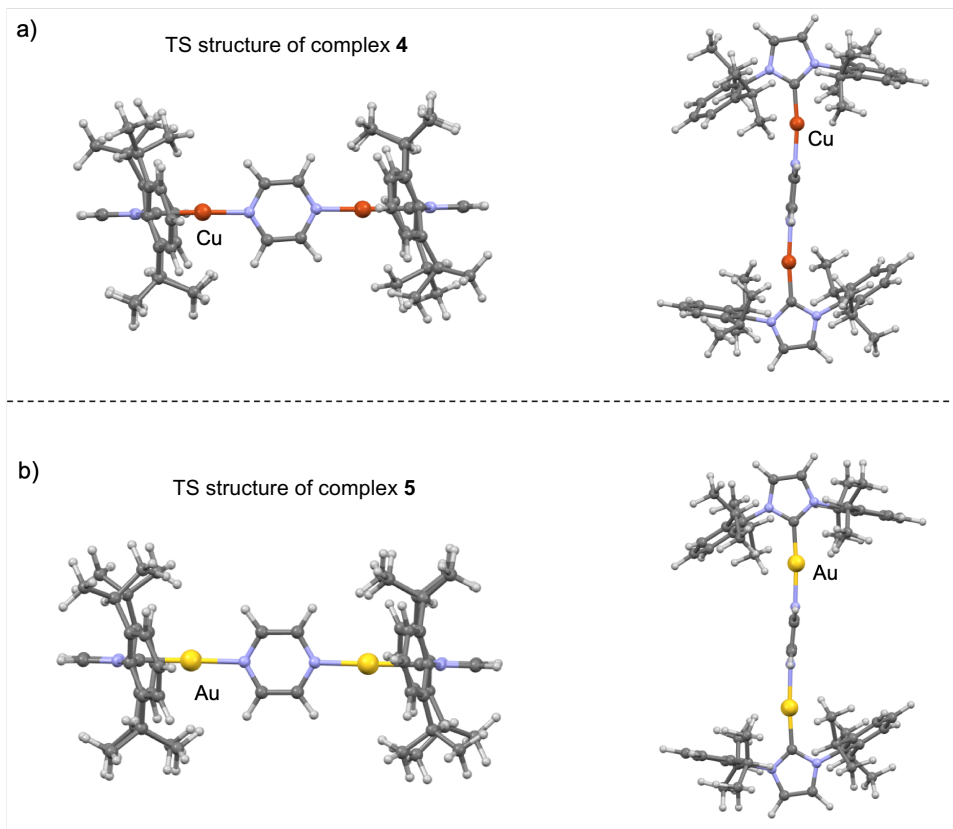


Figure 3-15. Geometries of the transition state (TS) of a) **4** and b) **5** obtained from the calculations.

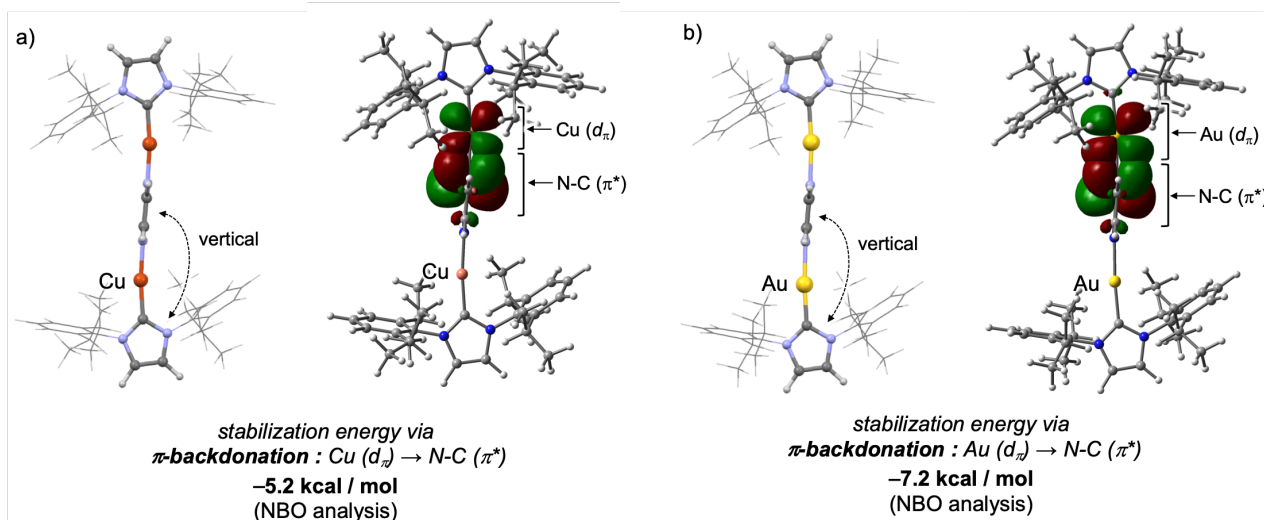


Figure S3-16. TS structures of the a) Cu(I) rotor **4** and b) Au(I) rotor **5** having vertical geometries between pyrazine and NHC plane (left), and the estimated p-backdonation by NBO analysis (right).

Quantitative interaction analysis using I-SAPT

To estimate the steric interactions between the IPr-NHC ligand and the pyrazine rotator, I employed the energy decomposition analysis between the diisopropylphenyl groups on the NHC ligand and the pyrazine rotator of four geometries from the ground and transition state of **4** and **5** by using intramolecular symmetry-adapted perturbation theory (I-SAPT) implemented in the PSI4 1.3 program package.^{36,37} This I-SAPT calculation can decompose the interaction energy between the two functional groups to physically meaningful components, including electrostatic interaction (Elst), exchange repulsion (Exch), induction effect (Ind), and dispersion interaction (Disp) terms. The reference wave function was recalculated at SAPT0 level of theory with Sapporo-DKH3-DZP-2012 basis set for Au and Def2-SVP basis set for the other atoms, and a series of default auxiliary basis sets; Def2-SVP-JKFIT, Def2-SVP-RI, and WTBS for Au and cc-pVTZ-MINAO for the other atoms. The multiplicities of the two functional groups were set to doublet, that of the other link structure was set to singlet, and that of the overall molecule was set to singlet. Finally, it was confirmed that two link bonds were assigned into the link structure as a result of automatic IBO localization and link bond selection in the I-SAPT calculations.

Two structural combinations (I and II) between the left or right site of IPr-NHC ligand (diisopropylphenyl moiety) and pyrazine were set for the energy decomposition analysis using I-SAPT (Figure 3-17). The results were summarized in Table 3-3. It should be noted that the exchange interactions, namely steric repulsion, in the **TS-1** shows ca. 1.6 kcal/mol of higher energy value than those of the **TS-2**. Furthermore, the gap of total SAPT energy value between the TS and ground state of Cu(I) rotor **4** also shows ca. 1.7 kcal/mol higher than those of Au(I) rotor **5** (Table 3-3). These results indicate that the difference in steric repulsion between TS-1 and TS-2 worked for a crucial factor in the different activation energy barrier for the two-fold pyrazine rotations between the Cu and Au rotors.

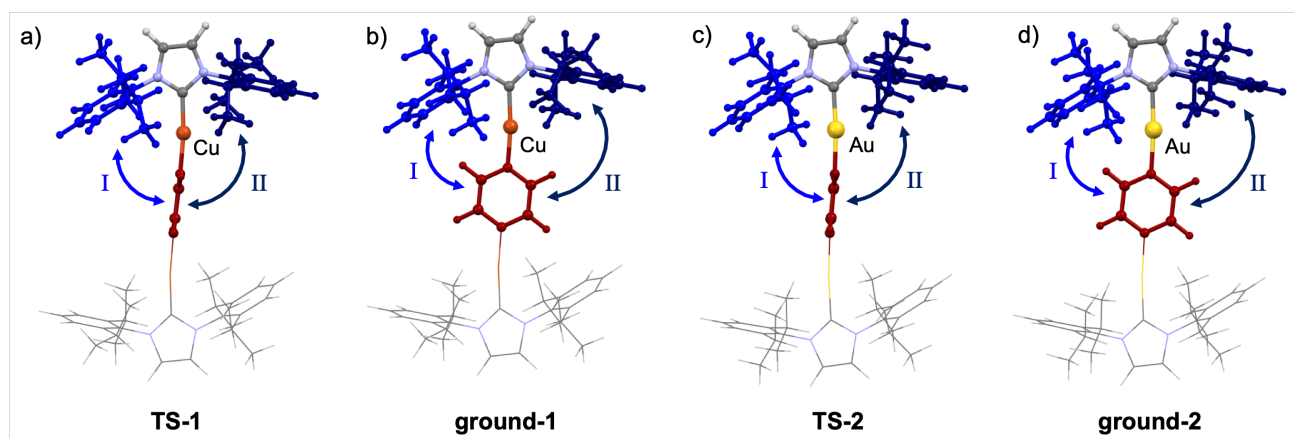


Figure 3-17. The calculated structures of a) **TS-1**, b) **ground-1**, c) **TS-2**, and d) **ground-2** with the defined structural combinations (I and II) between the diisopropylphenyl groups and pyrazine (left and right sites are illustrated in blue and dark blue, respectively).

Table 3-3. Results of energy decomposition analysis using I-SAPT.

structure	domain	Electrostatic [kcal/mol]	Exchange [kcal/mol]	Induction [kcal/mol]	Dispersion [kcal/mol]	Total [kcal/mol]
TS-1	I	0.72	3.80	-0.77	-2.52	
	II	0.71	0.41	-0.19	-1.12	
	I+II	1.43	4.21	-0.96	-3.64	1.03
ground-1	I	-0.94	1.86	-0.78	-2.49	
	II	0.30	0.26	-0.22	-0.99	
	I+II	-0.64	2.12	-1.00	-3.48	-3.01
TS-1 (I+II) – ground-1 (I+II)						4.04
TS -2	I	0.39	2.01	-0.34	-1.77	
	II	0.32	0.58	-0.12	-0.80	
	I+II	0.71	2.59	-0.46	-2.57	0.28
ground-2	I	-0.62	1.23	-0.41	-1.83	
	II	0.00	0.49	-0.14	-0.72	
	I+II	-0.62	1.72	-0.55	-2.55	-1.99
TS-2 (I+II) – ground-2 (I+II)						2.27

Details of calculation study using the modeled rotors

To confirm the contribution of π -backdonation on the molecular rotation, I performed the DFT calculation using the modeled rotors possessing non-bulky NHC ligand. The initial geometries of the modeled rotors are built from the ground state structures of Cu(I) rotor **4** and Au(I) rotor **5** with substituting diisopropylphenyl group to methyl group on the NHC ligand. It is followed by optimizing the positions of H atoms with fixing the geometries of heavy atoms using DFT calculation with B3LYP/6-31G level. The ground state and TS structures for the molecular rotations were obtained by the Locally Updated Planes (LUP) method using the GRRM17 program. The geometry optimizations were performed under wB97XD/6-31G(d) for organic atoms and LanL2DZ for metals with fixing whole atoms without pyrazine rotator. Interestingly, the structure having vertical geometry between pyrazine and NHC plane was

assigned as ground state in both rotors, which is opposite from the cases of rotor **4** and **5** (Figure 3-18a and b). NBO analysis using the ground state geometries of the modeled rotors revealed that the Au rotor shows ca. 1.5 kcal/mol of stronger p-backdonation energy than those of the Cu rotor, as shown in Figure S13c and d, which is almost the same with the cases using the TS structures of rotor **4** and **5**. These results indicated that the vertical geometry between pyrazine and NHC plane conduct stabilizing effect via π -backdonation from d_π of metals to π^* of pyrazine, and magnitude of the stabilized energy could be modulated by altering metal species which have different size of d_π orbitals.

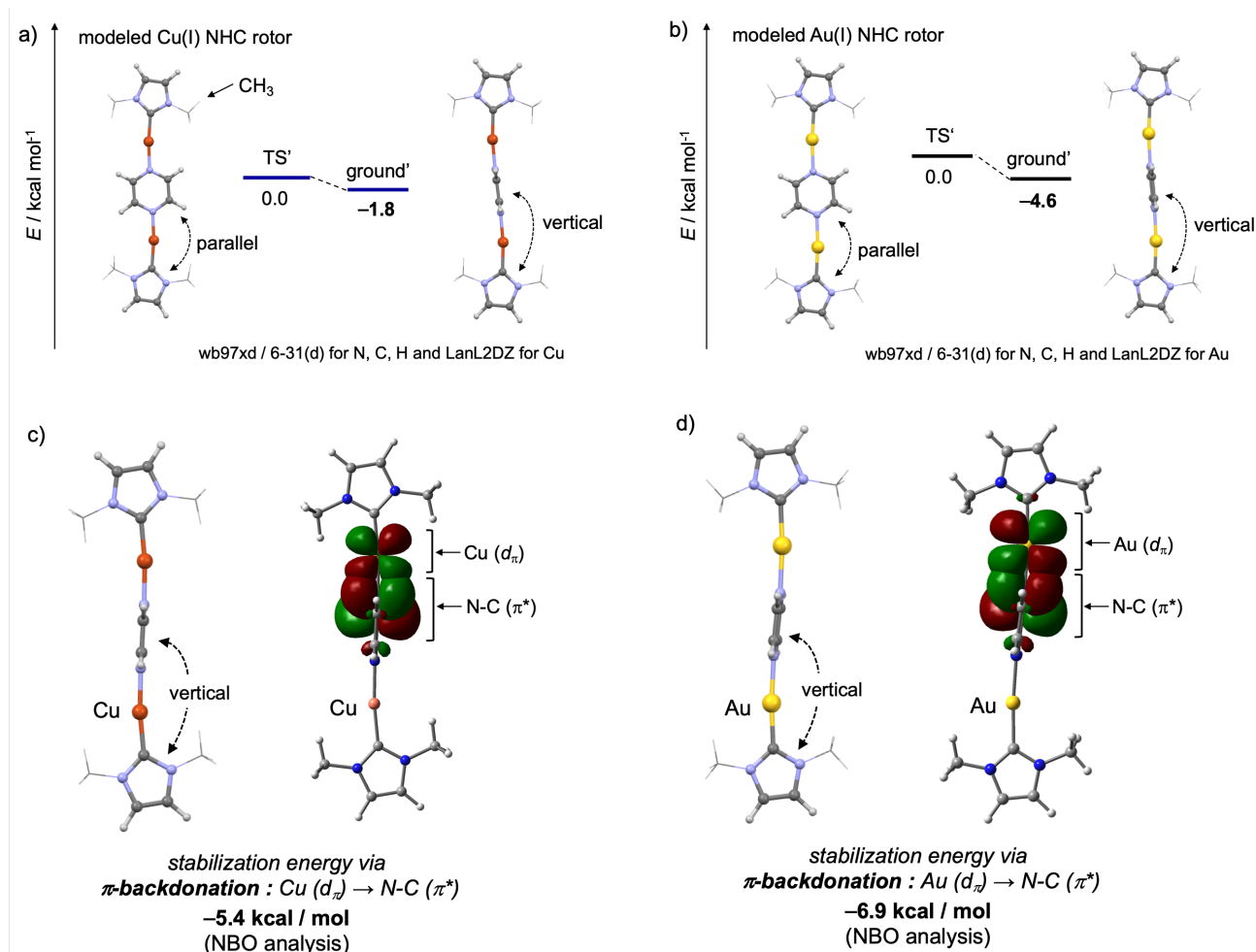


Figure 3-18. Energy diagrams and the obtained geometries of ground state and TS for molecular rotation in the modeled a) Cu(I) rotor and b) Au(I) rotor. Estimated p-backdonation energy of the c) Cu(I) rotor and d) Au(I) rotor by NBO analysis using the vertical geometry between pyrazine and NHC plane.

Optical Properties of Solution Phase of 4 and 5

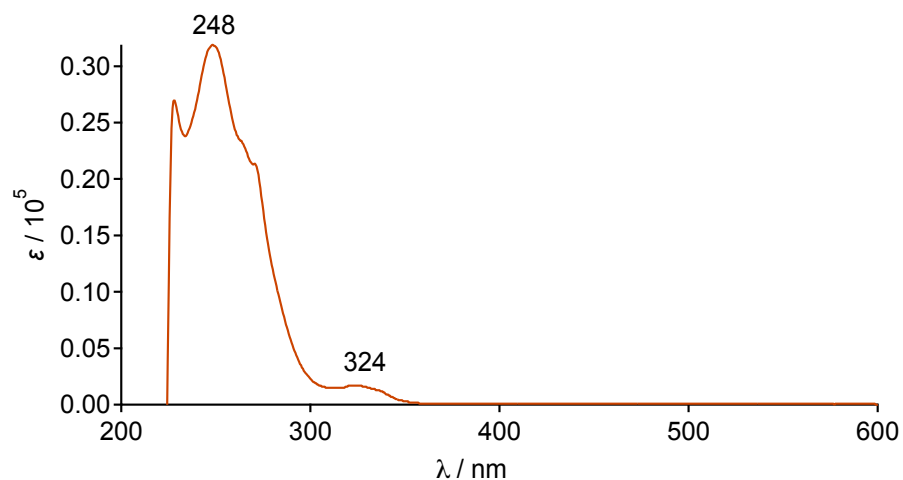


Figure 3-19. UV/vis of Cu(I) rotor **4** in CH₂Cl₂ ($c = 6.2 \times 10^{-6}$ M) at room temperature. The solution of **3** in CH₂Cl₂ exhibited no emission under UV light.

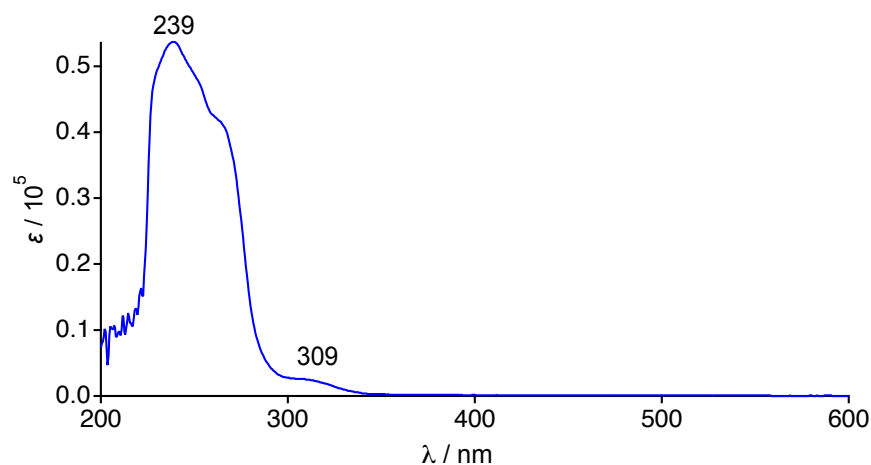


Figure 3-20. UV/vis of Au(I) rotor **5** in CH₂Cl₂ ($c = 3.6 \times 10^{-5}$ M) at room temperature. The solution of **4** in CH₂Cl₂ exhibited no emission under UV light.

TD-DFT Calculations

All calculations were performed using the Gaussian 16 (revision C.01 and E.01) program package.⁵ The singlet state TD-DFT calculations of the Cu and Au rotors in the crystal **4** and **5** were performed with the goal of understanding the origin of their emission properties. In the calculations, the B3LYP functional and the SDD basis set with an effective core potential for metals and the 6-31G* for the other atoms were used. The geometries of the rotor **4** and **5** with SbF₆ anion were taken from the single crystal structure of **4** and **5** at 195 K. The positions of the heavy atoms were fixed and only the positions of H atoms were optimized using the Spartan'10 MMFF force-field calculations before TD-DFT calculations.⁶ The simulated UV/vis absorption spectra and the excitation spectra from the experiments exhibited similar tendency on the traces (Figure 3-21).

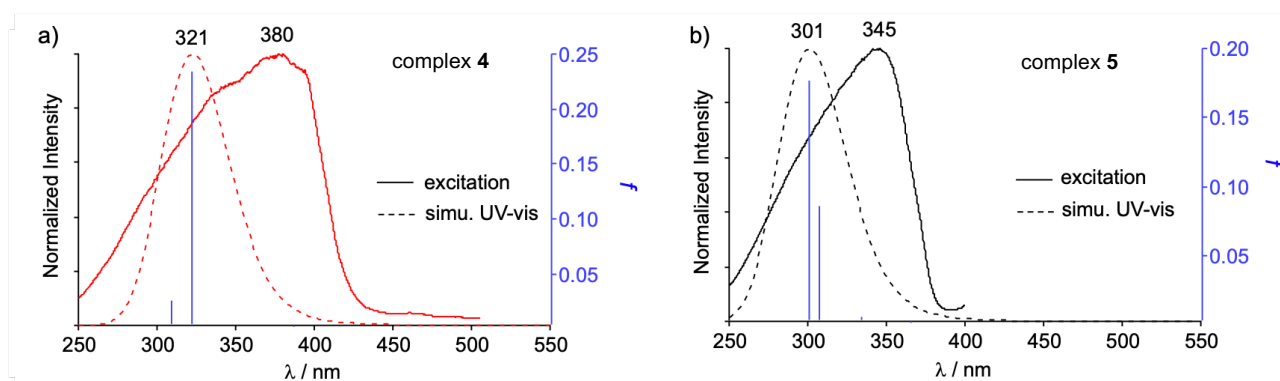
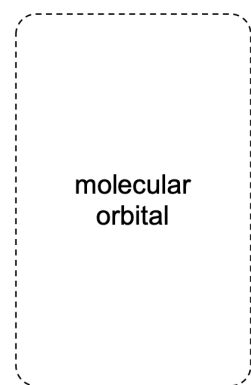


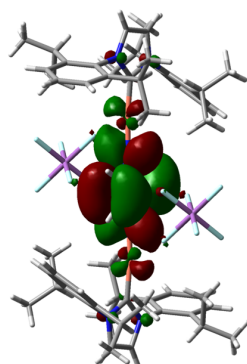
Figure 3-21. Comparison of experimental and theoretical studies on emission properties of the crystal a) **4** and b) **5**. Excitation spectra of the crystal **4** and **5** (red and black solid line, respectively) obtained at room temperature. Simulated UV/vis absorption spectra of the rotor **4** and **5** in the crystals (red and black dashed line, respectively) and oscillator strengths (blue sticks) based on the singlet state TD-DFT calculations of the geometries derived from the single crystalline structures of **4** and **5** measured at room temperature (B3LYP/6-31G* for C, H, N, F and SDD for Cu or Au).

Table 3-4. Selected singlet to singlet transitions of the Cu(I) rotor **4**

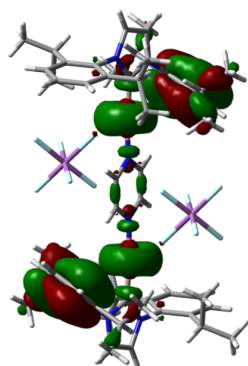
states	energy / eV	λ / nm	f / -	orbital transition	CI coefficients
S0 to S1	3.3025	387	0.0033	HOMO-10 $\rightarrow$ LUMO	0.11259
				HOMO-4 $\rightarrow$ LUMO	0.41064
				HOMO $\rightarrow$ LUMO	0.55397
S0 to S7	3.8525	321	0.2343	HOMO-8 $\rightarrow$ LUMO	0.38207
				HOMO-6 $\rightarrow$ LUMO	0.57334
S0 to S9	4.0075	309	0.0265	HOMO-10 $\rightarrow$ LUMO	-0.21415
				HOMO-8 $\rightarrow$ LUMO	0.55104
				HOMO-6 $\rightarrow$ LUMO	-0.37157



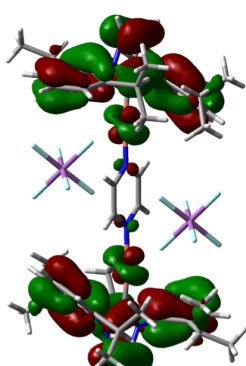
state
(hartree)



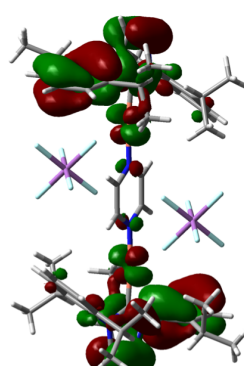
LUMO
(-0.09810)



HOMO
(-0.24692)



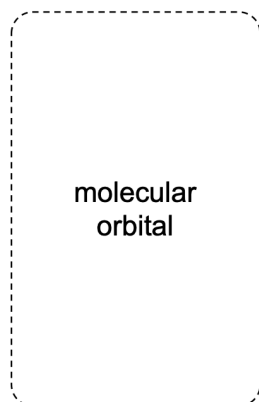
HOMO-6
(-0.26157)



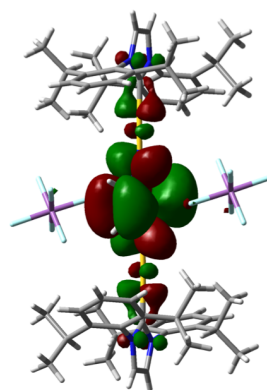
HOMO-8
(-0.26418)

Table 3-5. Selected singlet to singlet transitions of the Au(I) rotor **5**

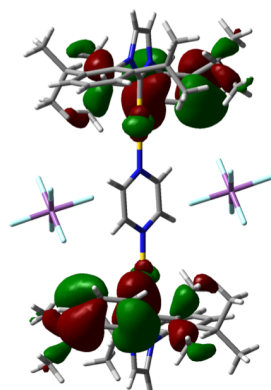
states	energy /eV	λ / nm	f / -	orbital transition	CI coefficients
S0 to S1	3.388	366	0.0027	HOMO-4 $\rightarrow$ LUMO	-0.10590
				HOMO $\rightarrow$ LUMO	0.69434
S0 to S7	4.0281	308	0.0858	HOMO-12 $\rightarrow$ LUMO	-0.17437
				HOMO-8 $\rightarrow$ LUMO	0.22488
				HOMO-6 $\rightarrow$ LUMO	0.60482
				HOMO-4 $\rightarrow$ LUMO	-0.21970
S0 to S9	4.1234	301	0.1763	HOMO-6 $\rightarrow$ LUMO	0.65359
				HOMO-4 $\rightarrow$ LUMO	-0.26012



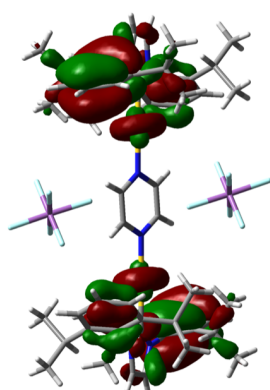
state
(hartree)



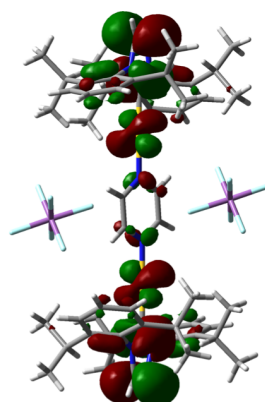
LUMO
(-0.10620)



HOMO
(-0.24967)



HOMO-6
(-0.27293)



HOMO-8
(-0.27599)

Photophysical Properties

For emission decay traces of crystal **4**, we used 370 nm as the excitation wavelength and detected kinetic traces at 600 nm. Emission decays of crystal **5** were detected at 420 nm under 370 nm excitation. The emission decays were measured under 10^4 counts. The obtained emission decays were fitted by using second order exponential decay function.

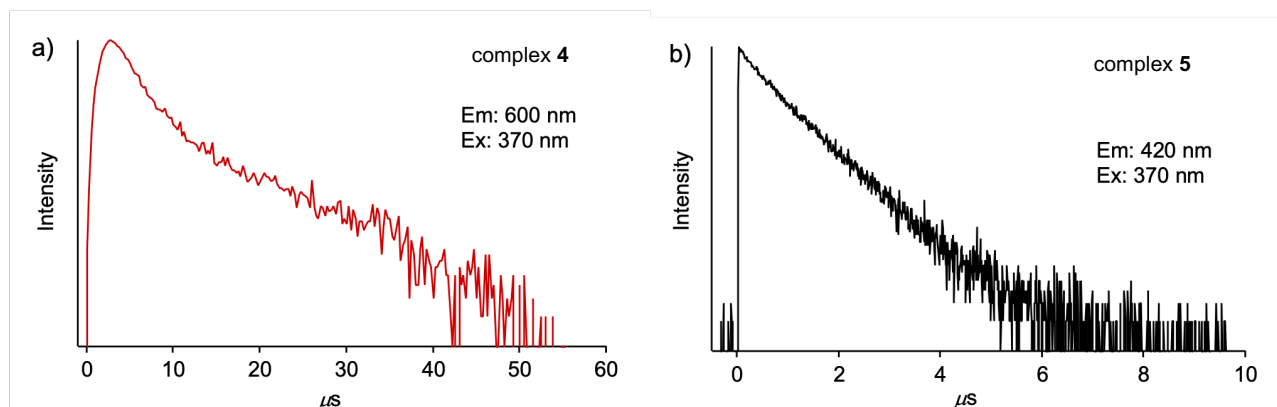


Figure 3-22. Emission decay profiles of the crystal a) **4** and b) **5** measured at room temperatures. The emission decays were monitored at a) 600 nm and b) 420 nm under 370 nm of excitation.

Table 3-6. Emission lifetimes fitted from the emission decays of the crystal **4** and **5**

Sample	$\tau_{av} / \mu s^{a,b}$	$\tau_1 / \mu s^a$ (A / -)	$\tau_2 / \mu s^a$ (A / -)	CHI
crystal 4	3.06	1.69 (0.92)	18.9 (0.08)	1.19
crystal 5	0.87	0.38 (0.13)	0.95 (0.87)	1.03

^a: $\lambda_{ex} = 370$ nm, $\lambda_{em} = 600$ nm for crystal **4** and $\lambda_{em} = 420$ nm for crystal **5**. ^b: $\tau_{av} = \sum \tau_n A_n$.

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Chapter 4.

Development of Giant Molecular Rotor Mediated by Large NHC Au(I) Complex

4.1 Introduction

Rotational dynamics of large size molecules having a three-dimensionally complicate structure such as protein are ubiquitous in nature, and often play the fundamental function of living systems.¹⁻⁵ In artificial molecules, iptycenes which are a class of aromatic compounds with arene units fused to the [2.2.2]bicyclooctatriene bridgehead system have been widely utilized as a key unit for developing molecular motions and functional properties such as photo-functions, electronics, and molecular assembly. In particular, triptycene and pentiptycene derivatives have wide applications by taking advantage of their unique structures that the aromatic moieties are three-dimensionally fused in molecules as well as the p-rich features (Figure 4-1a).⁶⁻⁸ Generally, fluid phases allow to occur the molecular dynamics, while solid phases are considered to be least suitable to show mechanical motion of the large size molecules. Origin of difficultness to show the molecular motion in solid state is a densely packed environment near the molecules. In case of triptycene and pentiptycene, the molecules have a large surface area and volume by the three-dimensionally fused multiple arylenes, resulting in formation of intermolecular π - π or CH- π interactions which suppress the mechanical motion in solid state (Figure 4-1b). However, design elements that generate sufficient volume near the large molecules may allow for large angular displacements, even in the solid phase.

In past two decades, molecular rotational motion in solid-state with functional properties have been intensely investigated by utilizing “amphidynamic crystals” that exhibit fast molecular rotations with highly ordered structures in solid phase (Figure 4-1c).⁹⁻¹⁵ The amphidynamic crystals capable of controlling physical properties by altering the molecular rotation represent a critical development in solid-state functional materials, as well as a promising strategy to transduce molecular-level functions to the macroscopic scale.^{10,16-22} The basic concept of blueprint for the crystalline materials is linking two bulky stators to the rotator via axis moiety. As the structural motifs, gyroscope-like molecular rotors, dumbbell-shaped molecules, and porous materials such as metal–organic frameworks (MOFs) have been employed.^{11,12,14,15} In many cases, the molecular rotations have been achieved with using phenylenes as rotators. However, construction of crystalline molecular rotors to rotate a large size molecule having a complex structure still remains a significant challenge.

When the rotator size increased comparing to phenylene, the larger rotational area is required in the solid-state. In general, large local volume is unlikely formed during the crystallization process. Thus, it is difficult to design the large local volume around the large rotator. Furthermore, large rotator will increase the large contact face and multiple interaction in the crystal, which is unfavorable factor for

showing molecular motion. Recently, Garcia-Garibay *et al.* have succeeded to rotate triptycene in solid state by utilizing dumbbell shape molecular design introducing bulky convex shape large stator as shown in Figure 3-1d.²³ Indeed, MOFs bearing the ligand that triptycene moiety is centrally introduced have been developed with observation of rotary motion of the triptycene in solid state (Figure 4-1d).²⁴ However, these approaches still have an issue inducing unfavorable effect to occur rotational motion of more large size triptycene such as pentiptycene in solid media. In the dumbbell shape molecular rotor, the bulky convex shape stators still allow to form intermolecular steric hinderance between the rotator unit and the nearly packed stators. MOF system have played a great role to construct free volume for the rotation. However, there is also unbeneficial effect that the large pore in MOF also allows to form the interpenetrated structure to fulfill the pore so that it becomes difficult to rotation in the solid-state. Recently, my group developed a new platform for crystalline molecular rotor by using concave shape *N*-heterocyclic carbene (NHC) metal complex as a stator that encapsulate the central rotator unit.^{25,26} Main effort of this approach is that the rotator moiety can be shielded by undesired intermolecular steric hinderance in crystalline media. From this feature, I envisioned that the larger and bulkier NHC ligand can build the large rotational volume for rotating large rotators such as triptycene or pentiptycene in crystal.

In order to realize this concept, herein, I designed the giant NHC Au(I) complexes molecular rotor **6** and **7** by using IPr# ligand [(1,3-bis(2,4,6-tri(diphenylmethyl))imidazo-2-ylidene)]²⁷ as the concave bulky stator with triptycene and pentiptycene rotators, respectively, and observed rotational motion of these triptycene derivatives in crystals. IPr# ligand was introduced because of its highly bulky and large structure which could prevent the close packing of rotator–rotator or rotator-ligand. Both crystalline rotors were characterized by single-crystal X-ray diffraction, revealing that the bulky NHC ligand afforded to construct loose packing environment near the rotators. The ²H spin-echo solid state NMR measurements for the crystalline samples confirmed that rotational motion of both rotators occurred in crystals above 293 K for rotor **6** and 233 K for rotor **7**, respectively.

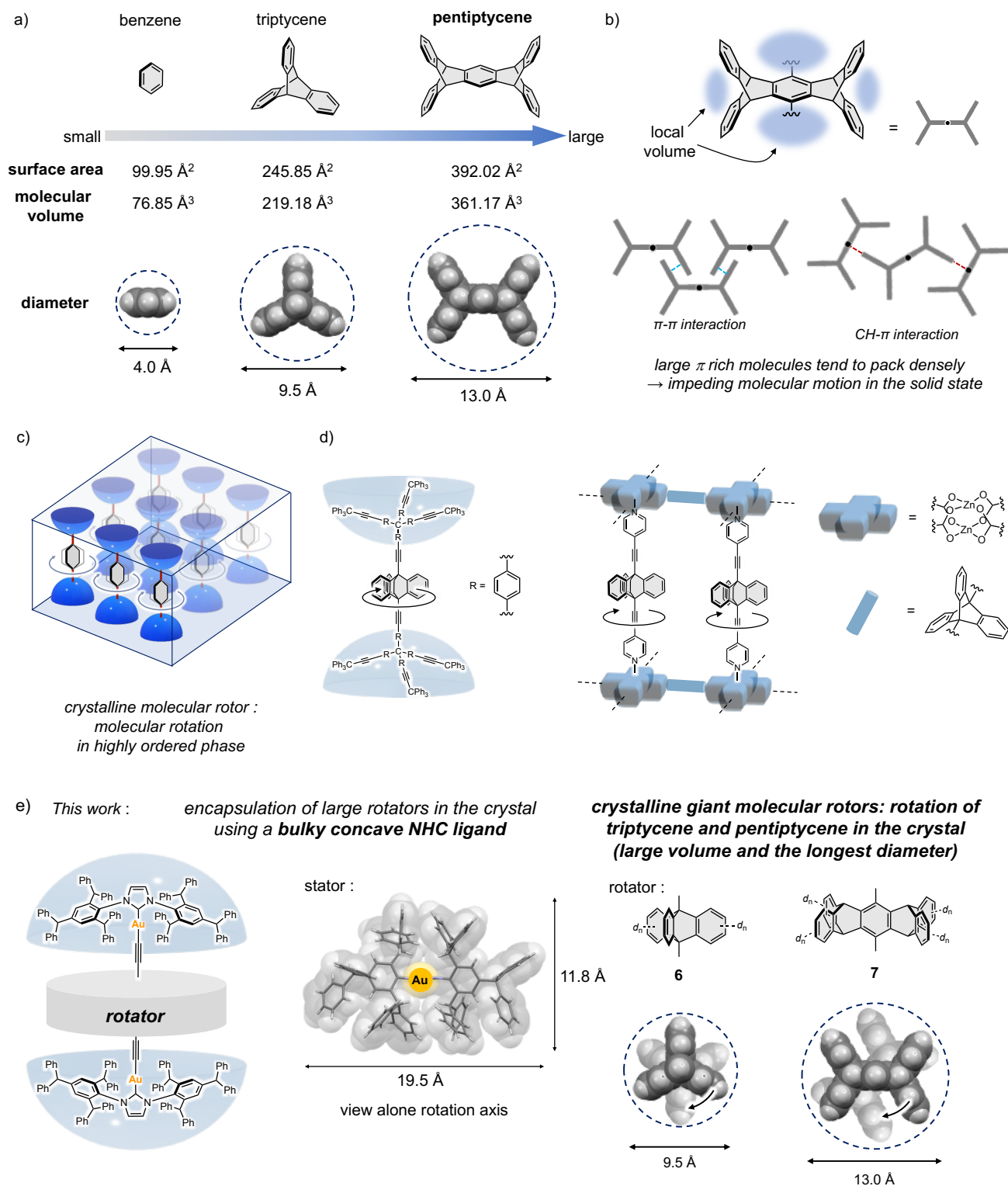


Figure 4-1. a) Molecular size differences (surface, volume, and rotational diameter) for benzene, triptycene, and pentiptycene. b) Schematic image of the packing arrangement for the crystal of pentiptycene. Multiple π - π and CH- π interaction could form dense crystal structure. c) The schematic

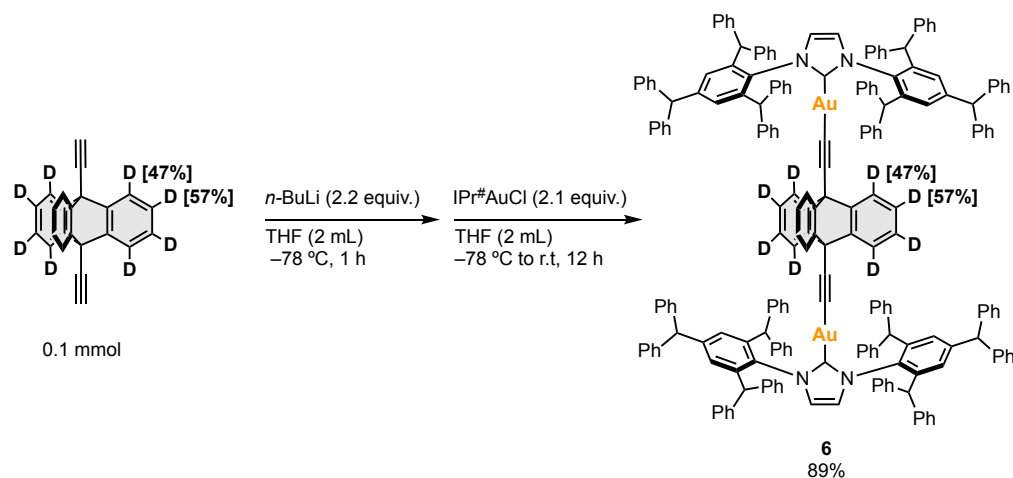
image of crystalline molecular rotor. d) Previously reported molecular rotors using triptycene as rotators. e) Chemical structure of molecular rotor **6** and **7**. The overlap area of IPr# ligand is estimated about 11.8 x 19.5 Å².

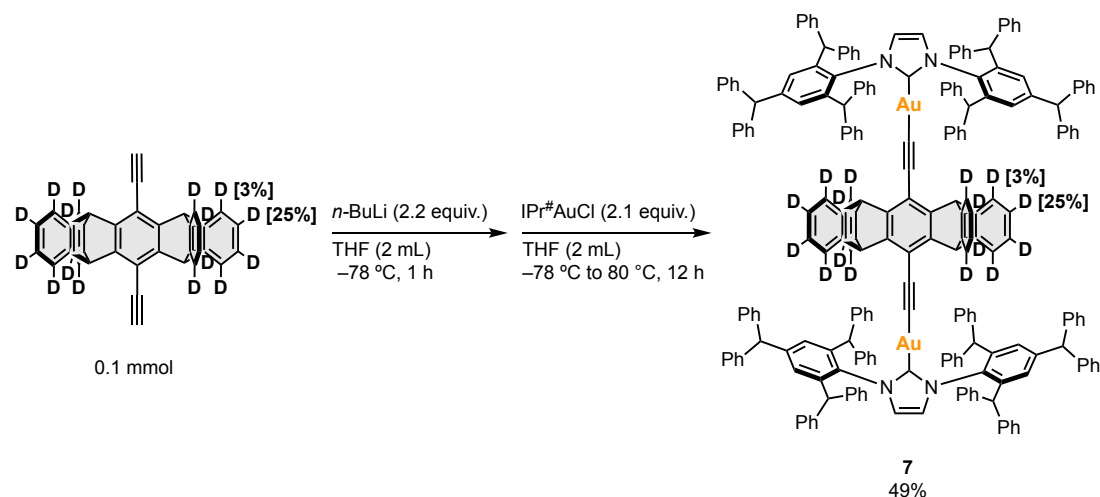
4.2 Result and discussion

Synthesis and preparation

Giant rotors **6** and **7** were synthesized from the diethynyl iptycene compounds and IPr[#] Au(I) chloride using standard alkylation conditions, as illustrated in scheme 6 and 7. The rotor **6** was obtained in 89% yield by the moderate reaction conditions while the synthesis of rotor **7** required high temperature during the reaction to obtain the compound in 49% yield. The rotor **6** was crystallized by solvent diffusion from the dichloromethane solution of **6** layered hexane while vapor diffusion method was conducted for **7** dissolved in CHCl₃ and exposure to the Et₂O vapor. The crystallization of rotor **7** yielded two polymorphs (solvated and non-solvated crystals) in the same vial confirmed by single crystal X-ray analysis (SC-XRD). The solvated crystal of rotor **7** altered to the non-solvated crystal by treating the crystal in vacuum (see Experimental Section). The rotor **6** and **7** was additionally characterized by ¹H, ¹³C nuclear magnetic resonance (NMR) spectroscopy, high resolution mass spectrometry, elemental analysis.

Scheme 4-1. Synthesis of giant rotor **6** and **7**





Single crystal X-ray Diffraction of **6** and **7**

Single crystal XRD measurements were performed to obtain the precise structural information of giant rotor **6**. The rotor **6** was crystallized in the triclinic space group $P2_1/c$ with four molecules per unit cell ($Z=4$). Hexane inclusion was found in the crystal structure with its chemical occupancy 0.5. (Figure 4-2a) Each C–C distance between the phenylene groups of NHC ligand and triptycene moiety is shown in Figure 6-2b. These distances are varied from 3.34 to 3.83 Å. Considering the Van der Waals radius of carbon and hydrogen atoms, the shortest C–C distance of the linear C–H...H–C groups without any interaction is about 4.0 Å, and its distance could be shortened to 2.8 Å when there was favorable interaction. In the rotor **6**, the shortest distance between C–C is 3.34 Å, that is smaller than the 4.0 Å but still longer than the 2.8 Å, indicates the less steric hindrance between the NHC ligand and the rotor, which is the favorable packing manner to show molecular motion of triptycene. The packing environment around the rotor **6** were shown in Figure 4-2c. There are two phenyl groups highlight in purple which are close to the rotator. The distances from these phenylene and the rotational axis of triptycene were ca. 5.59 and 5.91 Å. These distances were longer than the rotational radius of the triptycene (4.75 Å). These packing environment around the triptycene rotator indicates that rotation of triptycene should be affordable. However, hexane near the rotator can sterically disturb rotation of the triptycene despite the hexane is placed in close to the rotational center within 4.86 Å and its slightly longer than the rotational radius of triptycene. In order to promote rotational motion of the triptycene, the solvated crystal was treated under vacuums for 1 day to remove hexane near the rotator, and complete desolvation was proved by ^1H NMR and TGA analysis. The obtained PXRD pattern was well identical with the simulated pattern from the single crystal XRD indicates there was no phase transition during the desolvation and still maintain the crystallinity.

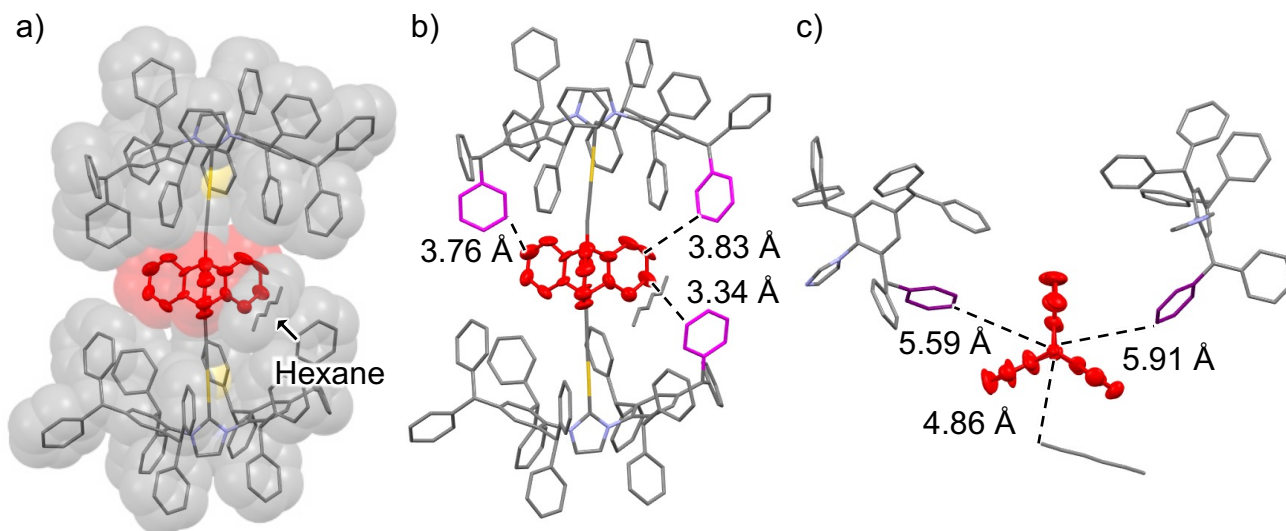


Figure 4-2. a) Crystal structure of giant rotor **6** b) several C–C distances from phenylene group of NHC moiety and triptycene. c) Packing geometry around the rotator. Phenylene groups highlight as purple are close to the rotator.

Single crystal XRD study of giant rotor **7** without solvent inclusion revealed that two independent rotors (denoted as rotor **7a** colored in green and **7b** colored in orange, respectively) were found in the unit cell ($z = 2$) which packed in the space group $P-1$ (Figure 4-3a). The pentiptycene rotator is slightly bent against the two NHC units because of the flexibility of the alkyne axis. In terms of the molecular packing structure, each rotor **7a** and **7b** were aligned along the b -axis and form columnar like structure. (Figure 4-3b) Each pentiptycene was placed in separate and almost no interaction each other. This result indicated that the bulky concave-shaped NHC ligand could prevent strong stacking between each pentiptycene units. (Figure 4-16–17) The distances between the rotator and phenyl groups of stators were shown in the Figure.3c. For the rotor **7a**, some phenylene groups were very close to the pentiptycene moiety. (phenylene was colored in pink) The distance from those phenylene group to the center of triptycene was 4.18 Å, and the nearest distance from phenylene to pentiptycene was 3.54 Å. In fact, these two phenylene could prevent the dynamic motion of pentiptycene because they were placed in the course of rotation. The molecular geometry of the rotor **7b** was different from the rotor **7a**. The closest distance from the rotator to the neighboring phenylene was found 3.68 Å as shown in Figure 4-3c, indicating that the steric hinderance between the phenylene of stator and rotator in **7b** should be smaller than that of **7a**.

The steric environment near the rotators was shown in Figure 4-3d. For rotor **7a**, two phenyl rings of the NHC ligand in the same molecule with the rotator and other two phenyl groups from the neighbored molecules were close to the rotator, colored in pink and purple, respectively. The distances from those units to the rotational center of the pentiptycene were 7.03 Å for purple phenyl groups and 4.18 Å for pink phenyl group, respectively. The distance between the purple phenyl groups is slightly longer than the rotational radius of the pentiptycene rotator 6.50 Å. However, those distances between two phenyl rings colored in pink is quite shorter than the radius of rotator and molecular motion could be prevented. Contrary, distinct packing environment was found for the rotor **7b**. The distance between the phenylene of adjacent molecules colored in purple and the pentiptycene was 4.31 Å, which is also shorter than the rotational radius of pentiptycene. These steric environment near the pentiptycene would prevent the rotational motion in crystals. However, the geometry of phenyl groups near the rotor **7a** were expected to be able to take different conformation via rotation, which may allow to exhibit the rotational motion of the pentiptycene in **7a** (Experimental Section). In contrast, the orientation of phenyl rings near the rotor **7b** would not allow to occur the rotation of **7b** because the rotation axis of the phenyl moiety is vertical from the rotation axis of **7b**, which should suppress the motion of rotor **7b**. From the crystal structure analysis, I assumed that the crystal of giant rotor **7** would exhibit mainly two different molecular motions attribute from the **7a** and **7b**.

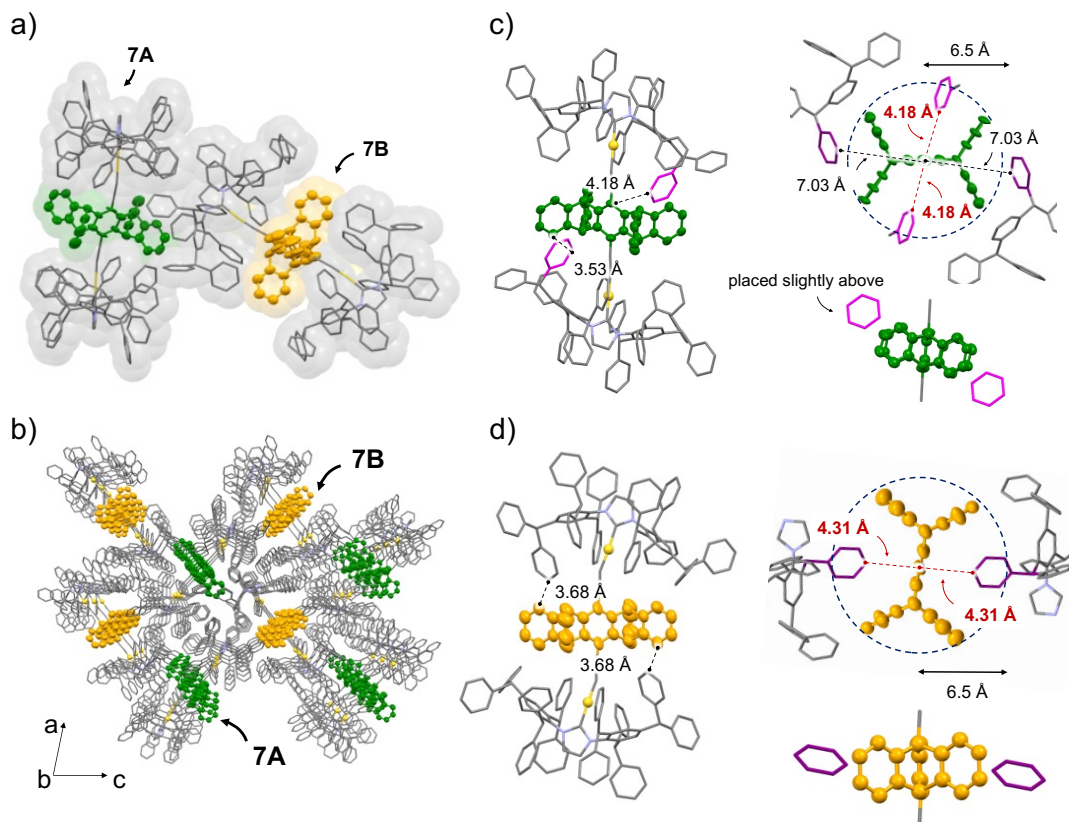


Figure 4-3. a) Crystal structure of giant rotor **7** (two independent rotors were denoted as rotor **7a** colored in green and **7b** colored in orange, respectively). b) Crystal packing arrangement of rotor **7**. c) Selected C–C distances from phenylene group of NHC moiety to pentyptycene, and d) packing geometry around the rotor **7a** and **7b** shown from the axis. Phenylene groups near of the rotators were colored in purple.

Solid-state ^2H NMR measurement and simulation studies

To investigate molecular motion of the crystalline rotor **6** and **7**, I carried out the variable temperature solid-state ^2H NMR spin-echo measurements with line shape simulation. It has been established that the method is ideally suited to determine the dynamics of deuterium-enriched moieties with site-exchange rates in the dynamic range of ca. 10^3 – 10^7 s $^{-1}$.²⁹ The key parameters for the rotation of the aromatic groups are the cone angle between the C–D bond and rotation axis. For rotor **6**, two different deuterium atoms would give the ^2H NMR spectrum, deuterium atoms at α -carbon (cone angle = 0°) and β -carbon (cone angle = 60°). The deuterium atoms at α -carbon do not give any line shape

change whether the molecular rotation occurred or not and give the Pake pattern with two shape peaks with two shoulders. By contrast, the ^2H NMR signal from the deuterium atoms at β -carbon give the molecular motion-dependent line shape change. From the ^2H NMR measurement for rotor **6** under variable temperature, clear line shape change was observed during the heating process from 295 to 348 K. The line shape simulation indicated that the dynamics of triptycene seemed to have multi component mode of motion with 3-fold 120° Brownian jumping and 3-site 30° . The simulated rotational frequency (k_{rot}) for 3-fold 120° jumping was 300, 600, 900, 1200 and 1800 kHz measured at 273, 295, 313, 333 and 348 K, respectively. The Arrhenius plots constructed from the rotational exchange frequencies observed at each of the experimental temperatures for rotor **6** (Figure 4-21). The activation energy (E_a) for rotor **6** was 4.3 kcal/mol and a preexponential factor (k_0) of $9.1 \times 10^8 \text{ s}^{-1}$ that is 3 orders of magnitude smaller than the value expected for theoretical, $5.6 \times 10^{11} \text{ s}^{-1}$.^{23,24} The relatively smaller k_0 obtained by the experiment may be reasoned by some correlated motion with the neighboring phenyl rings.

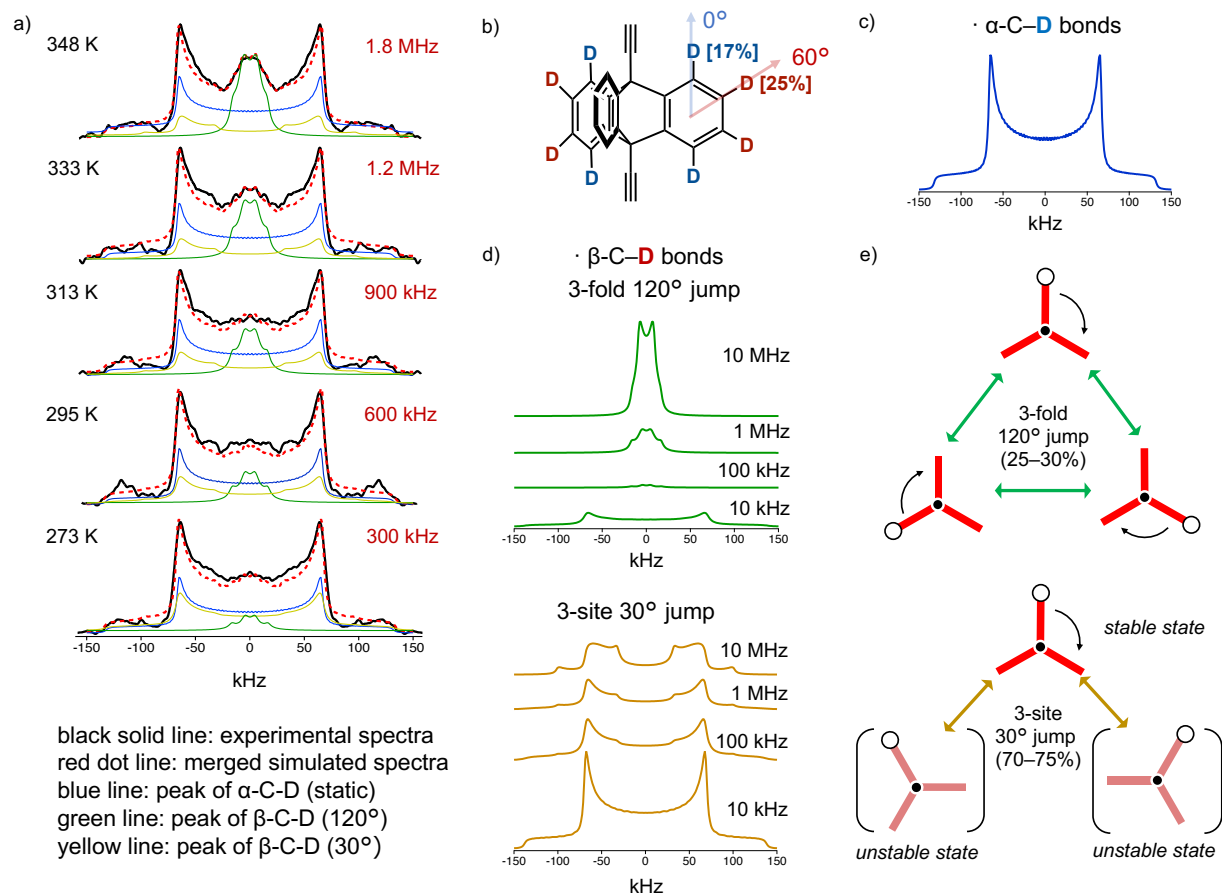


Figure 4-4. a) Various temperature (VT) solid-state (SS) ^2H NMR studies of rotor **6**. Experimental SS NMR spectra represented in solid black line, and the simulation spectra illustrated in red dashed line for superposition, blue solid line static spectra derived from α -D position, green and yellow solid line for 3-fold 120° jump and 3-fold 30° jump derived from β -D position, respectively. b) Cone angles experienced by the triptycene C–D bonds at the α - and β -positions highlighted in red and blue, respectively. Simulated ^2H NMR spectra for (c) the α -C–D bonds at all exchange frequencies and (d) the β -C–D bonds assuming a three-fold symmetric rotation, above one for 120° jump and below one for 30° jump, respectively. (e) Representation of the molecular rotation for 3-fold 120° jump (above) and 3-fold 30° jump (below).

The obtained spectra for the giant rotor **7** exhibited clear line shape change, especially around – 50 to 50 kHz from 233 K to 313 K, indicating that molecular motion of pentiptycene occurred in the solid-state. The line shape simulation of the spectra of giant rotor **7** was carried out considering that two pentiptycenes (**7a** and **7b**) were placed in the different packing environment as mentioned above. (Figure 4-3) The simulation patterns of rotor **7a** were assuming by 2-fold site exchanges and applied the different population site ratio. At lower temperature, rotor **7a** showed 2-fold 100° and/or 2-fold 80° jumping at K_{rot} for 100–150 kHz. These 2-fold motion become to 2-fold 90° jumping at 273 K and finally 4-fold 90° jumping was combined with 2-fold 90° jumping at 295 K and 313 K with its k_{rot} for 260 and 400 kHz, respectively. The molecular motion of rotor **7b** could not exhibit fully rotation due to the strongly stacked phenylene but could show motion with small angle, like libration. The line shape simulation suggested that 3-site 30° jump would occur from 233 K to 313 K for rotor **7b** with k_{rot} value at 300 to 1200 kHz. I note that owing to its unique structure of pentiptycene that possess the four phenyl blades and two different concave spaces, multiple metastable states would be existed in the crystal and resulted the site exchange with different population. These factors also would make it difficult to expect its molecular motion in the solid-state, and therefore I could not dismiss the possibility of other molecular motions. However, the clear line shape change of NMR spectra indicates the molecular motion of pentiptycene occur in the solid-state. The Arrhenius plot for rotor **7** was not achieved due to the different motions occurred at each temperature.

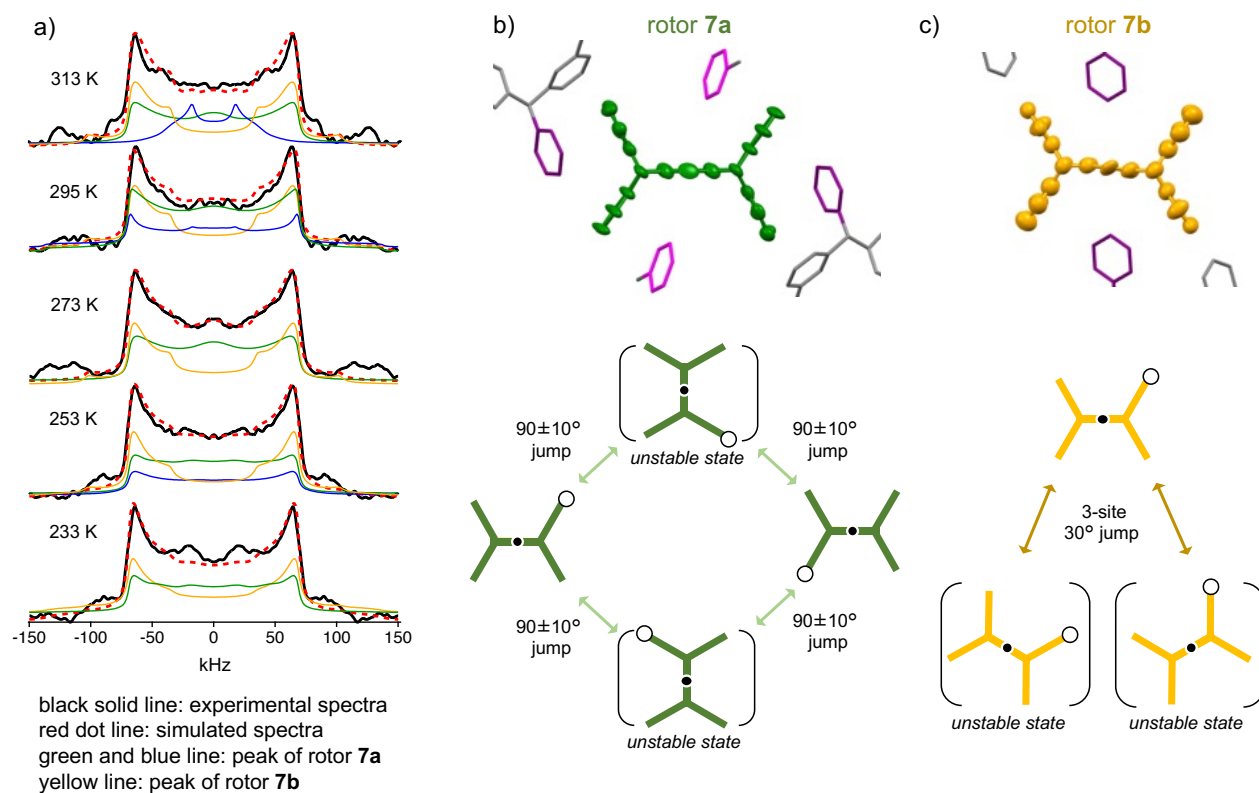


Figure 4-5. a) Various temperature (VT) solid-state (SS) ^2H NMR studies of rotor **7**. Experimental SS NMR spectra represented in solid black line, and the simulation spectra illustrated in red dashed line for merged one, green and blue solid lines for rotor **7a**, and yellow solid line for rotor **7b**, respectively. Packing environment around the rotators and representation of the molecular rotation for b) rotor **7a** and c) rotor **7b**.

Table 4-1. The simulated rotational motions and its frequency (k_{rot}) for rotor **7a** and **7b** at various temperature.

T [K]	rotor 7a		k_{rot} [kHz]	rotor 7b	
	green line	blue line		yellow line	k_{rot} [kHz]
313	2-fold 90° (0.8)	4-fold 90° (0.2)	400	3-site, 30°	1200
295	2-fold 90° (0.7)	4-fold 90° (0.3)	260	3-site, 30°	950
273	2-fold 90°	—	200	3-site, 30°	800
253	2-fold 100° (0.8)	2-fold 80° (0.2)	150	3-site, 30°	500
233	2-fold 100°	—	100	3-site, 30°	300

4.3 Summary

Here, I described the first example of a crystalline materials that exhibit rotational dynamics of bulky iptycene derivates (triptycene for **6**, pentiptycene for **7**) in solid state. Single crystal XRD measurement revealed that the encapsulation motif by the large concave shape NHC ligands provided reasonable rotational space around the central rotator with suppressing formation of intermolecular interaction between the rotators and the nearly packed moiety. ^2H solid state NMR studies suggested that multiple molecular motions occurred in both bulky rotors around 233 K to 348 K. These results strongly indicate that this platform will enable further study and design of rotational motion of large size and complicate molecular units, which structural integrity and high mobility of the molecular components, and greatly enhance the development of new functional materials based on the large size of molecular dynamics in the crystalline solid.

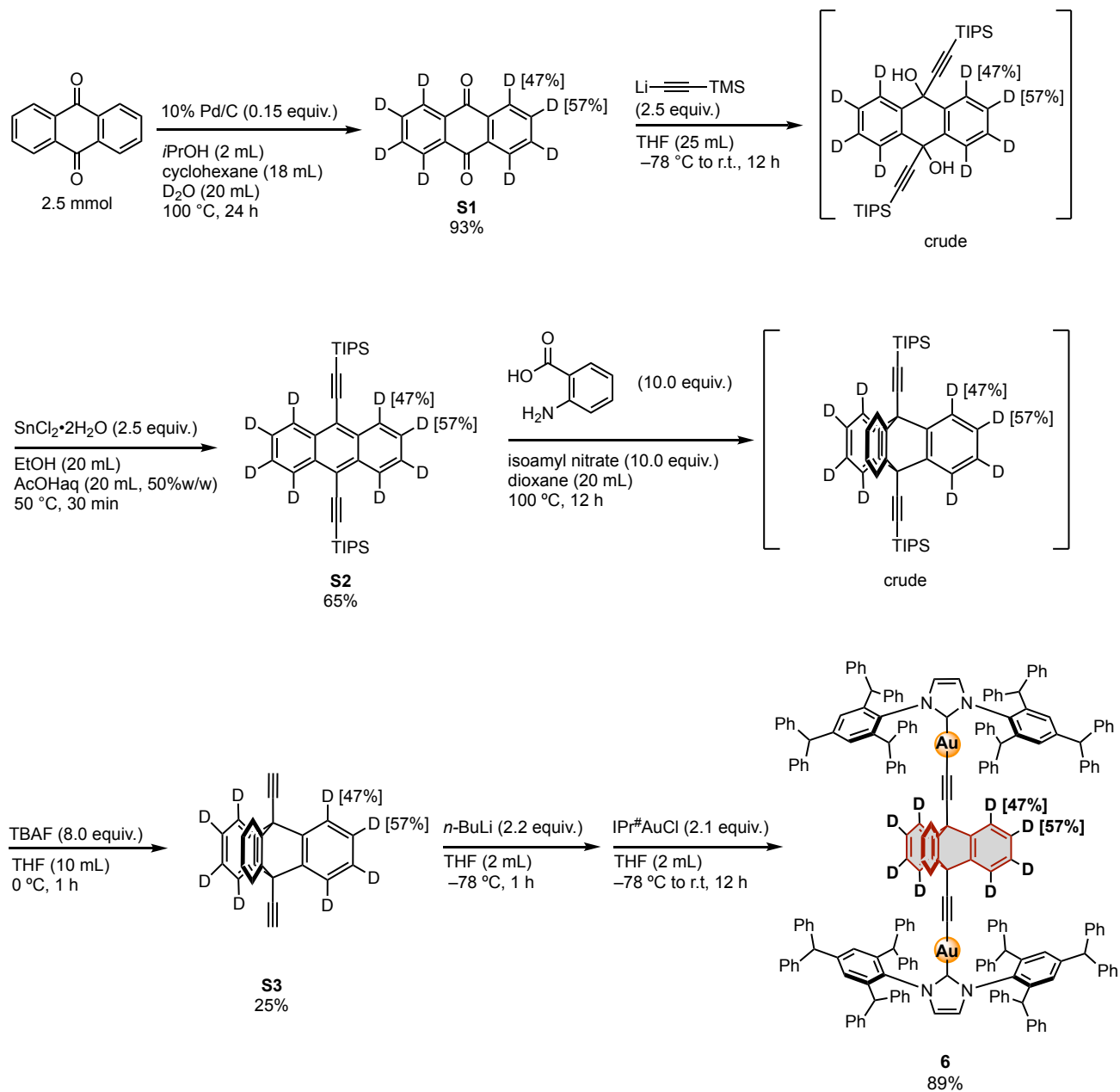
4.4 Experimental Sections

General

All commercially available reagents and solvents are reagent grade and were used without further purification unless otherwise noted. Solvents for the synthesis were purchased from commercial suppliers and dried over molecular sieves (4 Å). NMR spectra were recorded on a JEOL JNM-ECX400P, JNM-ECS400 (^1H : 400 MHz; ^{13}C : 99.5 MHz) using tetramethylsilane and CDCl_3 as internal standards, respectively. Solid-state ^2H NMR spectra were acquired on a Bruker AVANCE III HD 500 MHz (^2H : 76.77 MHz). Elemental analyses and low- and high-resolution mass spectra were recorded at the Global Facility Center at Hokkaido University. Thermal gravimetric analysis profiles were recorded on Bruker TG-DTA2010SAT. Differential Scanning Calorimetry (DSC) profiles were measured on DSC Q2000 V24.11. Powder X-ray diffraction (PXRD) data were obtained on a Rigaku SmartLab diffractometer with $\text{Cu-K}\alpha$ radiation and D/teX Ultra detector at room temperature. The raw data files were plotted on Igor Pro Version 6.37.

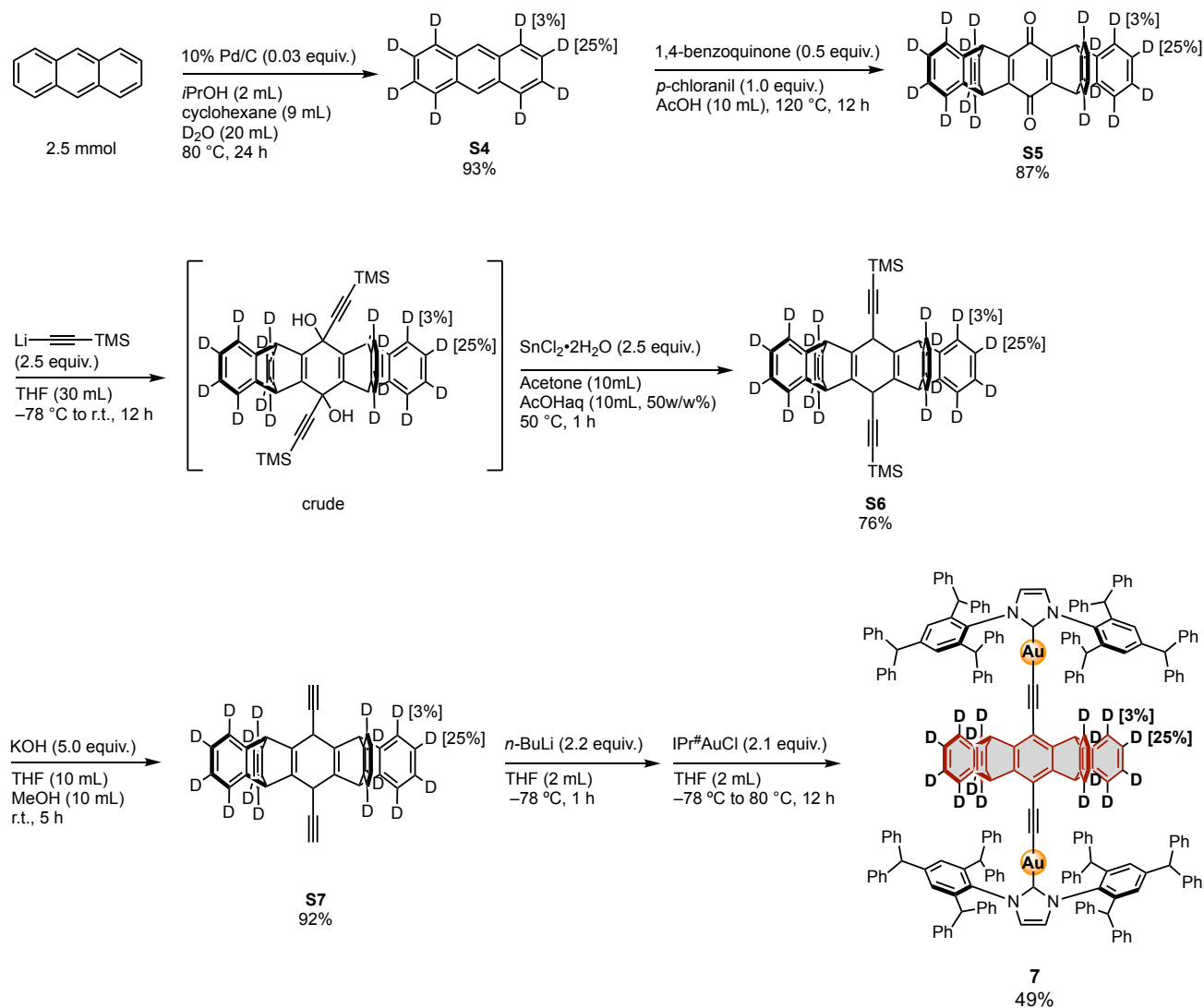
Synthesis

Scheme 4-2. synthesis of giant rotor **6**



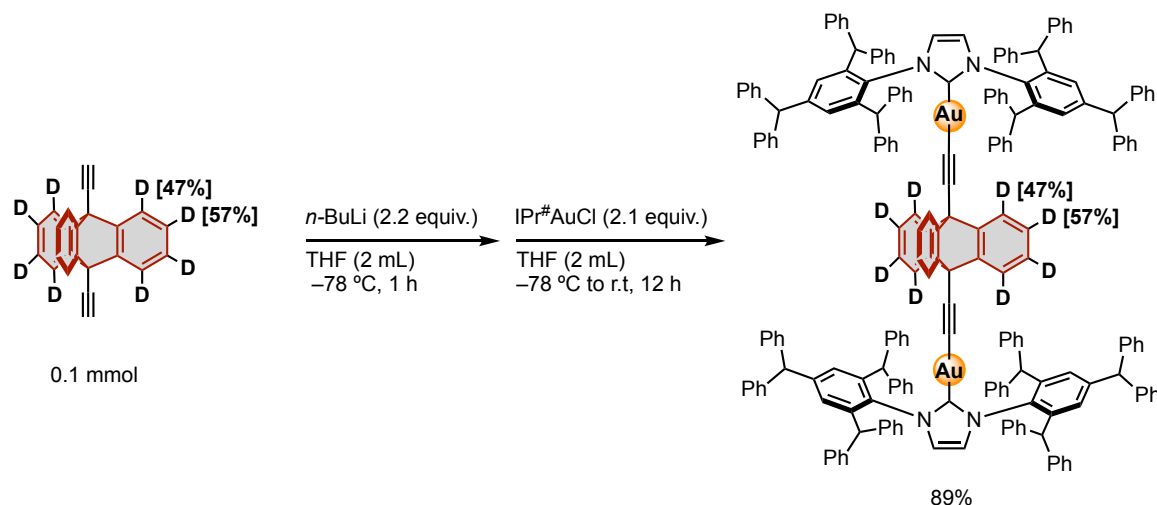
The compound IPr[#]AuCl¹, **S1**², **S2–S3**³ were prepared according to the previously reported literatures. The deuterated ratio of all compounds in scheme S1 was estimated via the compound **S3**.

synthesis of giant rotor **7**



The compound IPr[#]AuCl¹, **S4**², **S5–S7**⁴ were prepared according to the previous reports. The deuterated ratio of all compounds in scheme S2 was estimated based on the compound **S7**.

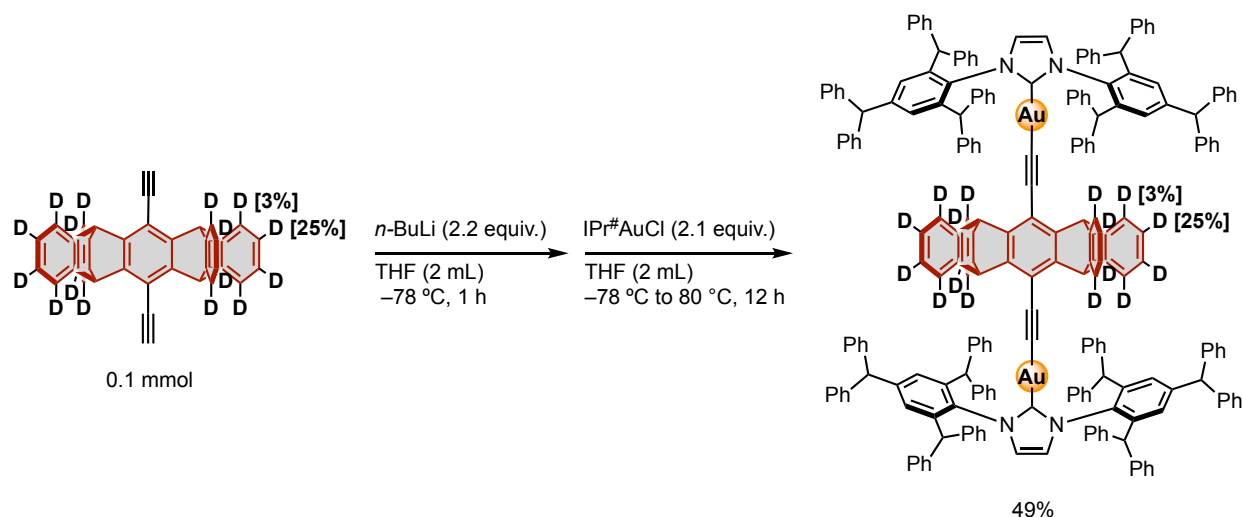
Synthesis of giant rotor **6**



To an oven-dried screw cap test tube was added diethynyltriptycene-*d* **S3** (21.4 mg, 0.07 mmol) and THF (10 mL), followed by cooling to −78 °C. 1.57 M of *n*-BuLi in hexane (0.10 mL, 0.15 mmol) was then added dropwise to the reaction mixture and stirred an hour at −78 °C. To the reaction mixture the IPr[#]AuCl (213.1 mg, 0.15 mmol) dissolved in THF (5 mL) was then added and reaction temperature was allowed to increase to room temperature for 12 h. The reaction mixture was passed through the short silica pad washed with DCM. The solvent was removed in vacuo and the crude product was purified by flash column chromatography using a mixture of hexane and DCM to afford the compound **6** as white solid. (194.7 mg, 89%). ¹H NMR (400 MHz, CDCl₃, δ): 5.43 (s, 4H), 5.48 (s, 8H), 5.92 (s, 4H), 6.82 (dd, *J* = 1.6 and 7.2 Hz, 16 H), 6.86 (s, 8 H), 6.96 (dd, *J* = Hz, 16 H), 7.02–7.08 (m, 17 H), 7.09–7.15 (m, 59 H), 7.20 (d, *J* = 7.6 Hz, 16 H), 8.14 (dd *J* = 5.8 and 3.8 Hz, 4.2 H). ¹³C NMR (100 MHz, CDCl₃, δ): 51.5 (CH), 56.4 (CH), 122.9 (CH), 123.3 (CH), 125.0 (CH), 126.4 (CH), 126.6 (CH), 126.6 (CH), 128.5 (CH), 128.6 (CH), 129.3 (CH), 129.5 (CH), 129.8 (CH), 131.0 (CH), 134.7 (C), 141.2 (C), 142.7 (C), 143.0 (C), 143.2 (C), 145.8 (C), 146.2 (C), 146.3 (C) 191.3 (C) MS-ESI (*m/z*): [M+H]⁺ calcd for C₂₁₀H₁₅₂D₄Au₂N₄H, 3134.20575; found, 3134.21. *Due to the variation of the deuterated ratio of compound, the exact mass was not able to evaluate from the high mass spectroscopy.* Elemental analysis (calcd. for C₂₁₀H₁₅₂D₄Au₂N₄ C, 80.25; H, 5.01; N, 1.76; Found: C, 80.49; H, 5.15; N, 1.79).

* Due to the highly overlap of the ¹H signal of triptycene and aromatic ¹H of phenyl moieties of NHC ligand, the average ratio of deuteration was determined from the diethynyltriptycene-*d* **S3**.

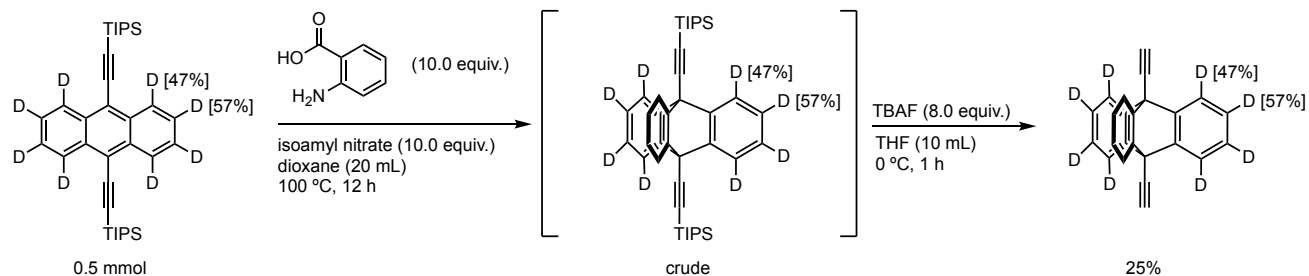
Synthesis of giant rotor **7**



To an oven-dried screw cap test tube was added diethynylpentptycene-*d* **S7** (48.1 mg, 0.1 mmol) and THF (2 mL), followed by cooling to −78 °C. 1.57 M of *n*-BuLi in hexane (0.14 mL, 0.22 mmol) was then added dropwise to the reaction mixture and stirred an hour at −78 °C. To the reaction mixture the IPr[#]AuCl (304.5 mg, 0.21 mmol) dissolved in THF (2 mL) was then added and reaction temperature was allowed to increase to 80 °C for 12 h. The reaction mixture was pathed through the short silica pad washed with DCM. The solvent was removed in vacuo and the crude product was purified by flash column chromatography using a mixture of hexane and DCM to afford the compound **7** as white solid. (162.1 mg, 49%). ¹H NMR (400 MHz, CDCl₃, δ): 5.42 (s, 4H), 5.48 (s, 8H), 5.94 (s, 4H), 6.26 (s, 4H), 6.83–6.86 (m, 22 H), 6.95 (d, *J* = 7.2 Hz, 16 H), 7.04 (t, *J* = 7.4 Hz, 8 H), 7.08–7.17 (m, 48H), 7.23–7.26 (m, 32 H), 7.34 (t, *J* = 4.0 Hz, 8H) ¹³C NMR (100 MHz, CDCl₃, δ): 51.5 (CH), 52.6 (CH), 56.3 (CH), 98.6 (C) 116.5 (C), 123.4 (CH), 123.9 (CD) 124.0 (CH), 124.5 (CD), 124.7 (CH), 126.4 (CH), 126.7 (CH), 128.5 (CH), 128.5 (CH), 128.7 (CH), 129.4 (CH), 129.5 (CH), 129.8 (CH), 130.9 (CH), 134.7 (C), 137.2 (C) 141.2 (C), 142.1 (C), 142.8 (C), 143.0 (C), 143.2 (C), 145.9 (C). 146.5 (C) 191.2 (C) MS-ESI (*m/z*): [M+Na]⁺ calcd for C₂₂₄H₁₆₂D₂Au₂N₂Na, 3330.23719; found, 3330.25. *Due to the variation of the deuterated ratio of compound, the exact mass was not able to evaluate from the high mass spectroscopy.* Elemental analysis (calcd. for C₂₂₄H₁₆₂D₂Au₂N₂ C, 81.34; H, 5.06; N, 1.69; Found: C, 80.83; H, 4.93; N, 1.70).

* Due to the highly overlap of the ¹H signal of pentptycene and aromatic ¹H of phenyl moieties of NHC ligand, the average ratio of deuteration was determined from the diethynylpentptycene-*d* **S7**.

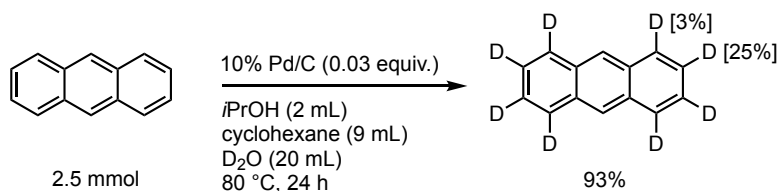
Synthesis of diethynyltritycene-*d* **S3**



S2 (271.5 mg, 0.5 mmol) was dissolved in anhydrous 1,4-dioxane (10 mL) in a 3-neck flask equipped with two dropping funnels and condenser. The solution was heated to 100°C and then a solution of anthranilic acid (685.7 mg, 5.0 mmol) and iso-amyl nitrite (585.8 mg, 5.0 mmol) in anhydrous dioxane (5 mL) were slowly added in via additional funnels over a period of 4 h. The reaction mixture was heated to 100°C another 8h before it was allowed to cool down to room temperature. The solvent was evaporated in vacuo. The residue was roughly purified by silica column with hexane and obtained as the mixture of desired product and byproduct which was used directly in the next reaction.

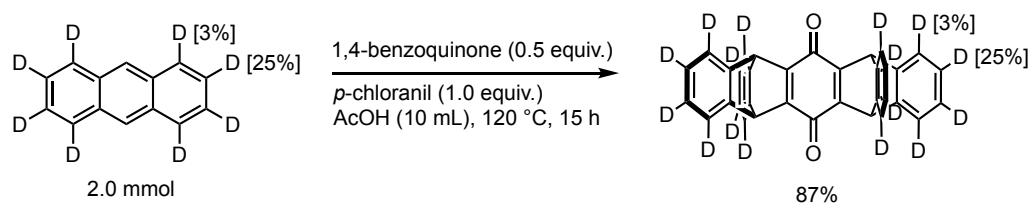
The crude product obtained from the previous reaction was dissolved in THF (10 mL) at 0 °C and TBAF (1.0 M solution in THF, 4.0 mL) was added into the reaction flask slowly. The reaction was stirred in an ice-water bath at 0 °C for 30 min before a saturated NH₄Cl solution was added in to quench the reaction. The product was extracted with diethyl ether (50 mL) twice. The combined organic layers were dried over anhydrous MgSO₄ and concentrated under vacuum to give a pale-yellow residue. The crude material was purified by silica column using hexanes as the eluent provided the desired product **S3** (39.3 mg, 25 %). The ¹H NMR spectra was well matched with the literature.³ The average ratio of deuteration was determined as 47% for alpha- and 57% for beta-position of the phenylene via comparison of the ¹H NMR spectra with the non-deuterated compound. ¹H NMR (400 MHz, CDCl₃, δ) 3.30 (s, 2H), 7.11 (dd, J = 3.2 and 5.6 Hz, 3.7H), 7.76 (dd, J = 3.4 and 5.0 Hz, 4.1H)

Synthesis of anthracene-*d* **S4**²



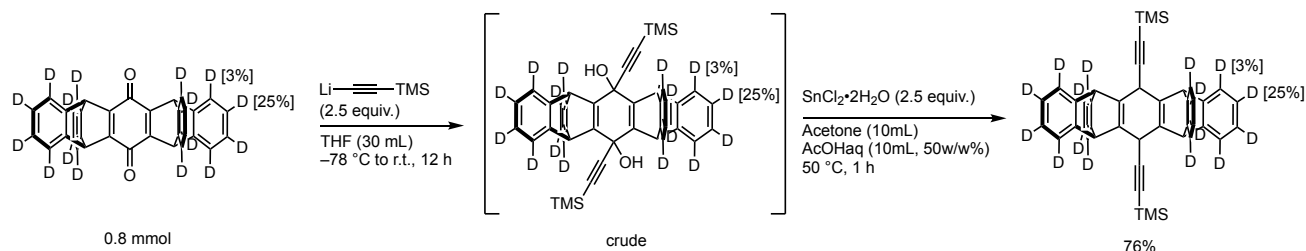
The deuteration of the anthracene was performed as literature.² To an oven-dried 50 mL pressure tube was added anthracene (445.6 mg, 2.5 mmol) and 10% Pt/C (146.3 mg, 0.075 mmol, 0.03 equiv.) followed by D₂O (20 mL), *i*PrOH (2 mL) and cyclohexane (9 mL). The reaction mixture was heat to 80°C for 24 h. The reaction mixture was pathed through the celite to remove the Pt/C and washed with DCM, and organic solvent was separated, and removed in vacuo to afford the compound **S4** as white solid which was enough pure to use for next reaction. (416.4 mg, 93%). ¹H NMR (400 MHz, CDCl₃, δ): 7.46 (dd, *J* = 2.8 and 6.8 Hz, 2.86H), 8.01 (dd, *J* = 4.0 and 5.6 Hz, 3.84H), 8.43 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 125.5(CH), 126.4(CH), 128.2(CD), 128.3(CH), 131.8(C) MS-EI (*m/z*): [M]⁺ calcd for C₁₄H₉D, 179.08453; found, 179.09. *Due to the variation of the deuterated ratio difference of compound, the exact mass could not calculate from the high mass spectroscopy.*

Synthesis of pentiptycene quinone-*d* **S5**



Acetic acid (10 mL) was added to a mixture of **S4** (358.5 mg, 2.0 mmol), 1,4-benzoquinone (108.1 mg, 1.0 mmol) and *p*-chloranil (491.8 mg, 2.0 mmol). The suspension was heated to 120°C overnight. The reaction mixture was then cooled to room temperature, and the yellow precipitate was isolated by the filtration, washed with diethyl ether (3 × 50 mL) and dried to give **S5** as a yellow powder. (402.1 mg, 87%). ¹H NMR (400 MHz, CDCl₃, δ): 5.77 (s, 4H), 6.97 (dd, *J* = 3.2 and 5.6 Hz, 5.9H), 7.36 (dd, *J* = 4.4 Hz, 7.8H) ¹³C NMR (100 MHz, CDCl₃, δ): 47.5 (CH), 124.3 (CD), 124.4 (CH), 125.5 (CD), 125.6 (CH), 143.8 (C), 151.1 (C), 180.1 (C) MS-EI (*m/z*): [M]⁺ calcd for C₃₄H₁₈D₂O₂, 462.15888; found, 463.16. *Due to the variation of the deuterated ratio difference of compound, the exact mass could not calculate from the high mass spectroscopy.*

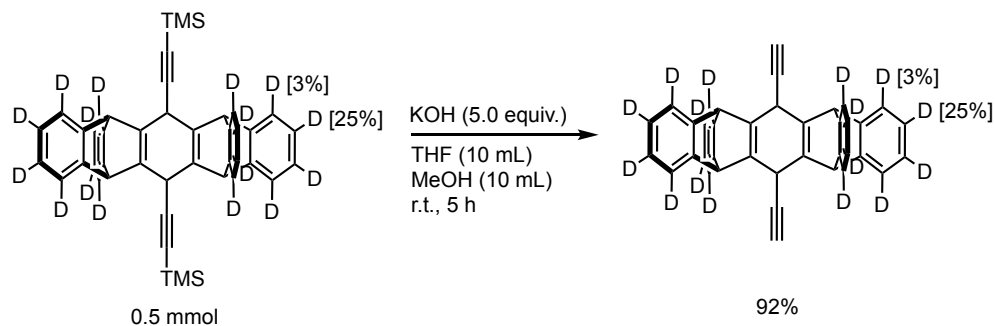
Synthesis of bis(TMS-ethynyl)pentiptycene-*d* **S6**



At $-78\text{ }^{\circ}\text{C}$, under a nitrogen atmosphere, *n*-BuLi in hexanes (1.57 M, 1.27 mL, 2.5 mmol) was added to a solution of TMS-acetylene (0.29 mL, 196.4 mg, 2.5 mmol) in THF (10 mL). The colorless mixture was warmed to room temperature and stirred for 1 h. It was then added to a solution of **S5** (370.0 mg, 0.8 mmol) in dry THF (20 mL) at $-78\text{ }^{\circ}\text{C}$. The resulting pale suspension was allowed to warm to room temperature and stirred overnight. After the reaction, water was added, the organic layer was taken, and the aqueous phase extracted with dichloromethane ($2 \times 50\text{ mL}$). The combined organic phases were dried MgSO_4 and taken to dryness under reduced pressure. The resulting pale-yellow powder was used to next reaction without further purification.

The crude was suspended in acetone (10 mL) and a solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (451.3 mg, 2.0 mmol) in 50% v/v AcOH(aq) (10 mL) was added dropwise. Once addition was complete, the suspension was stirred $50\text{ }^{\circ}\text{C}$ for 1 h. The reaction mixture was cooled to room temperature, and the precipitate was isolated by filtration washed with water ($3 \times 20\text{ mL}$) and petroleum ether ($5 \times 10\text{ mL}$) then dried thoroughly in vacuo to give **S6** as a white powder. (379.3 mg, 76%). ^1H NMR (400 MHz, CDCl_3 , δ): 0.48 (s, 18H), 5.77 (s, 4H), 6.94 (dd, $J = 3.0$ and 5.4 Hz , 6.0H), 7.32 (dd, $J = 4.4\text{ Hz}$, 7.8H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 0.5 (CH₃), 52.3 (CH), 100.7 (C), 102.6 (C), 115.0 (C), 123.8 (CD), 123.9 (CH), 125.2 (CD), 125.4 (CH), 144.2 (C), 145.0 (CH) MS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{44}\text{H}_{36}\text{D}_2\text{Si}_2\text{Na}$, 647.2530; found, 647.26. *Due to the variation of the deuterated ratio difference of compound, the exact mass could not calculate from the high mass spectroscopy.*

Synthesis of diethynylpentiptycene-*d* **S7**



S6 (312.5 mg, 0.5 mmol) was dissolved in THF (10 mL) and methanol (10 mL) and KOH (140.3 mg, 2.5 mmol) was added which causing a precipitate to form. The suspension was stirred at room temperature under for 5 h. The solid was then isolated by filtration, washed with ethanol (3×10 mL) and dried in vacuo to give **S7** as a white powder. (222.0 mg, 92%). The average ratio of deuteration was determined as 3% for alpha- and 25% for beta-position of the phenylene via comparison of the ^1H NMR spectra with the non-deuterated compound. ^1H NMR (400 MHz, CDCl_3 , δ): 3.70 (s, 2H), 5.82 (s, 4H), 6.95 (dd, $J = 3.0$ and 5.4 Hz, 6.0H), 7.36 (dd, $J = 4.2$ Hz, 7.8H). *Due to the low solubility of compound, ^{13}C NMR spectra could not obtained.* MS-EI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{38}\text{H}_{20}\text{D}_2$, 480.18470; found, 480.17. *Due to the variation of the deuterated ratio of compound, the exact mass could not calculate from the high mass spectroscopy.*

Crystal preparation of rotor **7**

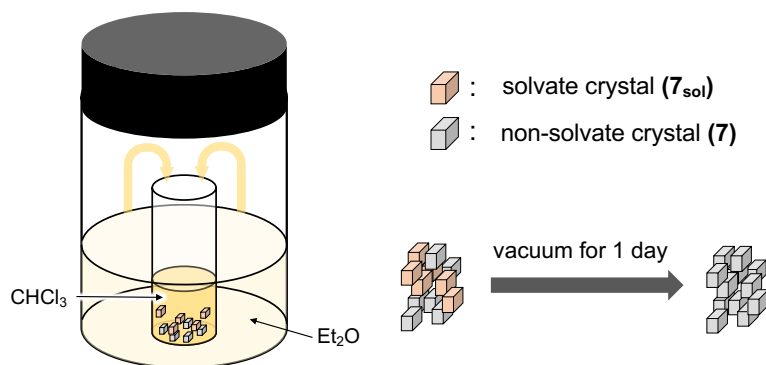


Figure 4-6. Schematic image of the crystallization process.

The single crystal of giant rotor **7** was obtained by $\text{CHCl}_3/\text{Et}_2\text{O}$ vapor diffusion method. In this case, we found two polymorphs in the same crystallization vial. (Figure 4-6) Both crystal structure was solved by SC XRD measurement, and we found one was crystallized without the solvent (crystal **7**) and another one was with CHCl_3 (crystal 7_{sol}). The crystal 7_{sol} may transform to the crystal **7** by vacuuming the crystal for 1 day at room temperature confirmed by PXRD measurement. (Figure 4-7)

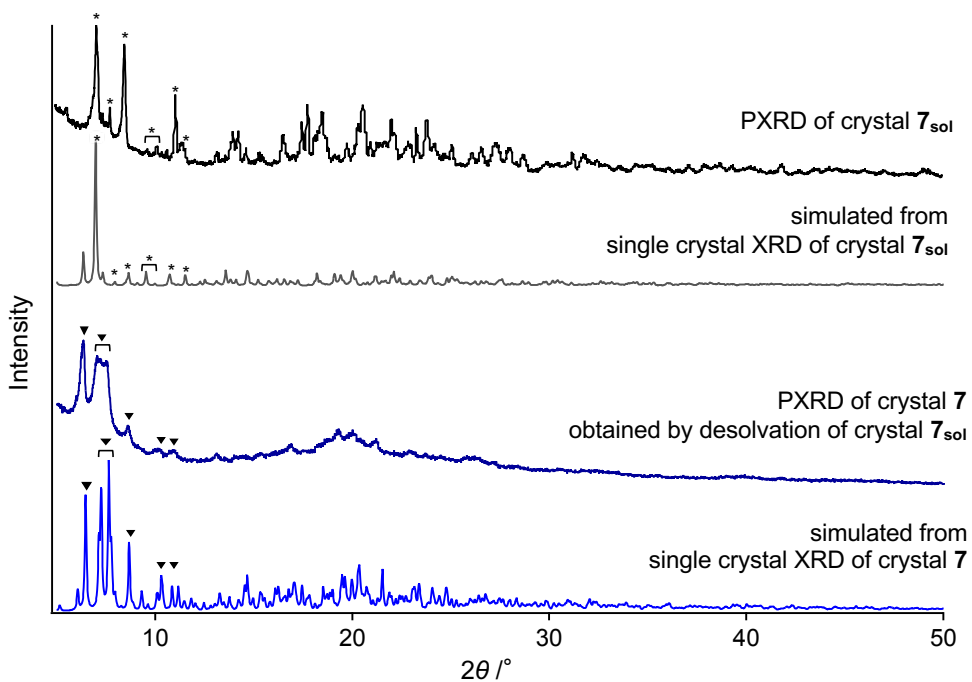


Figure 4-7. Measured powder XRD patterns of crystal 7_{sol} and 7. Details of the single-crystal data are summarized in Table 4-3.

Various Temperature Powder X-Ray Diffraction Study

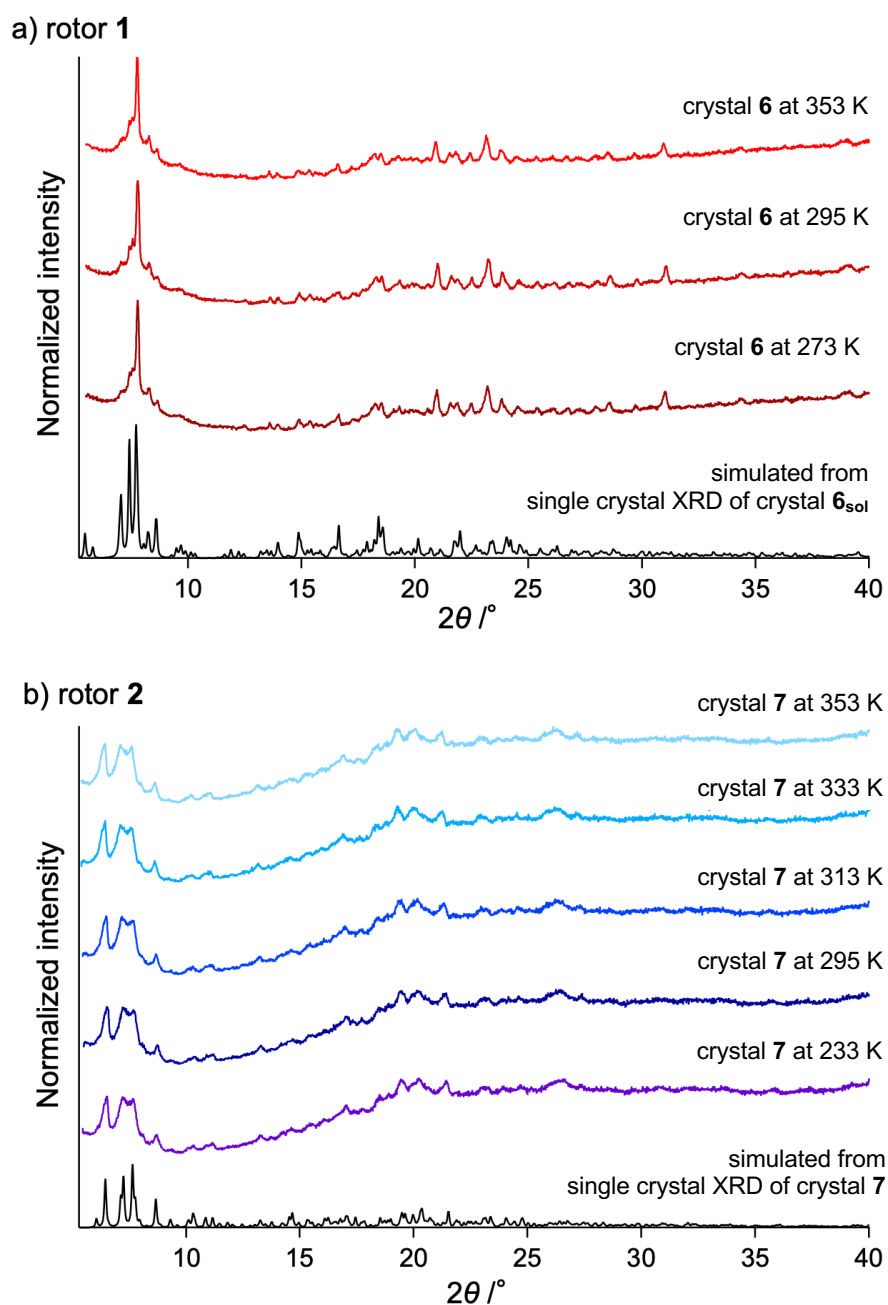


Figure 4-8. Various temperature powder XRD patterns of the crystalline samples of a) crystal 6 and b) 7, obtained by desolvation of crystal 6_{sol} and 7_{sol} via vacuum, respectively. Simulated patterns obtained by single crystal structure of crystal 6_{sol} and crystal 7.

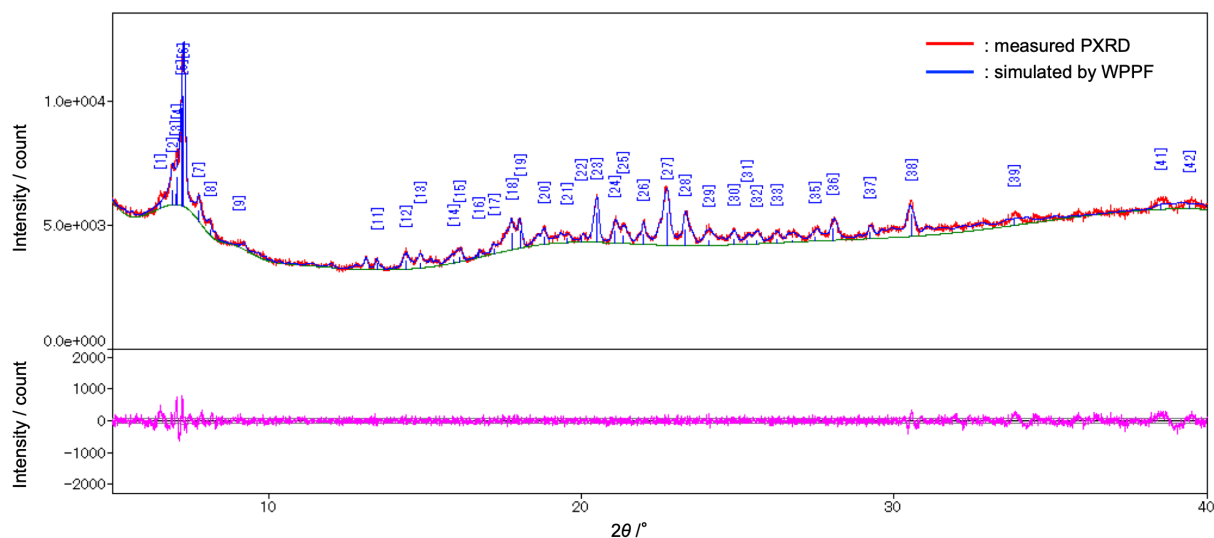


Figure 4-9. Powder XRD patterns of the crystalline samples (crystal **6**) obtained from the desolvation of crystal **6_{sol}** under reduced pressure (red solid line) and simulated using the WPPF method⁵ (blue solid line). The bottom pink solid line represents the deviation of the line-fitting.

Table 4-2. Summary of crystallographic parameters of the crystal **6** obtained from using the WPPF method and those obtained from the single-crystal XRD of crystal **6_{sol}**

compound	crystal 6 (powder sample)	crystal 6_{sol} ^a (single crystal)
<i>a</i> / Å	24.17	24.121(5)
<i>b</i> / Å	30.83	30.499(3)
<i>c</i> / Å	22.76	23.159(4)
α / °	90	90
β / °	108.12	107.76(2)
γ / °	90	90
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i> value	4	4

^a:Details of the single crystal XRD data are summarized in Table 4-3.

The crystallographic parameters of the desolvated powder crystal **6** were indexed by simulating and refining the PXRD patterns using the *Whole Powder Pattern Fitting* method (Figure 4-9 and Table 4-2).⁵ The refined crystal parameters of crystal **6** after desolvation are very similar to those of crystal **6_{sol}** obtained from the single-crystal XRD measurements, which indicates that the molecular packing mode of rotor **6** in crystal **6** is almost similar to that of crystal **6_{sol}**.

Thermogravimetric Analysis (TGA)

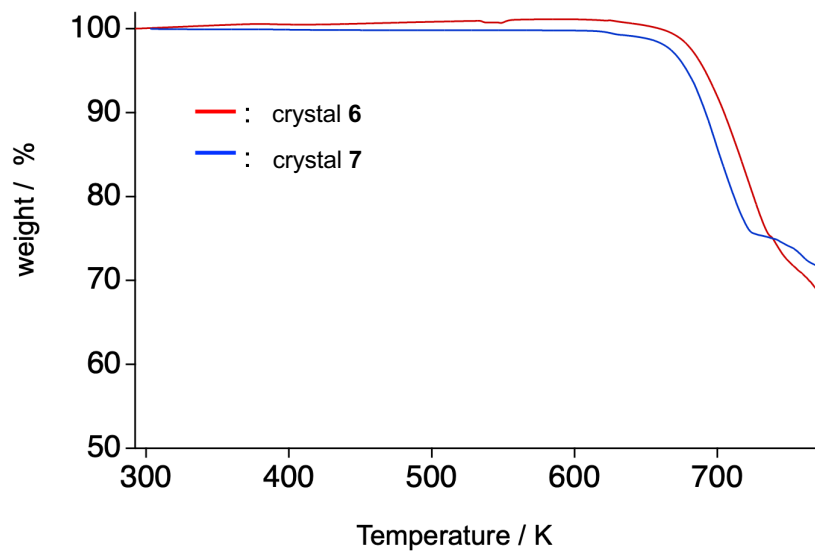


Figure 4-10. TGA profiles of the crystal after desolvation via vacuum (6 for red line and 7 for blue line). The heating rate is 5 °C/min. There was no decrease of weight of the samples until decomposition at approximately 650 K.

Differential Scanning Calorimetry (DSC) Study

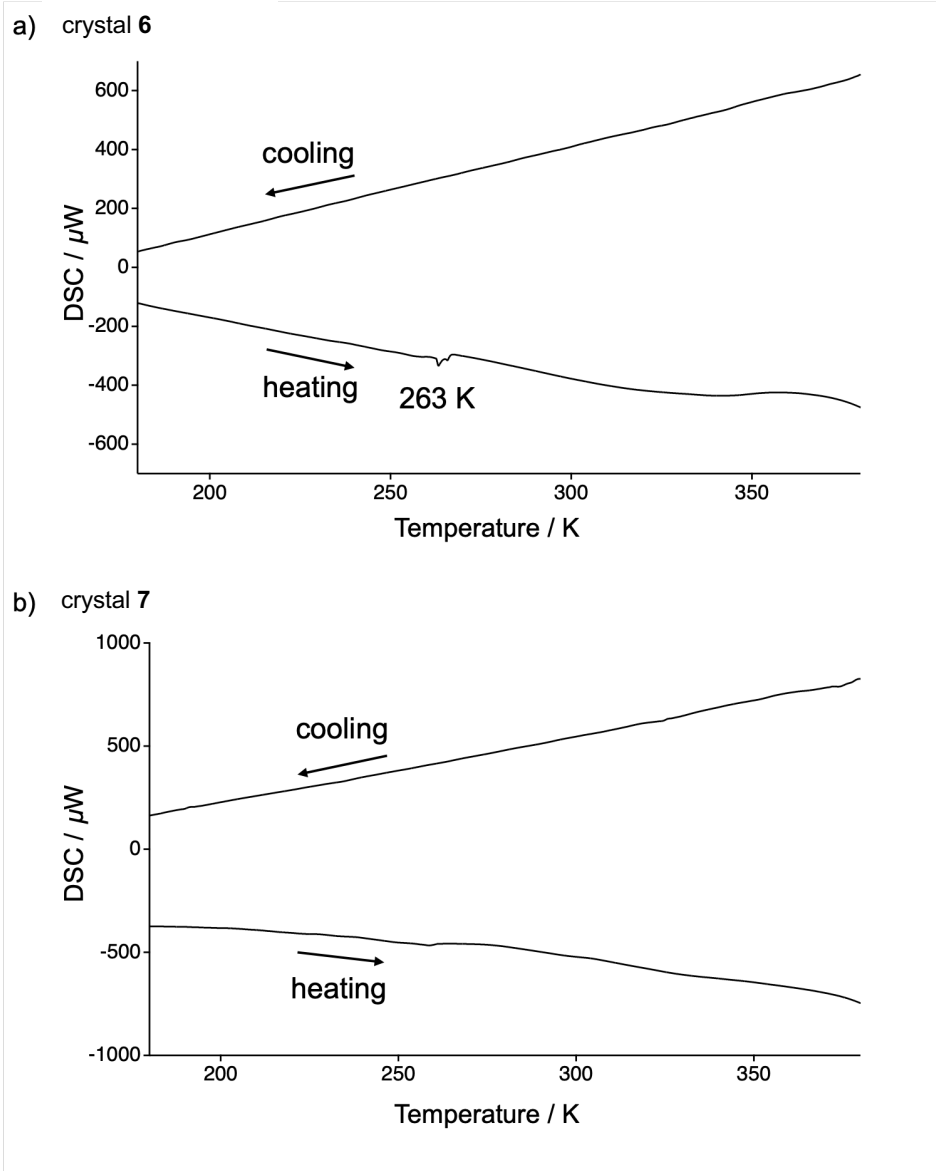


Figure 4-11. DSC profiles of a) the crystal 6 and b) 7. Heating and cooling rates were 10 °C/min. Some small peaks were observed during the heating process of crystal 6.

Data for Single-Crystal X-Ray Diffraction Analyses

Single-crystal X-ray diffraction analyses were carried out on a Rigaku XtaLAB PRO MM007 diffractometer using graphite-monochromated Mo-K α radiation or synchrotron radiation (Photon Factory beamline AR-NW12A). The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. All phenyl rings were confined by using the AFIX 66 constraint. Also, some moieties were confined by using the compatible restraints command such as SIMU for all crystals, RIGU and ISOR for crystal **7** and **7_{sol}**, respectively. Hydrogen atoms were refined using the riding model. All calculations were performed using the Olex2 crystallographic software package except for refinement, which was performed using SHELXL-2013.⁶

Table 4-3. Summary of X-ray crystallographic data of the crystals **6** and **7**.

compound	6_{sol}	7	7_{sol}
CCDC Number	2259660	2259662	2259661
Empirical Formula	C _{211.5} H _{159.5} Au ₂ N ₄	C ₂₂₄ H ₁₆₄ AuN ₄	C _{117.1} H _{91.3} AuC _{16.9} N ₂ O _{0.7}
Formula Weight	3150.85	3305.52	1979.19
Crystal System	monoclinic	triclinic	monoclinic
Crystal Size / mm	0.3×0.1×0.01	0.1×0.1×0.05	0.3×0.3×0.3
<i>a</i> / Å	24.121(5)	13.816	14.2365(8)
<i>b</i> / Å	30.499(3)	20.632	30.8543(13)
<i>c</i> / Å	23.159(4)	29.213	22.7441(9)
α / °	90	93.20	90
β / °	107.76(2)	89.43	101.968(5)
γ / °	90	98.06	90
<i>V</i> / Å ³	16255(5)	8232.1	9773.4(8)
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i> value	4	2	4
<i>D</i> _{calc} / g cm ⁻³	1.290	1.334	1.345
Temperature / K	123	95	123
2 θ _{max} / °	57.924	51.888	61.95
μ (Mo K α) / mm ⁻¹	1.864	1.388	1.745
No. of Reflections	Total: 104929 Unique: 33057 <i>R</i> _{int} = 0.3286	Total: 30788 Unique: 9306 <i>R</i> _{int} = 0.1055	Total: 78001 Unique: 24372 <i>R</i> _{int} = 0.1151
<i>R</i> ₁ ^a	0.1520	0.2340	0.1212
<i>wR</i> ₂ ^b	0.3666	0.5517	0.2684
GOF ^c	1.111	1.110	1.171
Max./Mini. peak <i>I</i> ^d / Å ³	4.80 e ⁻ / -3.07 e ⁻	2.59 e ⁻ / -1.25 e ⁻	3.73 e ⁻ / -2.84 e ⁻

^a: *I* > 2.00 σ (*I*). ^b: All reflections. ^c: Goodness of Fit Indicator. ^d: in Final Diff. Map.

Note: Large R_1 , wR_2 , and GOF value for each crystal due to the low crystallinity. Large electron peak come from the effect of Au atoms.

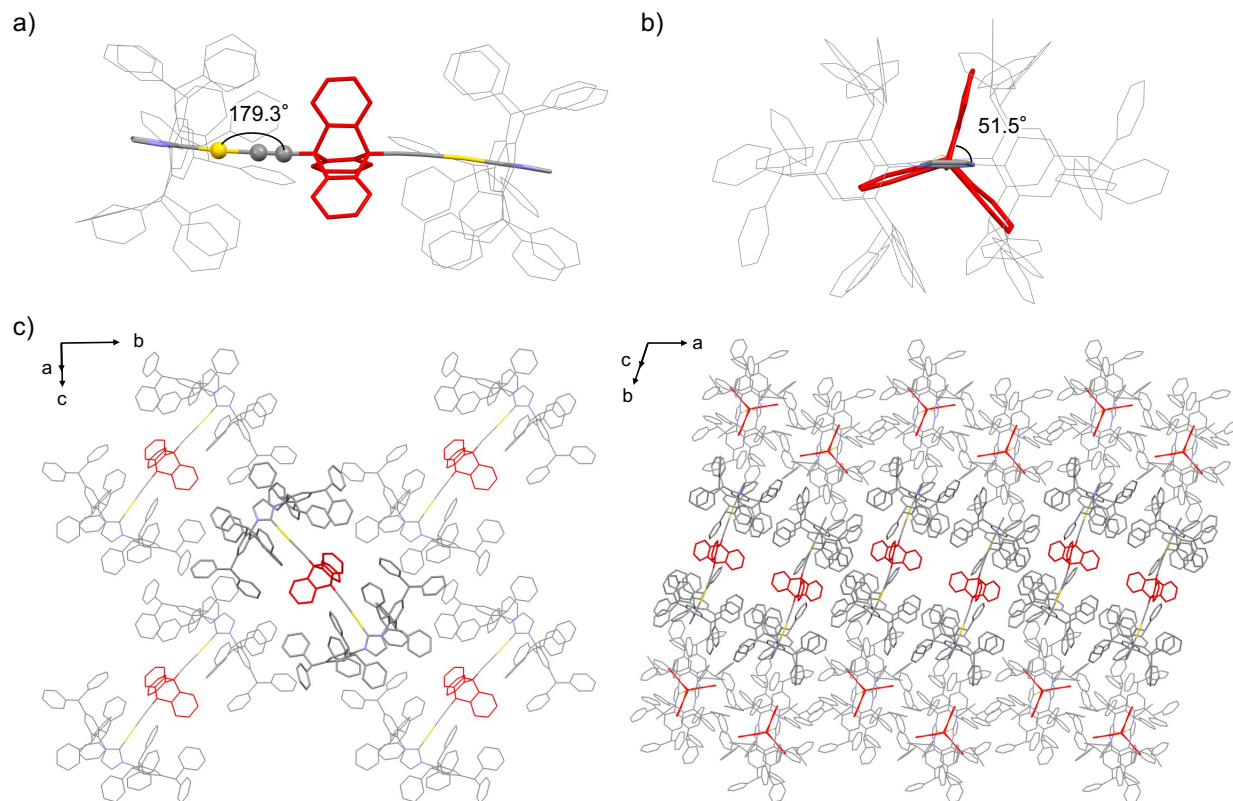


Figure.4-12. Molecular structure of molecular **6** in the crystal **6_{sol}**. Hexane was omitted for clarity. a) The angle between Au and ethynyl bond. b) Selected dihedral angle between the NHC plane and one of the phenylene plane of triptycene. c) Packing structure from each view.

Giant rotor **7_{sol}** was packed in the space group $P2_1/c$ and two CHCl_3 molecules per one rotor were found in the crystal structure. The distances between the rotator and phenyl groups of stators were shown in the Figure 4-12. Those distances are varied from 3.66 to 3.99 Å, which are shorter than those distances of giant rotor **6**. However, the shortest length (=3.66 Å) is still longer than the 2.8 Å which described above. From the packing structure, it was found that there were two phenyl groups and two solvated CHCl_3 molecules placed closely to the rotator. The distances from those units to the rotational center of the pentiptycene were 6.57 Å for phenyl groups and 3.96 Å for CHCl_3 , respectively. The distance between

the phenyl groups is slightly longer than the rotational radius of the pentiptycene rotator 6.50 Å. However, those distances between CHCl_3 are quite shorter than the radius of rotator and prevent the rotational motion in the solid state.

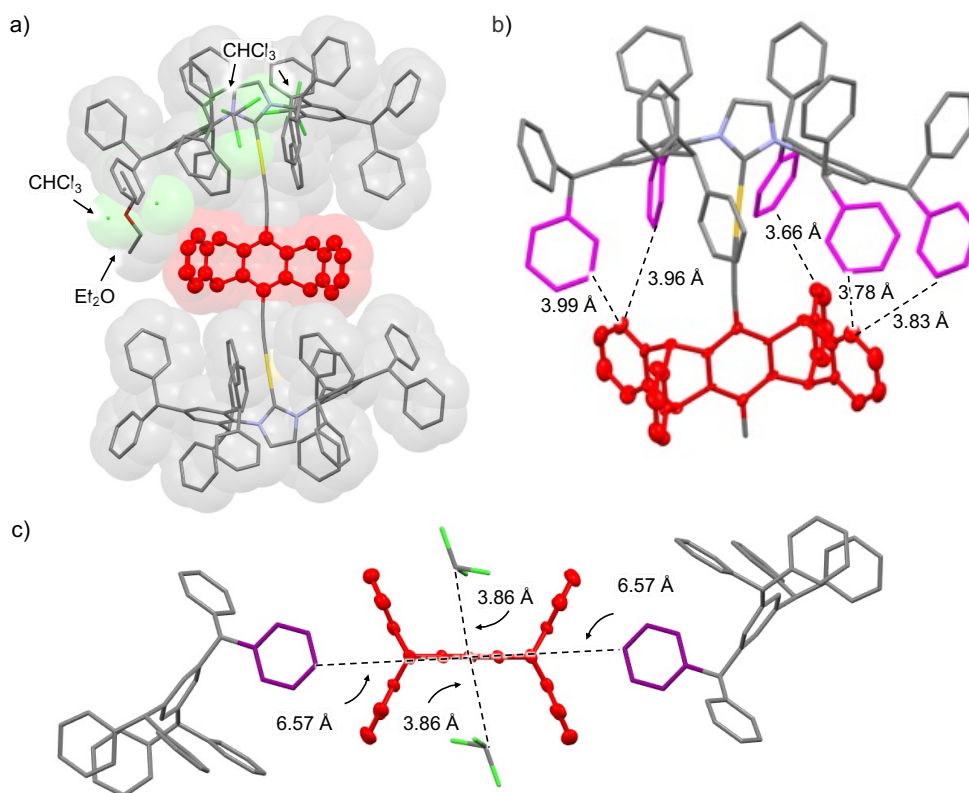


Figure 4-13. a) Crystal structure of crystal 7_{sol} b) several C-C distances from phenylene group of NHC moiety and pentiptycene. c) Packing geometry around the rotator. Phenylene groups highlight as purple are close to the rotator.

Crystal structure of 7

The detail of the packing environment of rotor **7a**, one of the diphenylmethyl unit (Ph_2C) of NHC was placed in the large cavity of pentiptycene and form ‘stack’ structure. However, the packing environment around the Ph_2C unit was very loose. The shortest distance between the phenyl groups of Ph_2C unit and neighbor phenyl group (blue) were 3.61 and 4.09 Å, respectively. These lengths are longer than the sum

of Van der Waals radius of carbon. Thus, molecular motion of Ph_2C unit along the $\text{C}_1\text{--C}_2$ bond is available. This motion can prompt the large rotation of the pentiptycene and therefore the rotor **7a** can exhibit the large angle rotation.

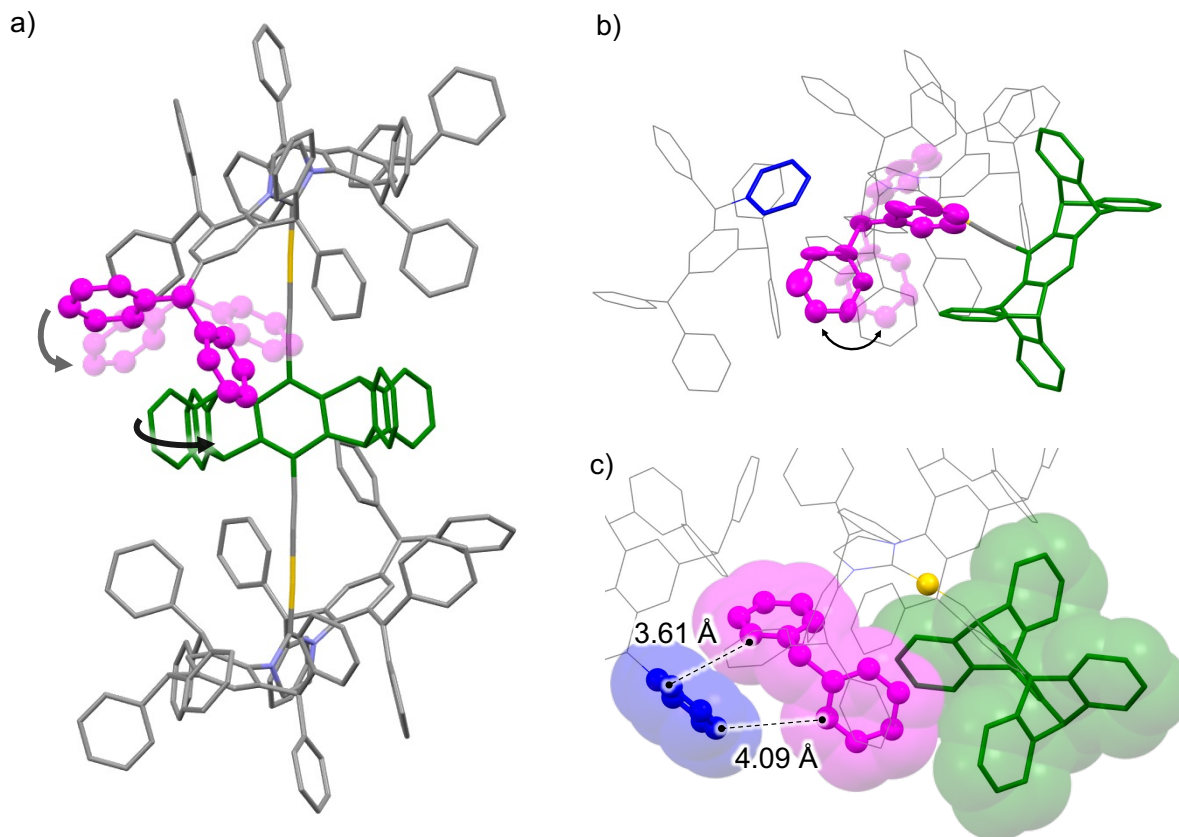


Figure 4-14. a,b) Crystal structure of **7a** in the crystal **7**. Black arrows indicate the rotational image of pentiptycene (green) and Ph_2C unit (pink). c) Packing geometry around the Ph_2C unit. Phenylene groups highlight as blue is close to the Ph_2C group.

For the rotor **7b**, there is also the Ph_2C group stacked into the large cavity of pentiptycene. However, the packing environment of this Ph_2C group is denser than that of in rotor **7a**. The shortest distances between the phenyl groups of Ph_2C unit and the adjacent phenyl group were 3.39 and 3.67 Å, respectively. Each length become shorter about ca 0.3 Å compared to the rotor **7a**. Therefore, rotor **7b** cannot exhibit fully rotation but only libration.

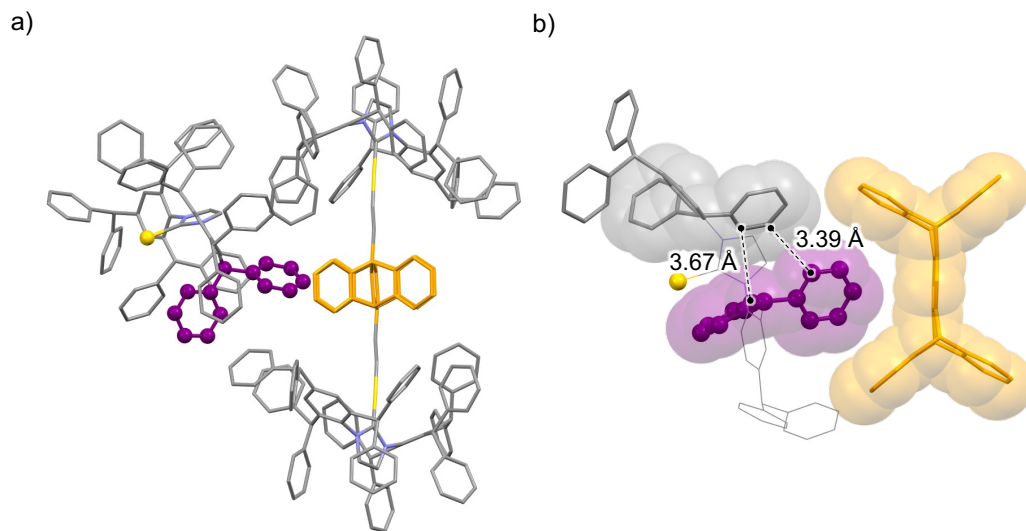


Figure 4-15. a) Crystal structure of **7b** in the crystal **7**. Adjacent Ph₂C unit was colored in purple. b) Packing geometry around the Ph₂C unit. Phenylene groups highlight as blue is close to the Ph₂C group.

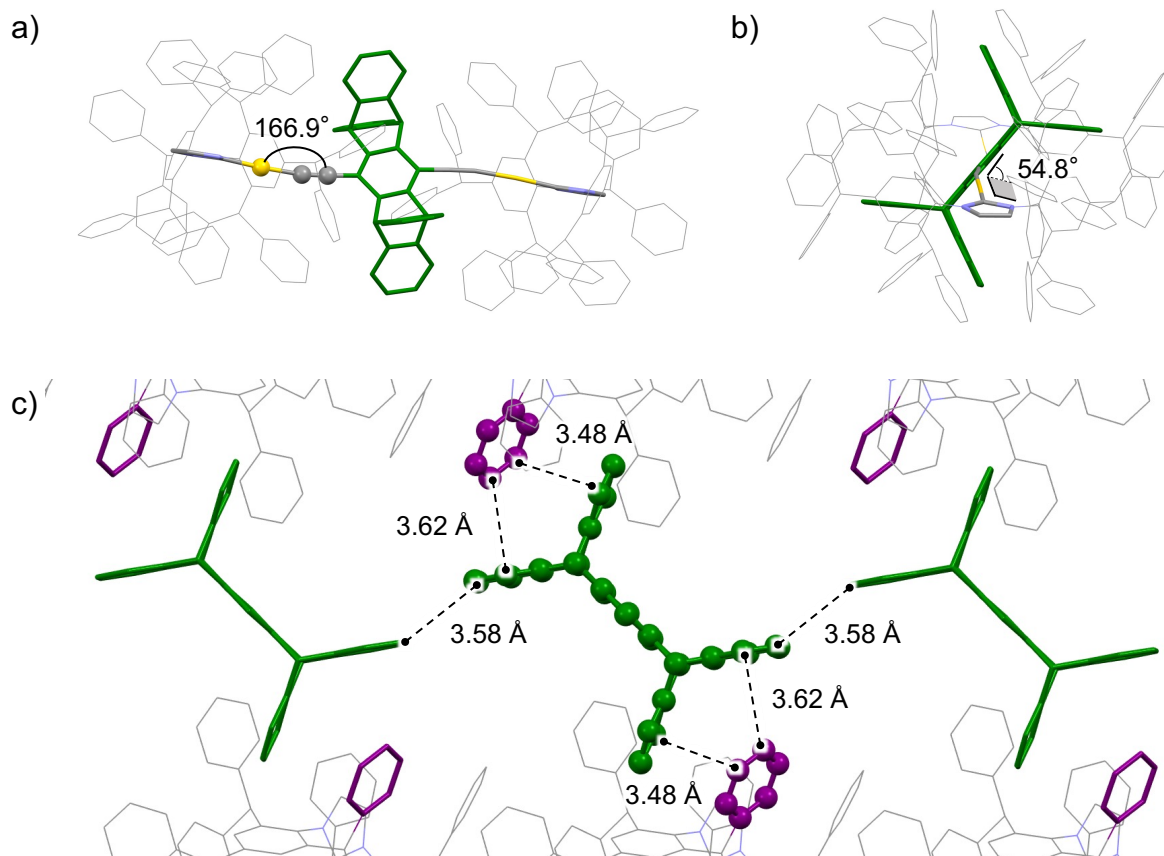


Figure 4-16. Molecular structure of molecular **7a** in the crystal **7**. a) The angle between Au and ethynyl bond. b) Selected dihedral angle between the NHC plane and the center phenylene plane of pentiptycene. c) Packing arrangement of the pentiptycene of **7a**.

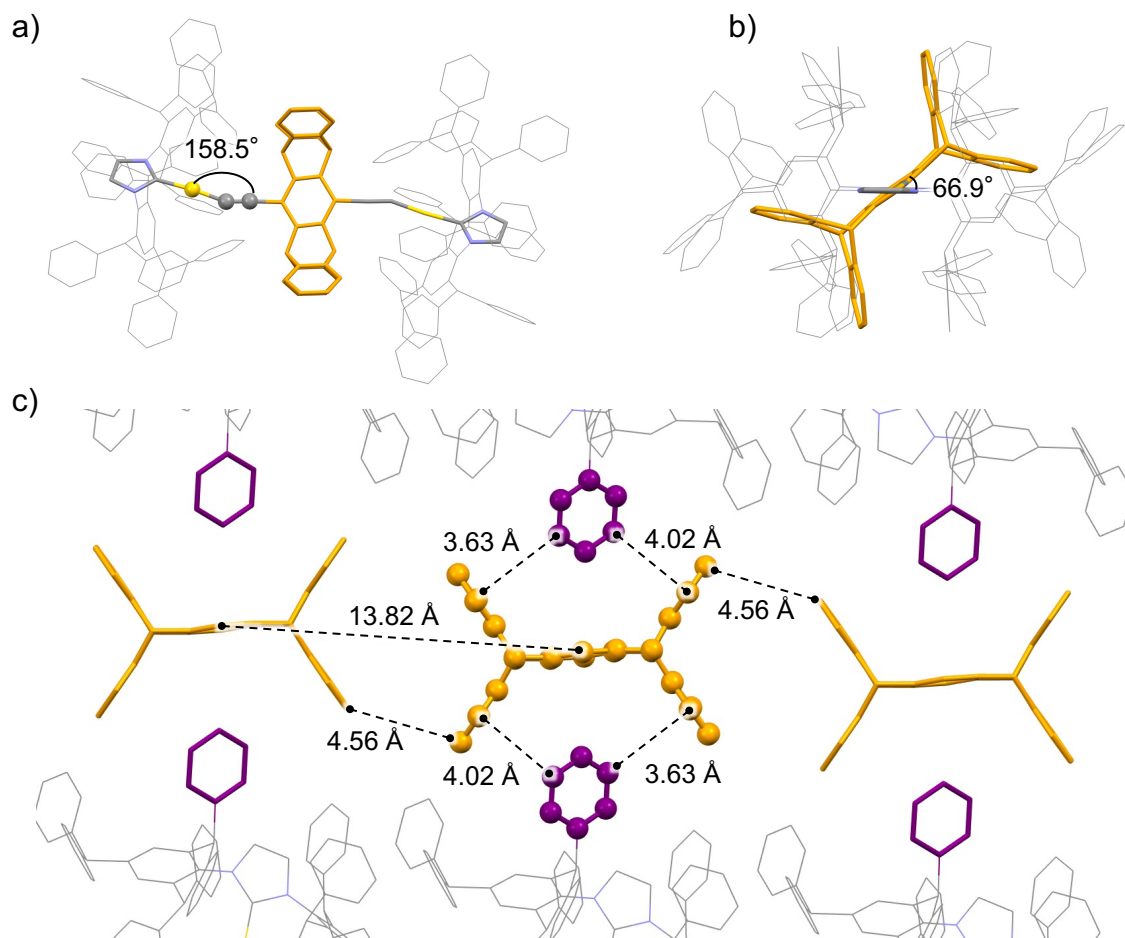


Figure 4-17. Molecular structure of molecular **7b** in the crystal **7**. a) The angle between Au and ethynyl bond. b) Selected dihedral angle between the NHC plane and the center phenylene plane of pentiptycene. c) Packing arrangement of the pentiptycene of **7b**.

Solid-State NMR Studies of Crystalline Rotor 6 and 7

Variable Temperature Solid-state ^2H NMR Spin-echo Experiments

The solid-state ^2H NMR (SS ^2H NMR) spin-echo experiments in this work were performed on a Bruker AVANCE NEO 500 MHz instrument at a ^2H frequency of 76.77 MHz (deuterium resonance frequency) and 90-degree pulse of 2.8 μs . For suppression of the undesired artifacts, a quadrupolar-echo sequence with phase recycling was used. An echo delay of 30 μs was used, and the recycle delay between pulses was 20 s. About 20 mg of sample was placed in a ZrO_2 NMR sample tube for each experiment. 1000 scans or more were used to acquire each spectrum. All spectra in this work were obtained using a line broadening of 4.0 kHz in the data processing.

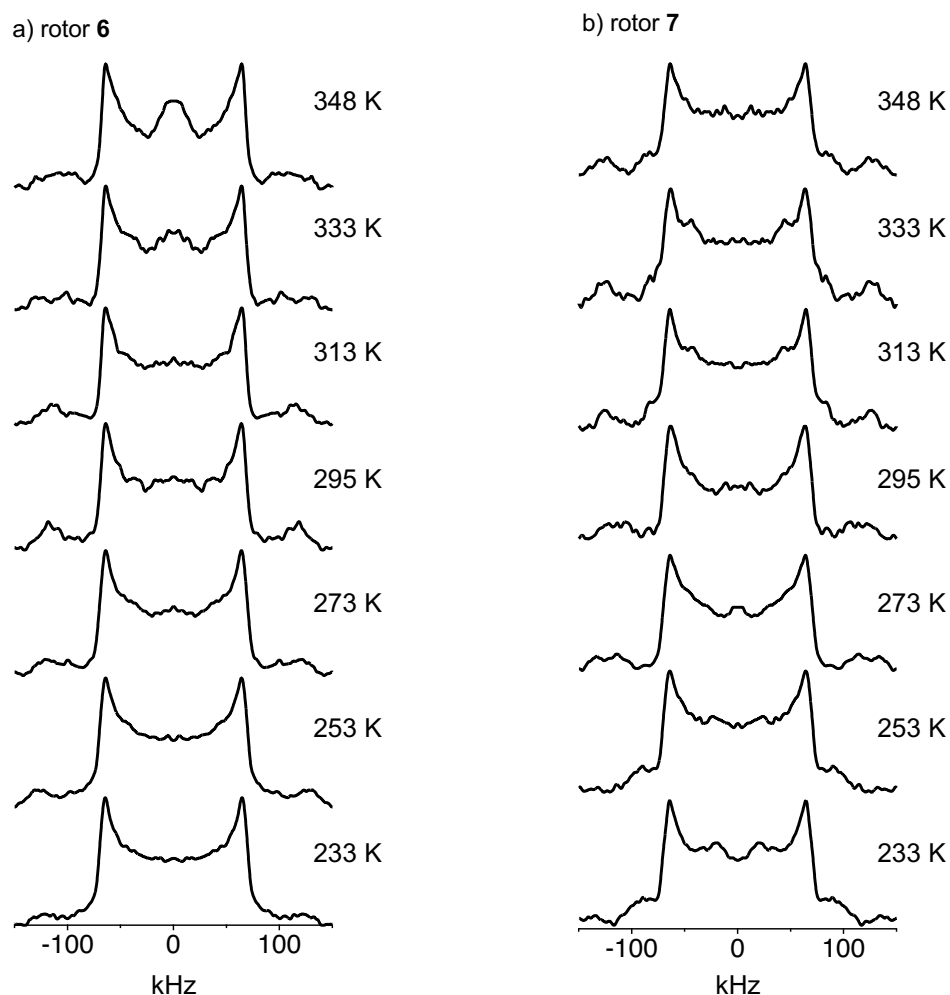


Figure 4-18. Variable temperature (VT) solid-state ^2H NMR spectra of the crystal a) 6 and b) 7 obtained from the experiment.

Simulation of the Experimental Spectra

All simulation was performed utilizing the online program offered by professor H. W. Spiess.⁶ The line shape simulation for both rotor **6** and **7** were conducted with delay time 30 μ s and line broadening 4 kHz.

Simulation for rotor 6

Basically, a quadrupolar coupling constant (QCC) of 134 kHz, a cone angle of 60° formed between the rotational 1,4-axis and C-D bond vector, and Brownian jumps of 120° of 3-fold were used. To demonstrate the 3-fold 30° with different population ratio, I used the transition matrix as shown in equation 1.

$$\begin{array}{ccc} - & 1 & 0 \\ 0.25 & - & 0.25 \\ 1 & 0 & - \end{array} \cdot \cdot \cdot (1)$$

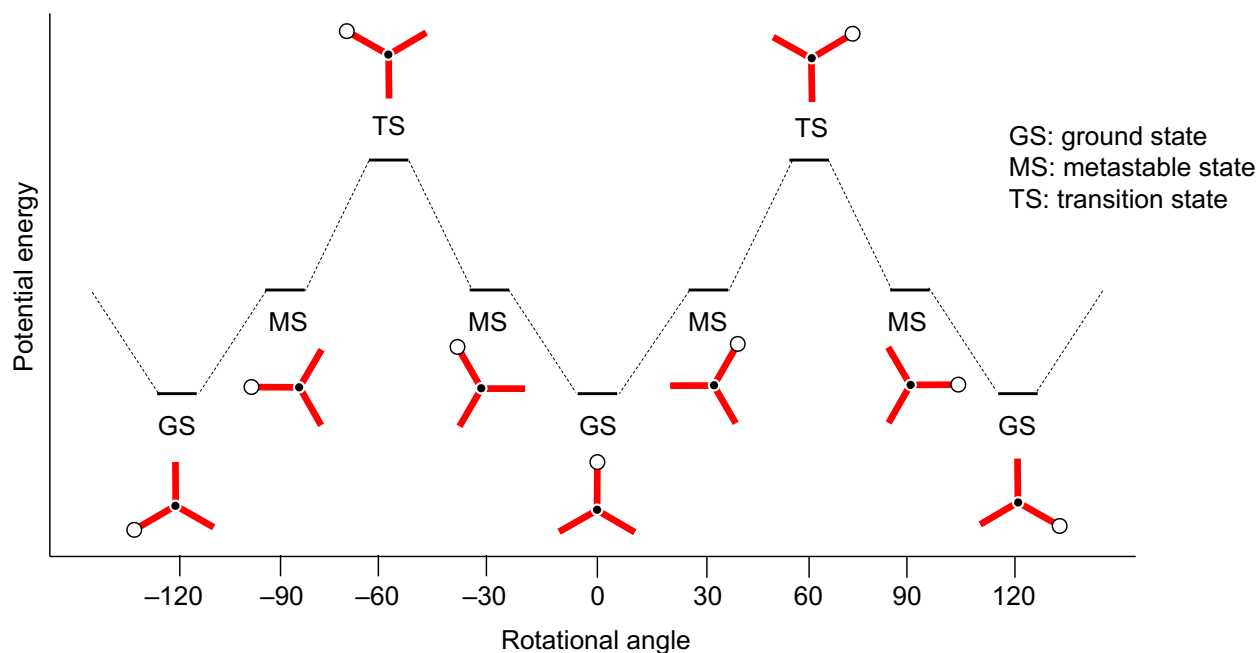


Figure 4-19. Schematic energy diagram for the rotation angle of triptycene in crystalline rotor **6**.

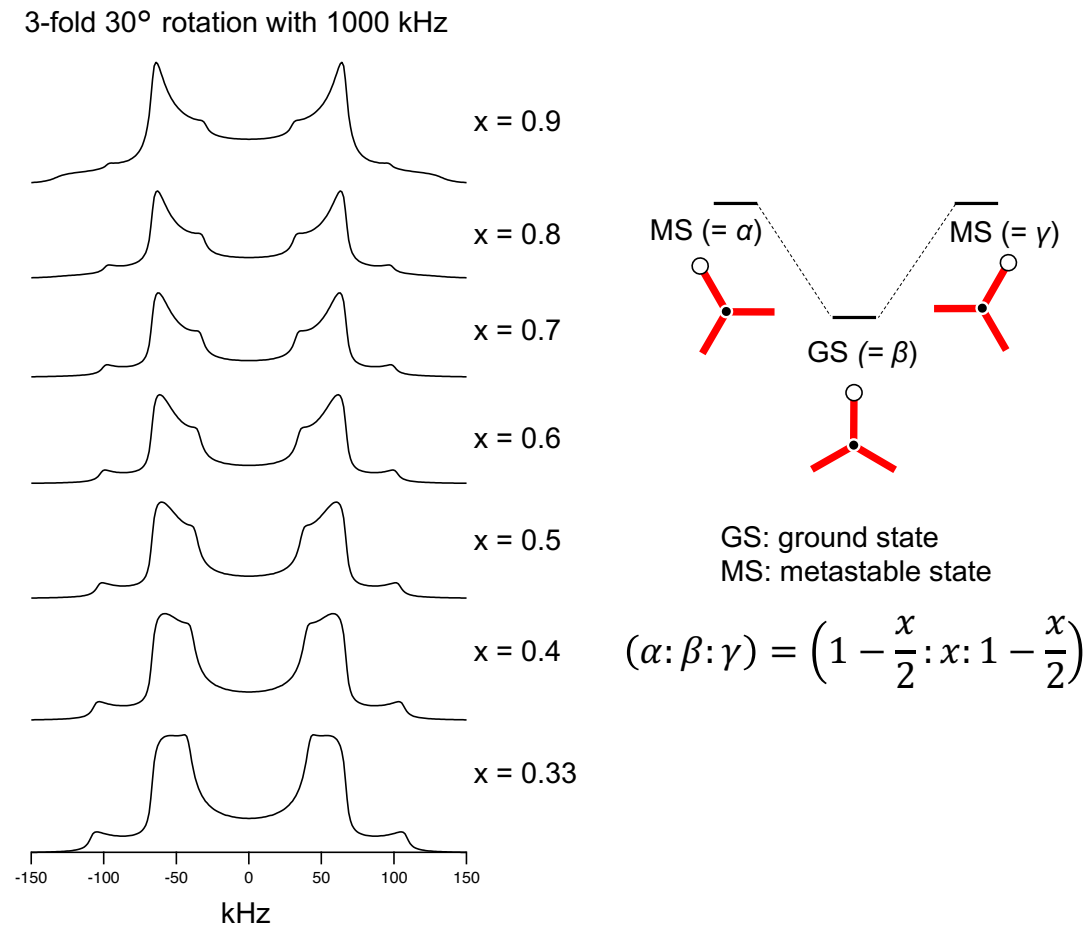


Figure 4-20. Simulated ^2H NMR of 3-fold 30° rotation of rotor **6** with different population ratio. Each population of the ground state ($= \beta$) and metastable state ($= \alpha$ and γ) were determined as shown.

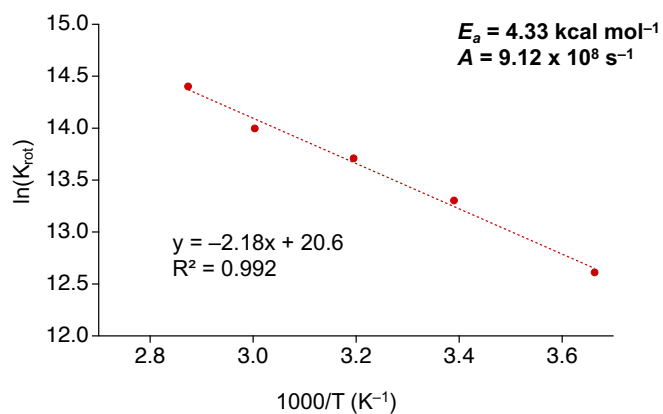


Figure 4-21. Arrhenius plot with evaluated energy barrier (E_a) and pre-exponential factor (A) of triptycene rotator dynamics in crystalline rotor **6**.

Simulation for rotor 7

The spectra obtained for rotor **7** was identified to be the result of 2-fold rotational model. Basically, a quadrupolar coupling constant (QCC) of 138 kHz, a cone angle of 60° formed between the rotational 1,4-axis and C-D bond vector, and Brownian jumps of various angles were used. Every molecular motion was applied for different population for each site (0.8/0.2) for the 2-fold rotation and (0.4/0.1/0.4/0.1) for the 4-fold rotation to demonstrate the stable and metastable site in the crystal.

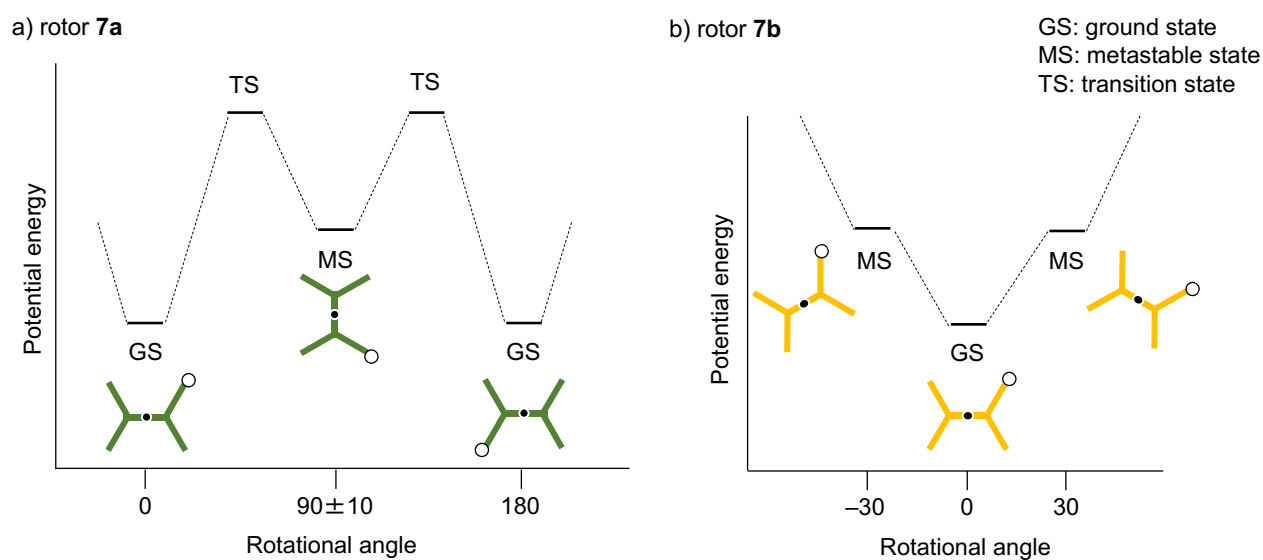


Figure 4-22. Schematic energy diagram for the rotation angle of a) rotor **7a** and b) rotor **7b** in crystal **7**.

2-fold 90° rotation with 200 kHz

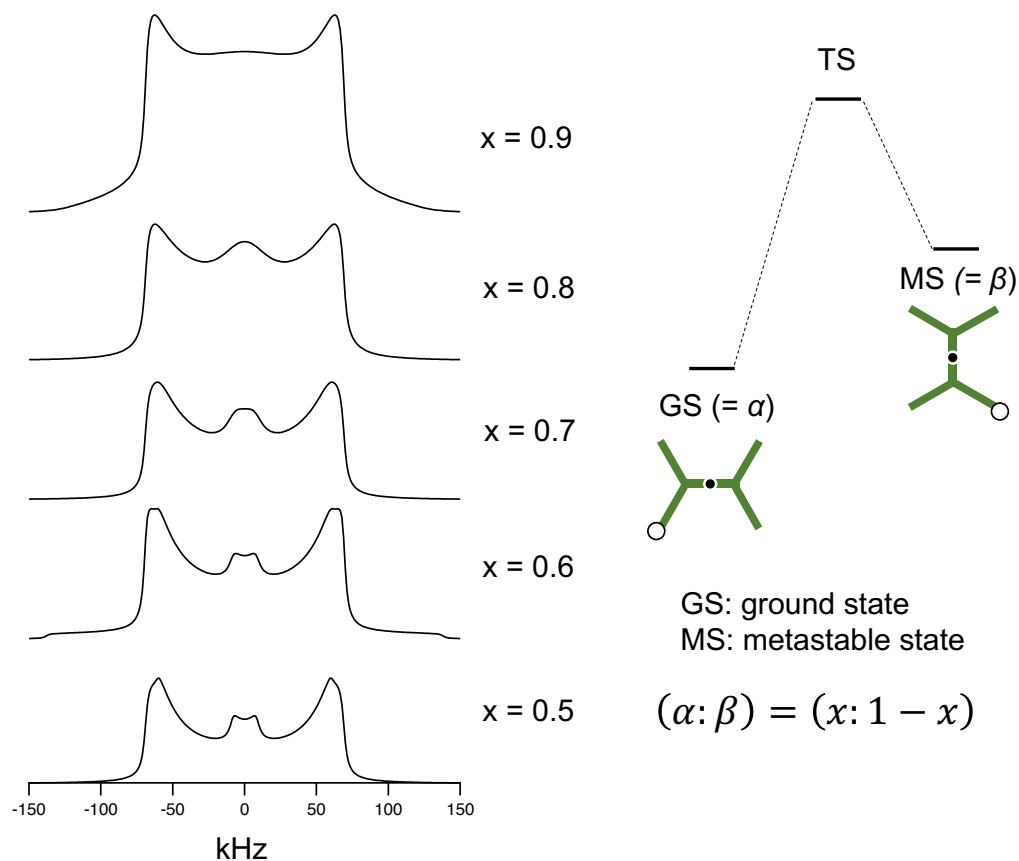


Figure 4-23. Simulated ^2H NMR of 2-fold 90° rotation of rotor **7a** with different population ratio. Each population of the ground state (= α and γ) (= β) and metastable state (= β) were determined as shown.

3-fold 30° rotation with 1000 kHz

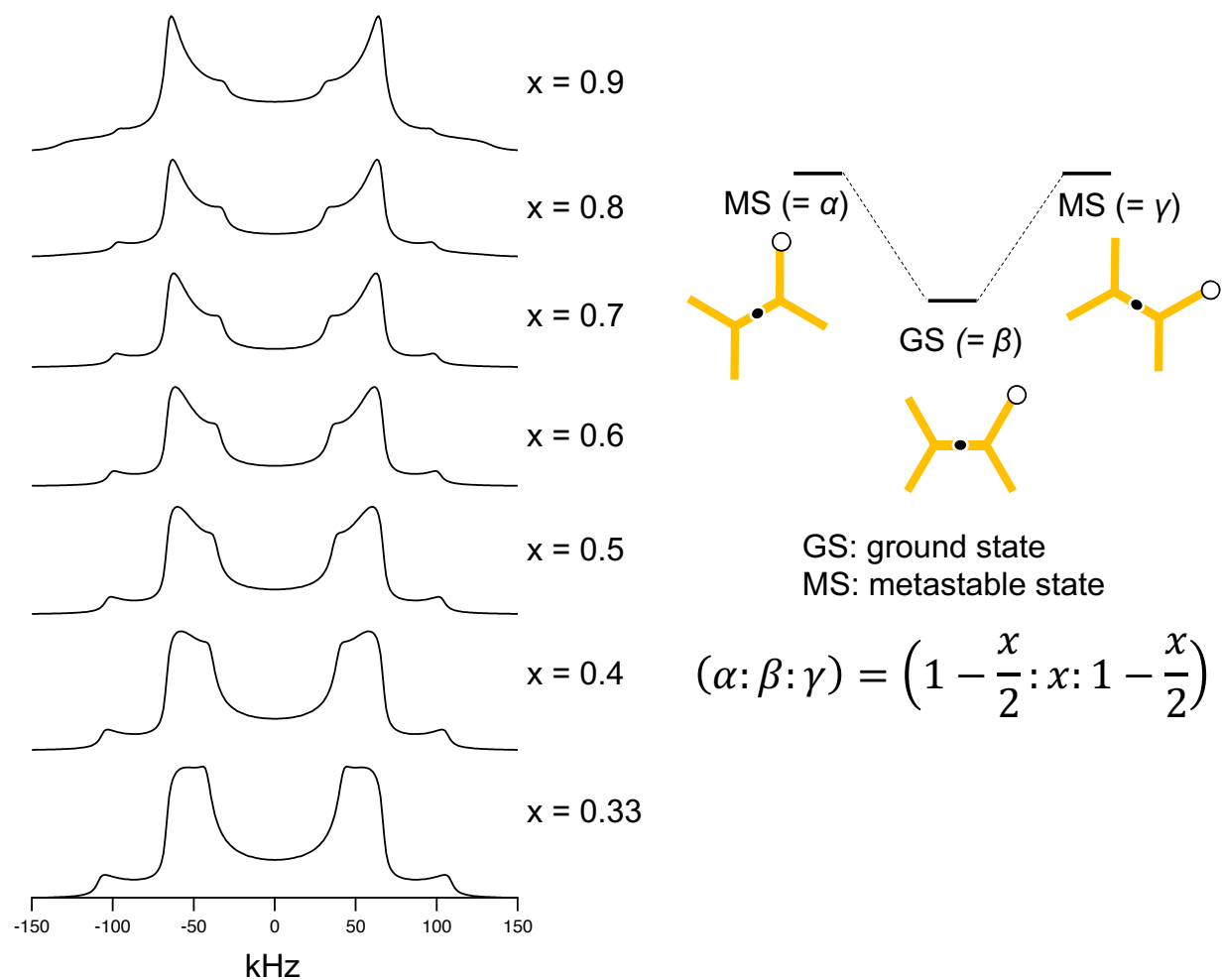


Figure 4-24. Simulated ^2H NMR of 3-fold 30° rotation of rotor **7b** with different population ratio. Each population of the ground state (= β) and metastable state (= α and γ) were determined as shown.

4.5. References

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V Summary of This Thesis

In this study, the rich molecular design capability and the steric and electronic properties of NHC ligands were utilized to rationally design molecular conformations in crystals and investigate the solid-state optical properties arising from these conformations. In Chapter 2, the helical structures and changes in solid-state luminescence properties of cationic coordination polymers consisting of NHC copper(I) complexes and pyrazine in crystals were discussed. Helical polymers are expected to have applications in fields such as ferroelectric liquid crystals (LCs), nonlinear optical materials, molecular detection, and enantiomer separation. However, rationally designing these structures remains a challenge. One-dimensional cationic coordination polymers are attracting attention as a promising platform for designing solid-state properties utilizing diverse coordination geometries. Previous studies have reported several examples of helical structures constructed using cationic coordination polymers. For example, Mak and colleagues demonstrated that the helical pitch length of silver(I)-based helical polymers could be tuned by changing the size of counteranions. While controlling helical structures by altering anions has been reported, achieving solid-state functionality such as photoluminescence remains a challenge. In this study, it was revealed that the helical structures of cationic coordination polymers composed of NHC copper(I) complexes and pyrazine vary depending on the type of counteranion. Octahedral-type SbF_6^- and PF_6^- counteranions formed quadruple helices (crystals **1** and **2**), whereas tetrahedral-type BF_4^- counteranions formed triple helices (crystal **3**). The differences in helical structure resulted in a redshift of the emission wavelength from 580 nm (crystals **1** and **2**) to 687 nm (crystal **3**). Chapter 3 describes the synthesis of cationic complexes composed of NHC copper(I) or gold(I) complexes, pyrazine, and SbF_6^- , and the investigation of molecular rotational motion of pyrazine and solid-state luminescence properties within crystals. Rotational motion in amphidynamic crystals is strongly influenced by the activation energy for rotation. The activation energy for rotational motion is determined primarily by two factors: the steric environment and the electronic environment around the rotating site. However, predicting and controlling the steric and electronic environments in crystals is difficult, making the rational design of activation energy for rotational motion a challenging issue. In this study, complexes **4** and **5** were synthesized using Au(I) or Cu(I), and the activation energy for pyrazine rotation was successfully designed. Single-crystal X-ray structure analysis revealed that both complexes had similar structures. Variable-temperature solid-state ^2H NMR measurements confirmed 180° rotational motion of pyrazine, and the activation energy for rotation was lower for Cu(I) complex **4** than for Au(I) complex **5**. Computational studies suggested

that the difference in activation energy between complexes **4** and **5** was due to destabilization caused by steric repulsion between pyrazine and NHC in the transition state and stabilization due to π -back donation between pyrazine and the metal. Furthermore, UV-irradiated crystals of complexes **4** and **5** exhibited orange and blue luminescence, respectively, with a decrease in luminescence intensity from low to high temperatures. Chapter 4 describes the molecular rotational motion of molecules with large rotational diameters within crystals, using bulkier NHC ligands compared to those used in Chapters 2 and 3. In general, amphidynamic crystals use rotation sites with diameters around 4.0 Å, such as phenyl groups. The largest rotation site reported to date is a triptycene with a diameter of 9.5 Å, reported by the Garcia-Garibay group. In this study, NHC gold(I) complexes were used to investigate the rotational motion of giant rotators (triptycene **6** and pentiptycene **7**) within crystals. Pentiptycene has a rotational diameter of 13.0 Å, about 3.0 Å larger than triptycene, making it the largest rotational site in amphidynamic crystals to date. Single-crystal X-ray structure analysis revealed that bulky NHC ligands allowed the formation of crystal structures with rotatable rotators. Variable-temperature solid-state ^2H NMR measurements evaluated the molecular motion in crystals **6** and **7**, showing clear spectral changes corresponding to triptycene's threefold rotational motion in crystal **6** and similar spectral changes for pentiptycene's molecular motion in crystal **7**. This dissertation highlights the rational design of molecular conformations and the synthesis of crystals with molecular mobility using NHC metal complexes, as well as the solid-state luminescence properties based on these features.

VI. List of Publication

Chapter II:

Distinct Fold-Mode Formation of Crystalline Cu(I) Helical Coordination polymers with Alternation of the Solid-State Emission Using Shape of the Counter Anions.

Jin, M.; Ando, R.; Ito, H. *Inorg. Chem.* **2022**, *61*, 3–9.

Chapter III:

Encapsulating N-Heterocyclic Carbene Binuclear Transition-Metal Complexes as a New Platform for Molecular Rotation in Crystalline Solid-State.

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

Chapter IV:

Giant Crystalline Molecular Rotors that Operate in the Solid State.

Ando, R.; Sato-Tomita, A.; Ito, H.; Jin, M. *Angew. Chem. Int. Ed.* **2023**, *135*, e202309694.

Other publication:

Charge-Transfer Crystal with Segregated Packing Structure Constructed with Hexaarylbenzene and Tetracyanoquinodimethane

Ando, R.; Jin, M.; Ito, H. *CrystEngComm* **2021**, *23*, 5564–5568.

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