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

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ABSTRACT One-dimensional cationic coordination polymers have been a promising platform for designing solid-state physical properties through diverse coordination geometries. In particular, the folding mode of the coordination polymers that form a helical structure directly determines the metal-centered coordination environment. Herein, we report *N*-heterocyclic carbene (NHC) Cu(I) cationic coordination polymers with pyrazine as the linker, which constructs 4-fold or 3-fold helical column in luminescent crystals using octahedral anions (SbF_6^- and PF_6^-) or a tetrahedral

anion BF_4^- , respectively. Single-crystal XRDs revealed that the folding modes depend on the structural shape of the counter anions, which form H–F interactions between ligands and anions. Indeed, the folding mode change from 4-fold to 3-fold by including a different shape of the counter anions resulted in red-shifted emission from approximately 580 nm to 687 nm, which is difficult to modulate in the solid-state.

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} We 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, we 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 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 PF₆) were included. However, a 3-fold helical columnar structure with a triangular planar on the vertical axis was constructed with the tetrahedral anion BF₄ (Figure 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 π -conjugated domain, inducing a red-shifted emission in the crystals (Figure 1e). To the best of our 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.

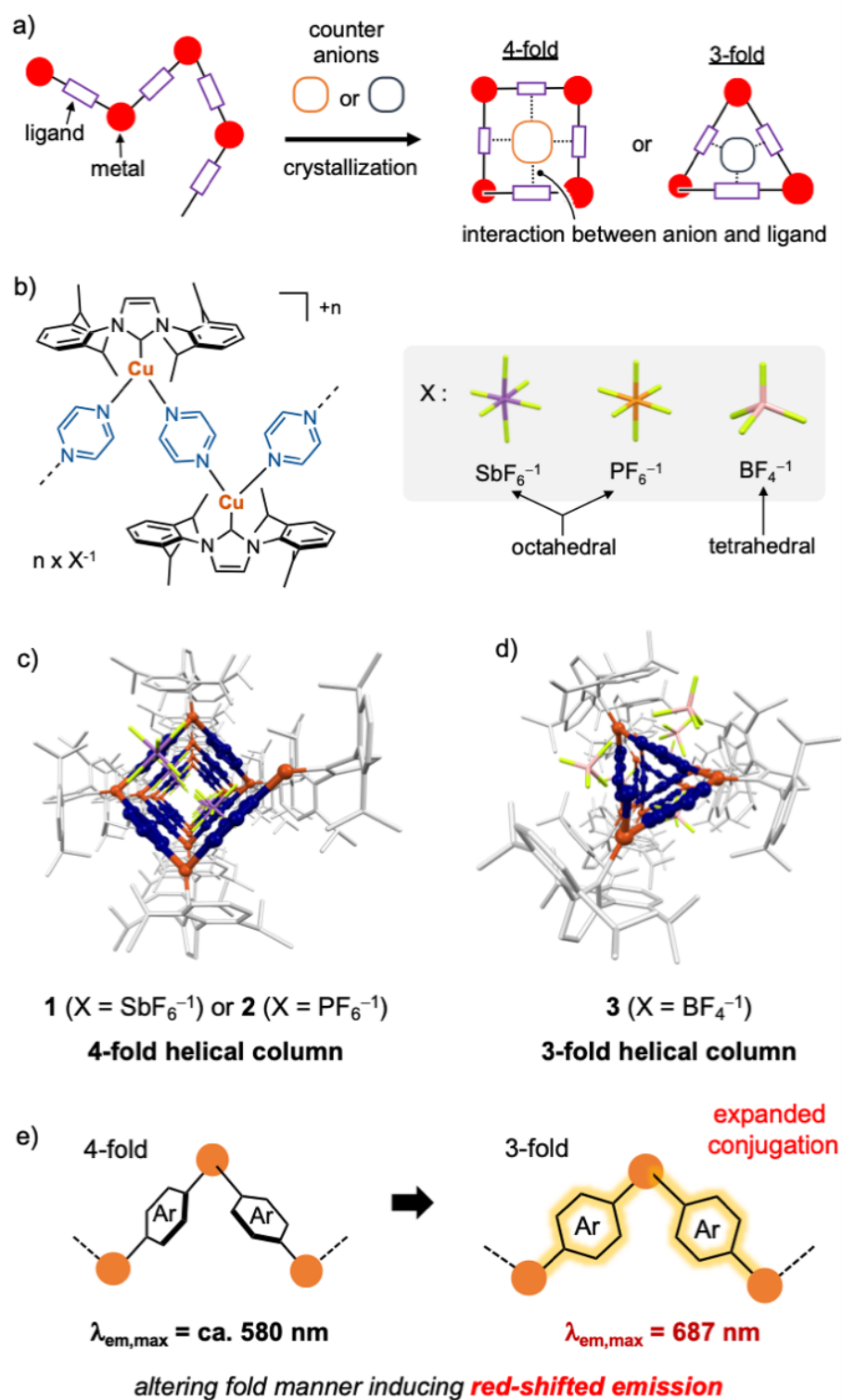


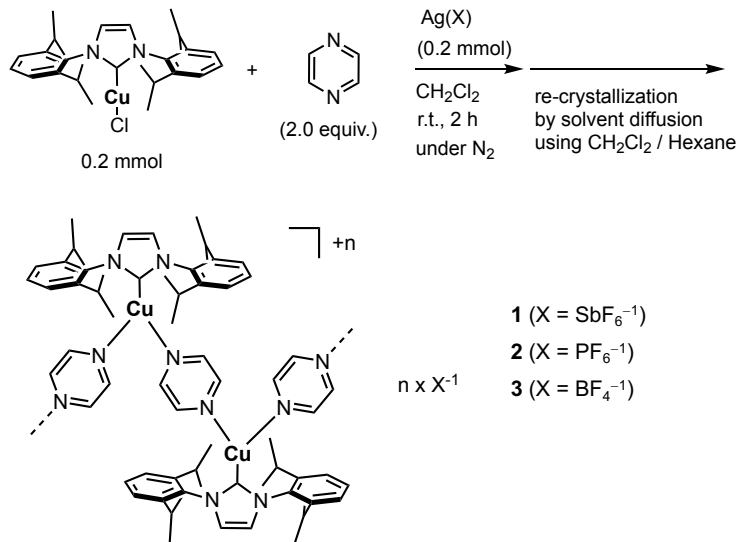
Figure 1. a) Representation of the fold-mode control of a coordination polymer using a distinct shape of counter anions. b) Prepared cationic NHC Cu(I) coordination polymers containing

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.

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 CH_2Cl_2 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 = SbF_6 , PF_6 , and BF_4), as shown in Scheme 1. Crystallization was performed through solvent diffusion using the CH_2Cl_2 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 CD_2Cl_2 solution and characterized through ^1H and ^{13}C 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 CH_2Cl_2 solvents were included in all crystals (see Supporting Information, Figure S1).

Scheme 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 2–4. 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 $P2_1/n$, 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 SbF₆⁻ as the counter anion with an octahedral structure, a 4-folded helical columnar coordination polymer was observed, as shown in Figure 2. The coordination polymers were packed into the $P2_1/n$ space group (Table S1). The Cu–C and Cu–N bond lengths of the Cu(I) complex **1** are 1.943 and 2.031 Å, respectively (Figure 2a). Two pyrazines were coordinated to Cu(I) at a binding angle of 101° (Figure 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 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 S2e). The bulky NHC groups were packed outside the column, and infinitely coordinated Cu(I) and pyrazines were folded with the included SbF₆ anions (Figures 2c–d). We observed that the fluorine atoms of octahedral SbF₆ 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 2c and S2a). Additionally, the angle of C–H–F were arranged in ca. 115°–168°, as shown in Figure S2f. This suggests that the octahedral shape of the SbF₆ 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 2d, e and S2b–d). The columnar structure in Figure 2d shows *P*-helicity and is surrounded by *M*-helical columns in the crystal (Figure S2d). The inclusion of CH₂Cl₂ solvent molecules was observed between the intercolumnar arrangements (Figure S2d).

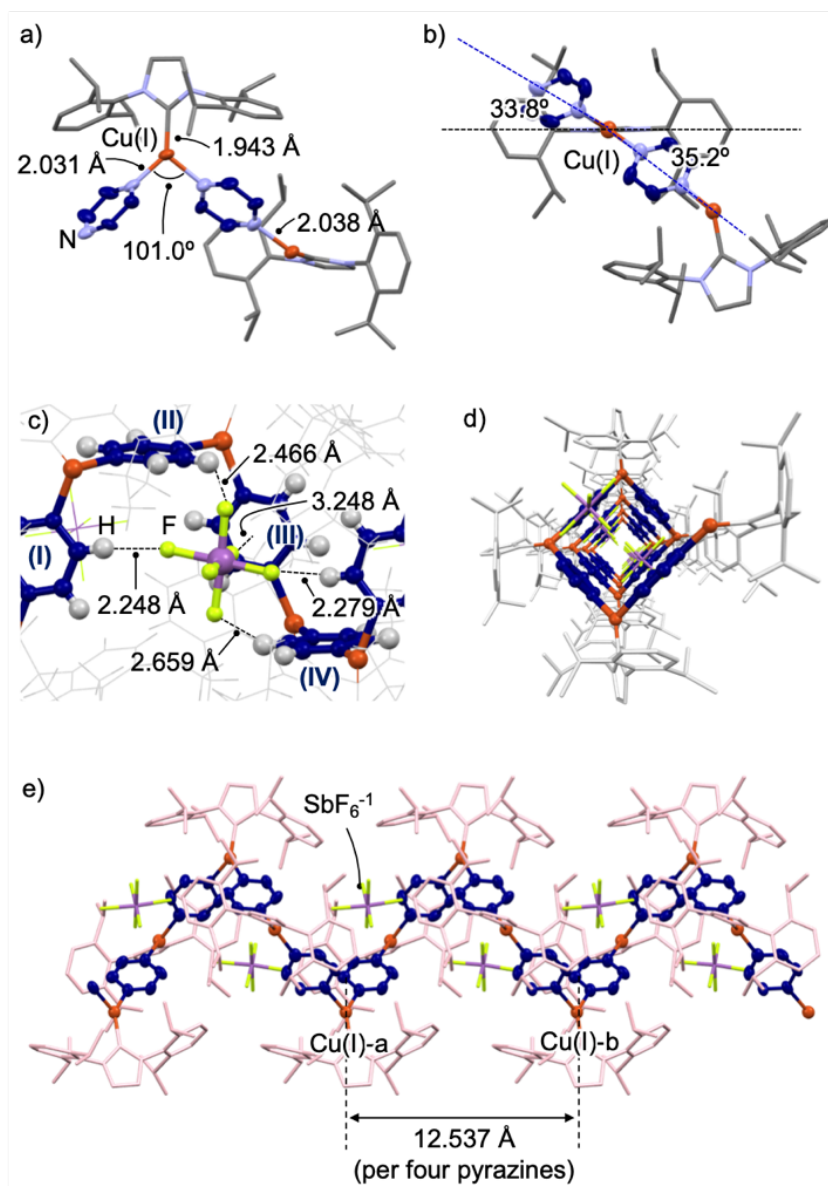


Figure 2. Crystal structure of the cationic NHC Cu(I) coordination polymer **1** containing SbF_6^{-1} . a), b) Coordination geometry near Cu(I) atoms. c) Observed H–F interactions between pyrazines and SbF_6^{-1} . d) Axial and e) side views of *P*-helicity of the 4-fold helical columnar structure of **1**.

Crystal **2**, which included octahedral PF₆ as the counter anion, also formed a 4-folded helical columnar structure in the *P2₁/n* space group, similar to crystal **1** (Figure 3 and Table S1). As described in Figure 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 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 S3e). 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 3c and S3). In addition, we observed that the angle of C–H–F ranged in ca. 100°–156° (Figure S3f). 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 3e and S3d). 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 3d exhibits *P*-helicity, and the *M*-helical columns are nearly packed as illustrated in Figure S3d. CH₂Cl₂ molecules were included in the intercolumnar packing environment (Figure S3d).

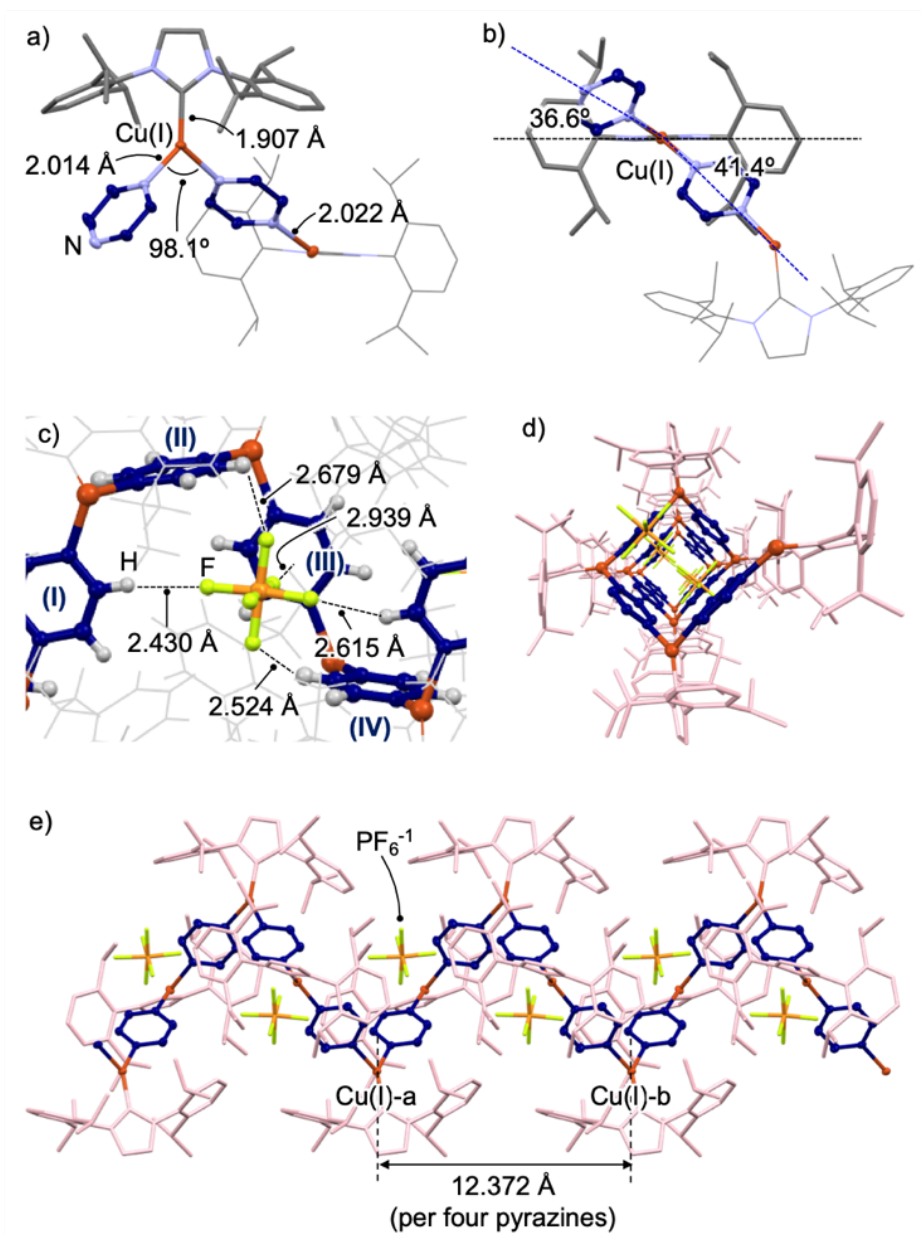


Figure 3. Crystal structure of the cationic NHC Cu(I) coordination polymer **2** containing PF₆. a) and b) Coordination geometry near the Cu(I) atoms. c) Observed H–F interactions between pyrazines and PF₆. d) Axial and e) side views of *P*-helicity of the 4-fold helical columnar structure of **2**.

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 4 and Table S1). 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 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 4b). Furthermore, we 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 S4d). The tetrahedral BF_4 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 S4e). Moreover, the 3-fold coordination pattern was elongated and formed a trigonal shape (Figures 4c–d and S4). 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 4e and S4). The observed helical column in crystal **3** showed *M*-helicity, and no counter-helical structure was confirmed in the crystal structure (Figure S4c).

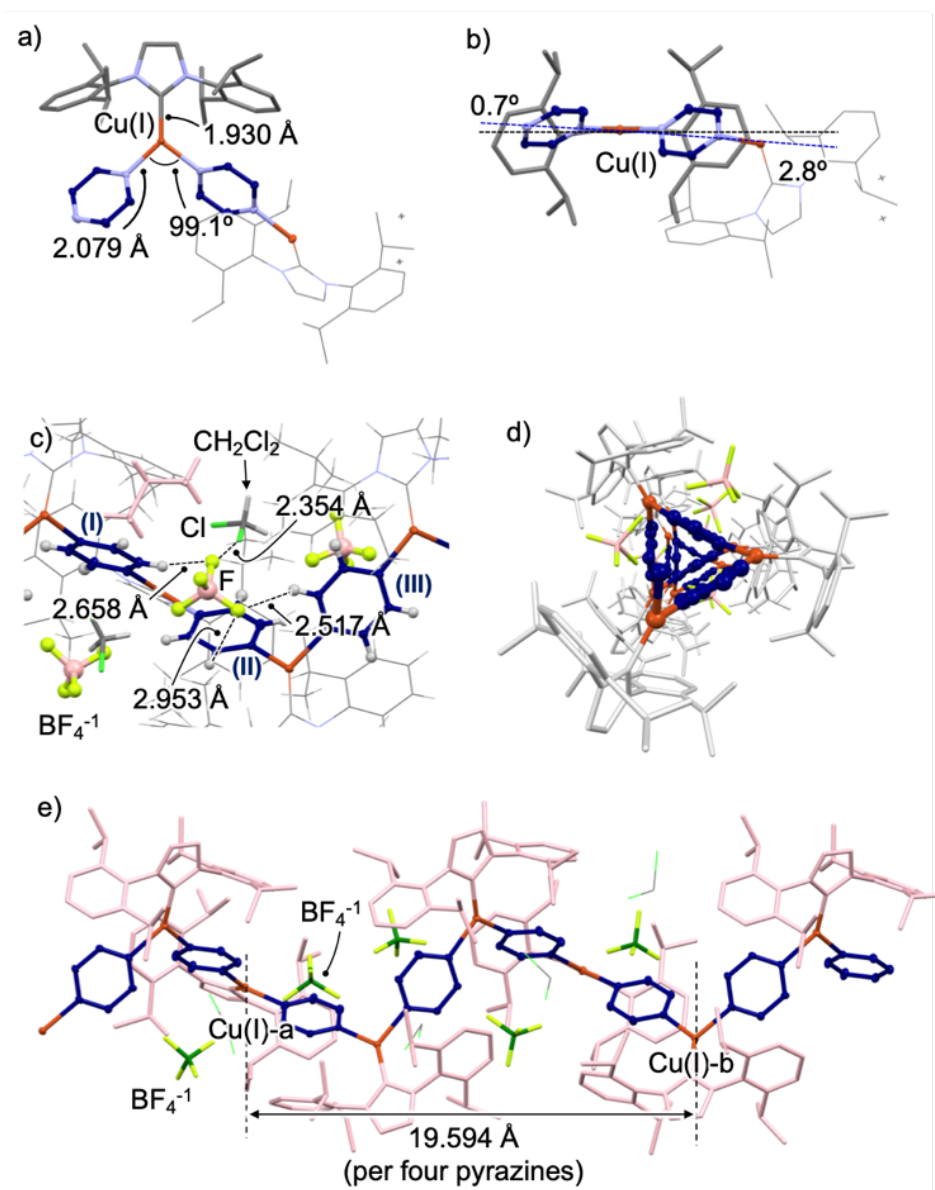


Figure 4. Crystal structure of the cationic NHC Cu(I) coordination polymer **3** containing BF_4^- . a) and b) Coordination geometry near the Cu(I) atom. c) Observed H-F interactions between hydrogen atoms in pyrazines and the NHC ligand and fluorine atoms in BF_4^- . d) Axial and e) side views of *M*-helicity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

We 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 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 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.

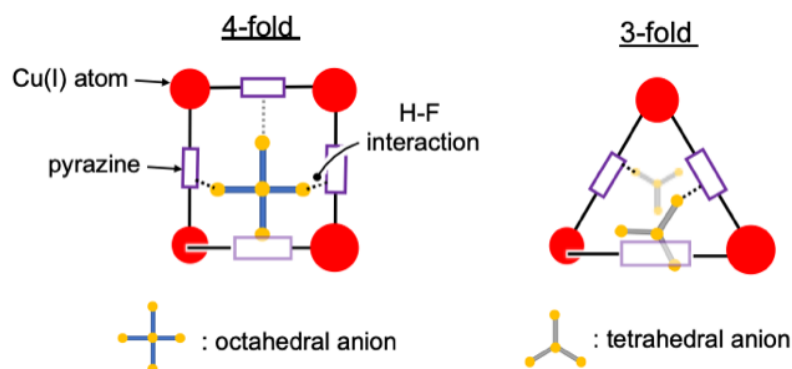


Figure 5. Illustrations showing the observed folding modes of the cationic NHC Cu(I) coordination polymers **1** to **3** in crystals, the interactions between the counter anions and pyrazines, and geometrical shape of the anions.

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 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 CH₂Cl₂ 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 S5–7 and Table S2).^{21,22,23,24} Crystals **1** and **2** showed a broad emission with maximum intensity ($\lambda_{em,max.}$) at 573 and 586 nm, respectively, under 365 nm irradiation (Figure 6b). Interestingly, the emission of crystal **3** has the $\lambda_{em,max.}$ at 687 nm, which is longer than those of crystals **1** and **2** (Figure 6b). The excitation spectra of crystals **1** and **2** monitored for each $\lambda_{em,max.}$ were very similar broad bands with $\lambda_{ex,max.}$ of the maximum excitation at 365 nm (Figure 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 6c). The emission decay and emission lifetimes ($\tau_{av.}$) 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 S2 and Figure S8). However, the relatively shorter emission lifetime of crystal **3** was detected as $\tau_{av.} = 4.6$ μ s, suggesting that the red-shifted emission should be yielded from different structural or electronic environments (Table S2 and Figure S8).

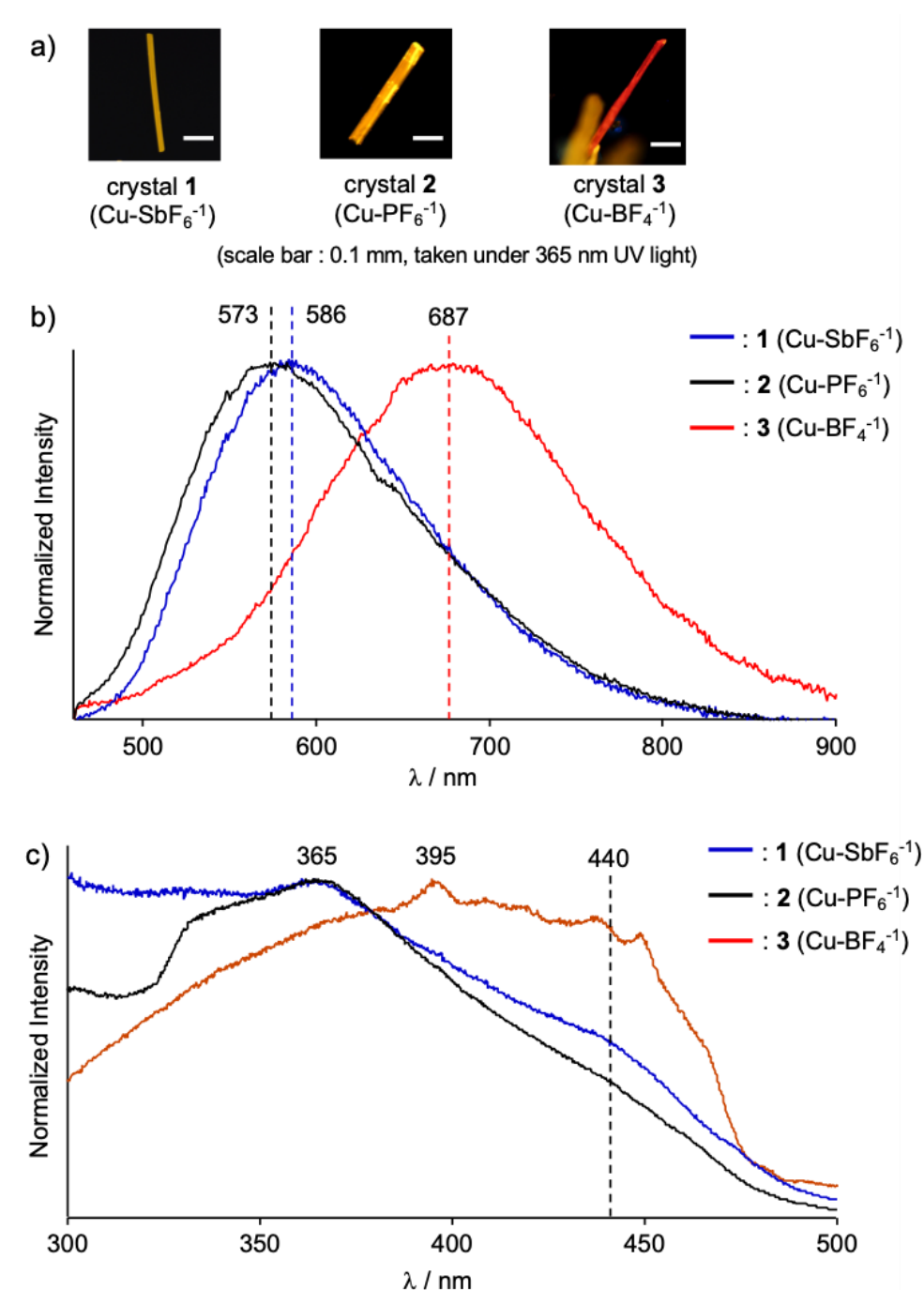


Figure 6. a) Photographs of crystal **1**, **2**, and **3** taken under UV light. b) Emission spectra of crystals **1**, **2**, and **3** measured by 365 nm of excitation (represented by blue, black, and red solid lines, respectively). c) Excitation spectra of crystals **1–3** monitored at each $\lambda_{em,max}$.

Based on the observed emission properties and crystal structures of the cationic NHC Cu(I) coordination polymers **1–3**, we 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 2c and 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 π planes with central coordination of Cu(I). We 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 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 S9). The calculated UV/vis absorption spectra showed qualitatively good agreement with the measured excitation spectra (Figure S9), and the involved molecular orbitals were identified as transitions from HOMO or HOMO-1 to LUMO or LUMO+1 (Figures 8 and S9–S12). 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 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.

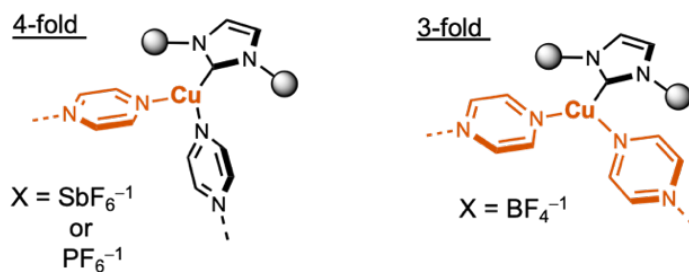


Figure 7. Schematic representation of the expected relationship between the coordination geometries built by 4-fold or 3-fold helical structures and the electronic conjugation shown in red.

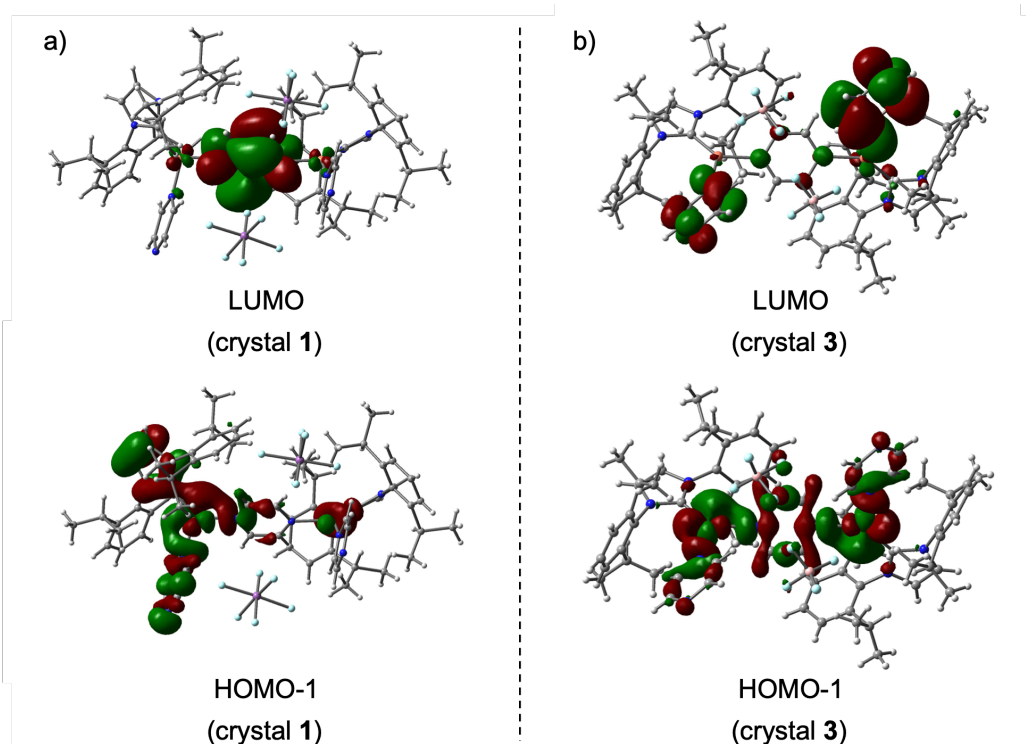


Figure 8. Selected orbitals dominantly involved in the singlet transitions of the NHC Cu(I) complex a) **1** (4-fold) and b) **3** (3-fold).

Conclusions

Herein, we 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. We 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.

ASSOCIATED CONTENT

Supporting Information. Spectroscopy, X-ray crystal graphic, thermal analysis, NMR profiles and other additional information. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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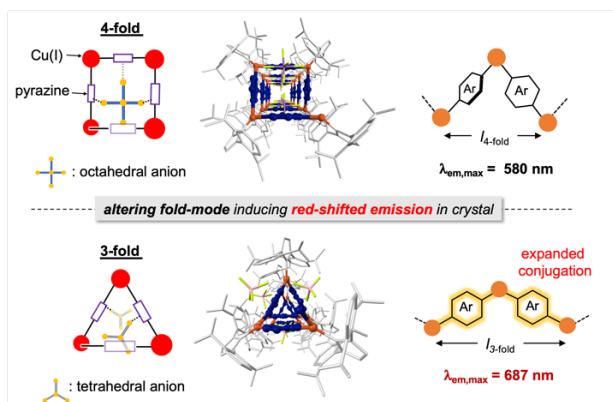
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Herein, we describe a novel way to form different fold-mode helical structure of cationic NHC Cu(I) coordination polymers in crystals by using the structural features of the counter anions, which also induce clear distinct emission properties in solid-state.