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Construction of sterically bent π -conjugated arylene by implanting into bulky NHC Cu(i) coordination polymers in crystalline media[†]

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One-dimensional π -conjugated coordination polymers are promising platforms for tailoring solid-state physical properties through diverse coordination geometries and structural arrangements. Their tunability arises from the precise design of building blocks such as metal nodes, π -conjugated organic ligands, and counter anions, which collectively influence the coordination geometry and packing structure. While distorted π -conjugated systems such as helicenes, fullerenes, corannulenes, and cycloparaphenylenes (CPPs) exhibit unique electronic properties distinct from planar π -conjugated systems, their incorporation as ligand linkers within coordination polymers remains challenging. Herein, we report the synthesis and structural modulation of cationic N-heterocyclic carbene (NHC) Cu(i) coordination polymers bearing bis(4-pyridyl)acetylene as a π -conjugated linker and sterically bulky counter anions. By leveraging the steric effects of counter anions and modifying the π -backbone on NHC ligands, we succeeded to yield two coordination polymers possessing sterically distorted π -conjugated linkers, which are generally difficult to achieve in coordination polymers. Single-crystal X-ray diffraction (XRD) studies revealed that highly bulky counter anions inhibit close packing of NHC ligands between neighboring coordination polymer columns, leading to a tilt in the trigonal planar orientation relative to the column axis.

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Introduction

One-dimensional π -conjugated coordination polymers are a promising class of materials with tunable structural and electronic properties.^{1,2} This tunability arises from the rational design of metal nodes, π -conjugated organic ligands, and counter anions.^{3,4} By carefully selecting these components, significant structural diversity can be introduced.^{5,6} The choice of the metal center, ligand architecture, and counter anions influences coordination geometry, crystal packing, and electronic properties.^{7,8} These tunable characteristics make π -conjugated coordination polymers highly attractive for applications in electronic devices,⁹ light emitting devices,^{10–12} and sensing technologies.^{13–15}

Distorted π -conjugated systems such as helicenes,¹⁶ fullerenes,¹⁷ corannulenes,¹⁸ and cycloparaphenylenes (CPPs),¹⁹

unlike conventional planar π -conjugated systems, exhibit unique electronic properties. These distinctive characteristics have consistently attracted significant attention in the field of materials science.^{20–22} If such distorted π -conjugated systems could be incorporated into one-dimensional π -conjugated coordination polymers, the integration afforded by the infinite coordination framework could potentially amplify their unique electronic properties, making this approach highly intriguing. Despite the extensive development of one-dimensional π -conjugated coordination polymers, construction of sterically distorted π -conjugated systems as a ligand linker within a coordination polymer network in the crystalline solid remains significantly challenging due to the thermodynamically unstable conformation.

We have previously reported the formation of various fold modes of cationic N-heterocyclic carbene (NHC) Cu(i) coordination polymers by using the structural features (shape, bulkiness) of counter anions, which can determine the coordination geometry.²³ These results indicated that by using cationic NHC Cu(i) coordination polymers, a wide variety of counter anions and NHC ligands can be selected as building blocks. The structural and steric characteristics of the counter anions and the concave-shape of the bulky NHC ligands have the potential to tune the local packing environment near the linker ligand and arrangement of the coordination polymers in crystalline media.^{23–32} In this study, we hypothesized that increasing the steric bulk of counter

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anions and modifying the π -backbone of N-heterocyclic carbene (NHC) ligands could modulate the tilt of NHC ligands relative to the column elongation axis. This structural modulation could, in turn, influence the arrangement of coordination polymers within the crystal lattice, potentially inducing distortions in the π -conjugated linkers.

To investigate this, we synthesized cationic NHC-Cu(I) coordination polymers incorporating two types of NHC ligands, bis(4-pyridyl)acetylene as a π -conjugated ligand linker, and sterically demanding counter anions (Fig. 1). Notably, the introduction of highly bulky counter anions, which hinder close packing interactions between adjacent

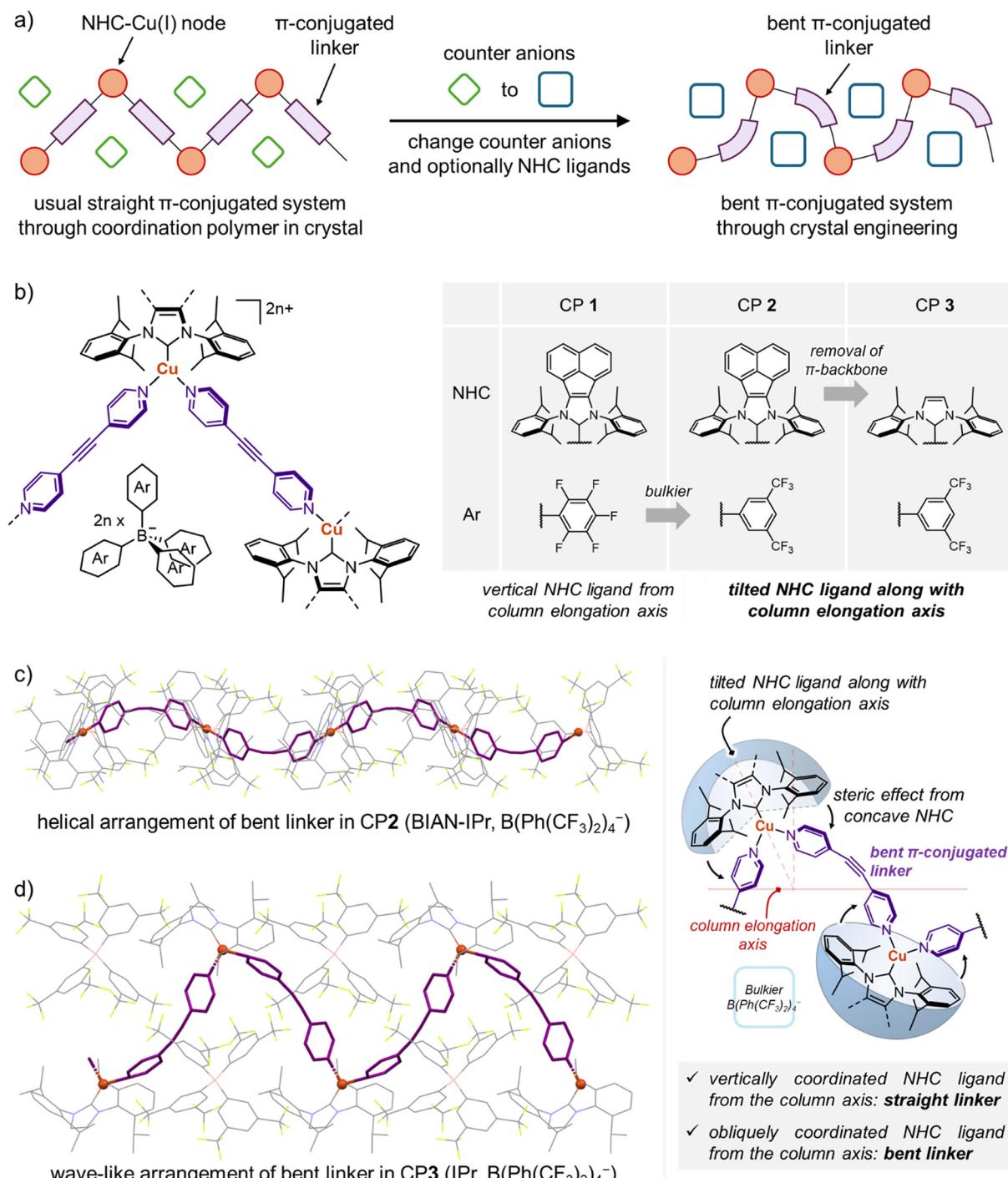


Fig. 1 (a) Representation of linker arrangement control of coordination polymers using different bulkiness of the counter anions. (b) Preparation of cationic NHC copper(I) coordination polymers (CP 1–3) containing bis(4-pyridyl)acetylene in combination with two different counter anions ($B(PhF_5)_4^-$ and $B(Ph(CF_3)_2)_4^-$) and two different NHC ligands (BIAN-IPr and IPr). Observed bent linker structures in (c) crystals 2 and (d) 3; and illustration of the plausible effect via the bulky NHC ligands and counter anions.

NHC ligands, or the removal of the NHC ligand backbone responsible for such packing, induced a tilt in the trigonal planar geometry. This tilting, occurring relative to the axis perpendicular to the polymer column elongation, facilitated the formation of distorted π -conjugated arylene in crystalline coordination polymers.

Results and discussion

Synthesis and preparations

Cationic trigonal planar NHC Cu(i) coordination polymers **CP 1–3** were prepared as crystalline solids through an anion exchange reaction²³ in CH_2Cl_2 solution from bis(4-pyridyl)acetylene, two different NHC Cu(i) chloride (bis(imino)acenaphthene (BIAN)-IPrCuCl or IPrCuCl), and two different sodium borate salt (sodium tetrakis(pentafluorophenyl)borate, $\text{NaB}(\text{PhF}_5)_4$ or sodium tetrakis[3,5bis(trifluoromethyl)phenyl]borate, $\text{NaB}(\text{Ph}(\text{CF}_3)_2)_4$) at room temperature for 2 h under a N_2 atmosphere, as shown in Scheme 1. Recrystallization was carried out through slow evaporation after solvent diffusion using the CH_2Cl_2 solution of each compound layered with ethanol at room temperature, yielding analytically pure yellow single crystals **1–3**. The crystalline powder sample of **1** was dissolved in acetone- d_6 , while those of **2** and **3** were dissolved in CDCl_3 , and characterized by ^1H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction (XRD).

Single-crystal XRD of **1–3**

Single-crystal X-ray diffraction (XRD) analysis at 153 K of NHC Cu(i) complexes **1–3** revealed the formation of cationic, trigonal planar N-heterocyclic carbene (NHC) Cu(i) complexes, which assemble into one-dimensional infinite coordination polymers in the crystalline state (Fig. 2–4). In all cases, the Cu(i) center is coordinated by one NHC ligand and two bis(4-pyridyl)acetylene linkers, forming a trigonal planar coordination geometry. The remaining pyridyl nitrogen of bis(4-pyridyl)acetylene bridges to an adjacent Cu(i) center,

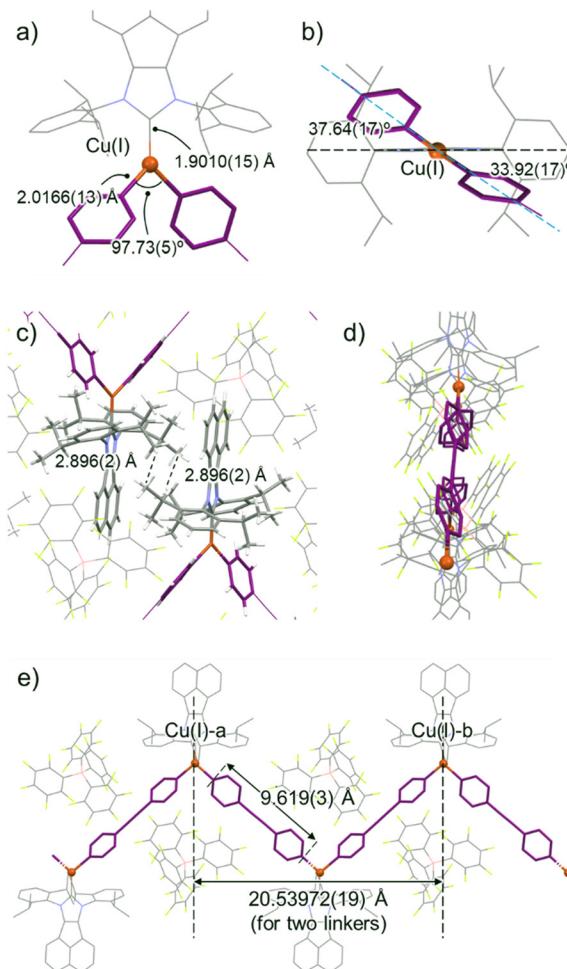
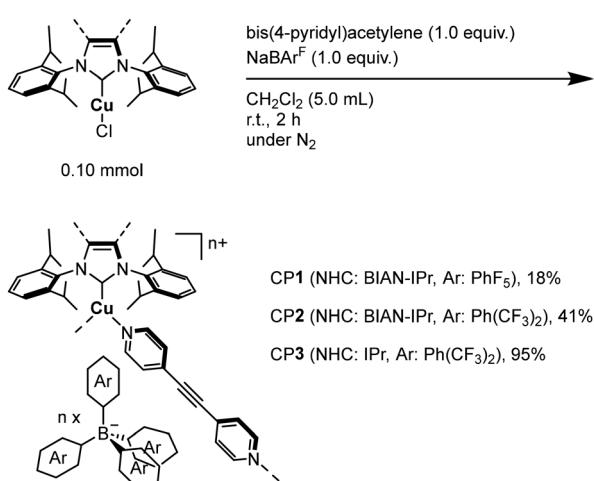


Fig. 2 Crystal structure of the cationic NHC Cu(i) coordination polymer **1** containing $\text{B}(\text{PhF}_5)_4^-$: (a) top view of the NHC backbone plane. (b) Side view of the NHC backbone plane. (c) Packing structure around the NHC ligand. (d) Axial and (e) side views of the zigzag arrangement of the straight linker in the plane structure of **1** at 153 K.



Scheme 1 Synthesis of cationic NHC Cu(i) coordination polymers.

propagating the polymeric structure. Additionally, the corresponding counter-anions are positioned in proximity to the main coordination columns.

Crystal **1** consists of the BIAN-IPrCu(i) complex as a metal node and the $\text{B}(\text{PhF}_5)_4^-$ anion as a counter anion, and a planar zigzag arrangement of straight π -conjugated ligand linkers was observed in the one-dimensional infinite coordination polymer structure, as shown in Fig. 2. The coordination polymers were packed into the $P\bar{1}$ space group (Table S1†). The Cu–C and Cu–N bond lengths of the Cu(i) complex **1** are 1.9010(15) and 2.0166(13) Å, respectively (Fig. 2a). Two pyridine moieties were coordinated to Cu(i) with a binding angle of 97.73(5)° (Fig. 2a). The torsion angles between pyridines and the NHC ring were 37.64(17) and 33.92(17)° (Fig. 2b). The bulkier NHC groups were also packed outside the column, and infinitely coordinated Cu(i) and bis(4-pyridyl)acetylene were folded with the nearly included $\text{B}(\text{PhF}_5)_4^-$ anions (Fig. 2c–e). Additionally, densely stacked intercolumn packing between neighboring coordination polymers was observed. Focusing on the packing



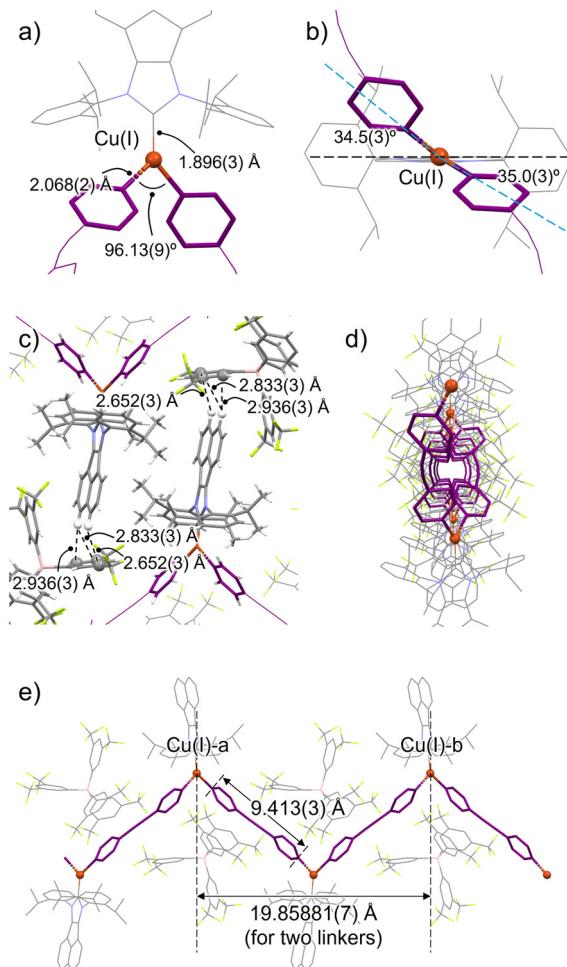


Fig. 3 Crystal structure of the cationic NHC Cu(I) coordination polymer **2** containing $\text{B}(\text{Ph}(\text{CF}_3)_2)_4^-$: (a) top view of the NHC backbone plane. (b) Side view of the NHC backbone plane. (c) Packing structure around the NHC ligand. (d) Axial and (e) side views of the helical arrangement of the bent linkers in the columnar structure of **2** at 153 K.

environment around the NHC ligand, parallel stackings of NHC π -backbones were observed, with interactions between isopropyl groups of 2.896(2) Å (Fig. 2c). Indeed, the planar shape characteristics of the NHC backbone contribute to an effect that enables parallel close packing. These may be attributed to the orientation of the NHC ligand perpendicular to the elongation axis of the coordination polymer. This coordination network was infinitely arranged, which constructed a 2-fold zigzag structure with 20.53972(19) Å of repeating pitch between Cu(I)-a and Cu(I)-b including two bis(4-pyridyl)acetylene linkers. Furthermore, the distance between the nitrogen atoms at both ends of the linker was 9.619(3) Å (Fig. 2d and e).

Crystal **2** consists of the BIAN-IPrCu(I) complex as a metal node and $\text{B}(\text{Ph}(\text{CF}_3)_2)_4^-$ as a counter anion, and the crystal with a helical arrangement of bent π -conjugated ligand linkers was observed in the one-dimensional infinite coordination polymer structure, as shown in Fig. 3. The

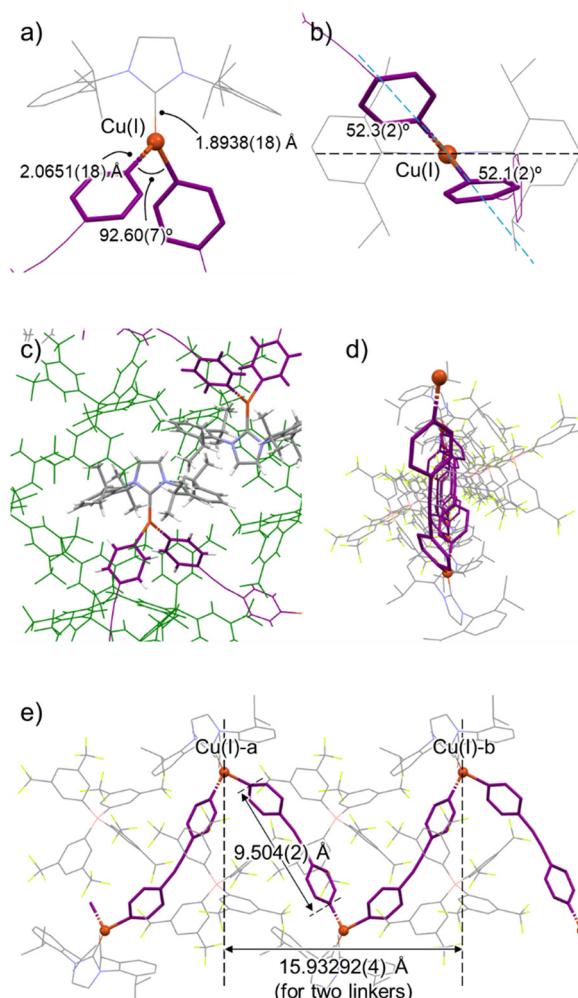


Fig. 4 Crystal structure of the cationic NHC Cu(I) coordination polymer **3** containing $\text{B}(\text{Ph}(\text{CF}_3)_2)_4^-$: (a) top view of the NHC backbone plane. (b) Side view of the NHC backbone plane. (c) Packing structure around the NHC ligand. (d) Axial and (e) side views of the wave-like arrangement of the bent linkers in the columnar structure of **3** at 153 K.

coordination polymers were packed into the $P2_1/c$ space group (Table S1†). When attention is paid to the details of the coordination geometry around the copper atoms, the Cu–C and Cu–N bond lengths of the Cu(I) complex **2** are equal to 1.896(3) and 2.068(2) Å, respectively (Fig. 3a). Two pyridine moieties were coordinated to Cu(I) with a binding angle of 96.13(9)° (Fig. 3a). The torsion angles between pyridines and the NHC ring were 34.5(3) and 35.0(3)° (Fig. 3b). The bulkier NHC groups were also packed outside the column, and infinitely coordinated Cu(I) and bis(4-pyridyl)acetylene were folded with the nearly included $\text{B}(\text{Ph}(\text{CF}_3)_2)_4^-$ anions (Fig. 3c–e). Additionally, the CH– π interactions between the π -backbone of the NHC ligand and $\text{B}(\text{Ph}(\text{CF}_3)_2)_4^-$ anions were clearly observed with C–H distances ranging around 2.652(3)–2.936(3) Å (Fig. 3c). The coordination polymer network was formed in a 2-fold zigzag structure with 19.85881(7) Å of repeating pitch between Cu(I)-

a and Cu(i)-b including two bis(4-pyridyl)acetylene linkers. Furthermore, the distance of the straight line connecting the nitrogen atoms at both ends of the linker was equal to 9.413(3) Å (Fig. 3d and e).

Crystal 3 consists of the IPrCu(i) complex as a metal node and $\text{B}(\text{Ph}(\text{CF}_3)_2)_4^-$ as a counter anion, and the wave-like arrangement of bent π -conjugated ligand linkers was observed in the one-dimensional infinite coordination polymer structure, as shown in Fig. 4. The coordination polymers were packed into the $P2_1/c$ space group (Table S1†).

The Cu–C and Cu–N bond lengths of the Cu(i) complex 3 were 1.8938(18) and 2.0651(18) Å, respectively (Fig. 4a). Two pyridine moieties were coordinated to Cu(i) with a binding angle of 92.60(7)° (Fig. 4a). The torsion angles between pyridines and the NHC ring were 52.3(2) and 52.1(2)° (Fig. 4b). The NHC groups were also packed outside the column, and infinitely coordinated Cu(i) and bis(4-pyridyl) acetylene were folded with the nearly included $\text{B}(\text{Ph}(\text{CF}_3)_2)_4^-$ anions (Fig. 4c–e). Additionally, the CH–F interactions between the NHC Cu(i) complex and $\text{B}(\text{Ph}(\text{CF}_3)_2)_4^-$ anions

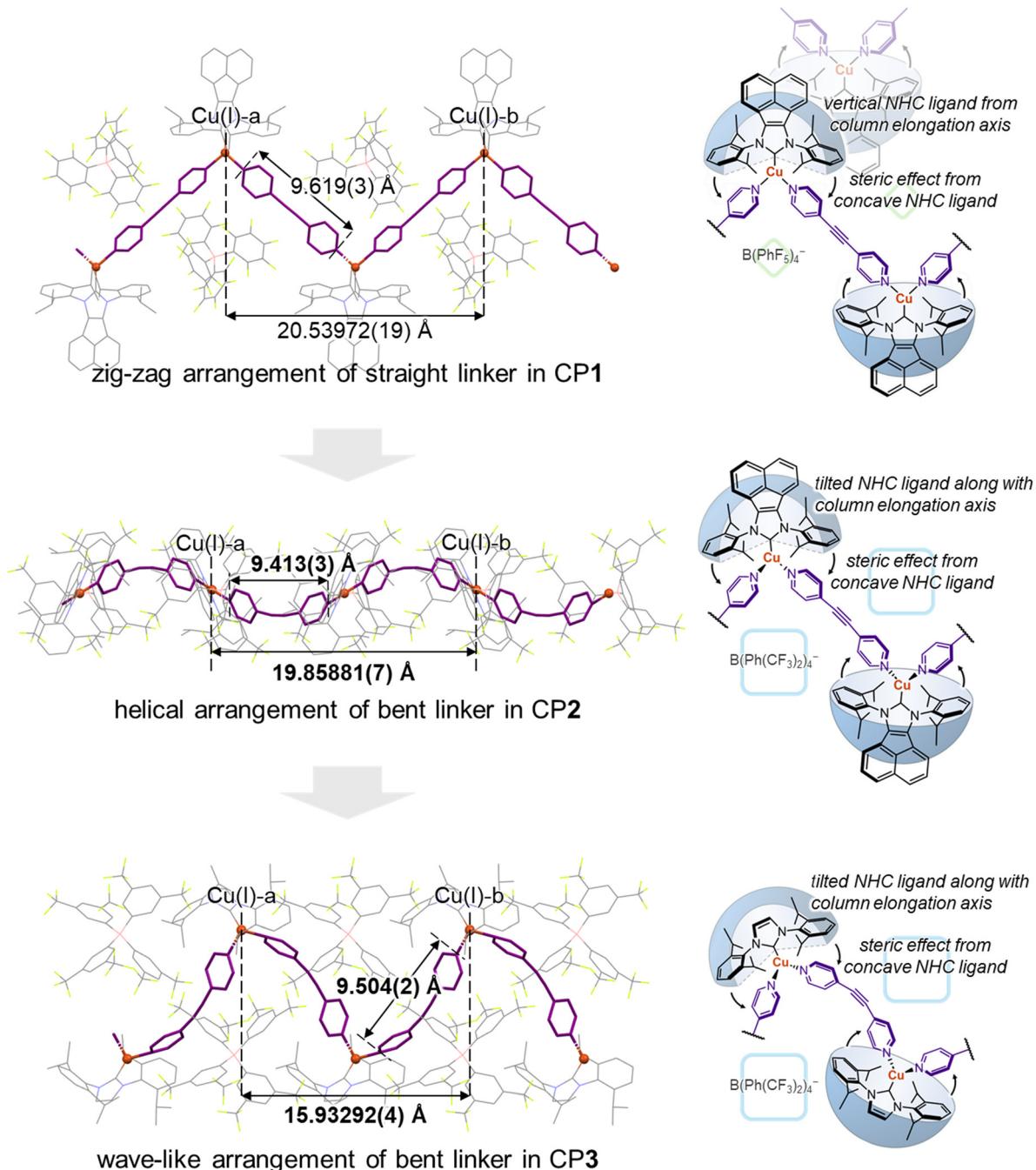


Fig. 5 Representation of the plausible effects via the bulky NHC moiety and counter anions to form the bent π -linkers and the distinct shape of arrangements.



were clearly observed with the C–H distances ranging around 2.4587(17)–3.177(4) Å (Fig. 4c). This packing was infinitely arranged, which constructed a 2-fold zigzag structure with 15.93292(4) Å of repeating pitch between Cu(i)-a and Cu(i)-b including two bis(4-pyridyl)acetylene linkers. The distance between the nitrogen atoms at both ends of the linker was 9.504(2) Å (Fig. 4d and e).

Comparison of the coordination polymer structures 1, 2 and 3

We have investigated the origin of the observed sterically bent structure of the π -conjugated linker in crystals 2 and 3. In crystal 1, the NHC ligands of the target coordination polymer and those of neighboring polymer columns assemble in a parallel fashion due to the planar shape character of the NHC π -backbone. Notably, as previously mentioned, these ligands extend outward perpendicular to the elongation axis of the coordination polymer columns. This packing mode of the NHC ligands may lead to the zigzag arrangement of the straight linkers in the crystal. On the other hand, in crystal 2, the counter anion was replaced with the bulkier $\text{B}(\text{Ph}(\text{CF}_3)_2)_4^-$ anion, which could disrupt the close packing of NHC ligands between coordination polymer columns. The resulting indirect intercolumn interactions caused a deviation in the outward orientation of the NHC ligands from their original alignment perpendicular to the elongation axis of the coordination polymer columns. This deviation, combined with the steric influence of the wing-side group on the NHC ligands, might induce a helical arrangement of the bent linkers in the crystal. In crystal 3, the NHC ligand was modified by replacing BIAN-IPr with IPr, possessing a smaller π -backbone. Consequently, the orientation of the NHC ligands has a significant deviation from the alignment perpendicular to the elongation axis of the coordination polymer columns, which may induce the bent event of the π -conjugated linker. Additionally, we envision that the hindered orientation of the NHC ligand with a steric influence of the wing-side substituents has induced the wave-like arrangement of the bent linkers (Fig. 5).

Conclusions

In this work, we achieved the construction of a bent π -conjugated molecular system in coordination polymers by modulating counter anions and NHC ligands. Cationic trigonal planar NHC–Cu(i) complexes formed one-dimensional zigzag structures with π -conjugated ligand linkers and counter anions ($\text{B}(\text{PhF}_5)_4^-$ or $\text{B}(\text{Ph}(\text{CF}_3)_2)_4^-$). Crystal 1 ($\text{B}(\text{PhF}_5)_4^-$) exhibited a zigzag linker arrangement due to NHC steric effects and parallel close packing. In contrast, bulkier $\text{B}(\text{Ph}(\text{CF}_3)_2)_4^-$ in crystal 2 disrupted the packing mode, inducing a helical bent linker arrangement *via* CH– π interactions. Crystal 3, lacking a large π -backbone in the NHC ligand, showed a wave-like linker conformation dominated by CH–F interactions. These results indicate that the fine tune of angular deviation of the NHC ligands in the

crystal structure by modulating the bulkiness of the counter anion and the size of the π -backbone of the NHC ligand can implant distorted π -conjugated molecules into the linker moiety of the coordination polymer network, which is generally challenging to achieve.

Data availability

The data supporting this article have been included as part of the ESI.† CCDC 2435084, 2435085 and 2435086 contain the supplementary crystallographic data for this paper.

Conflicts of interest

There are no conflicts to declare.

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