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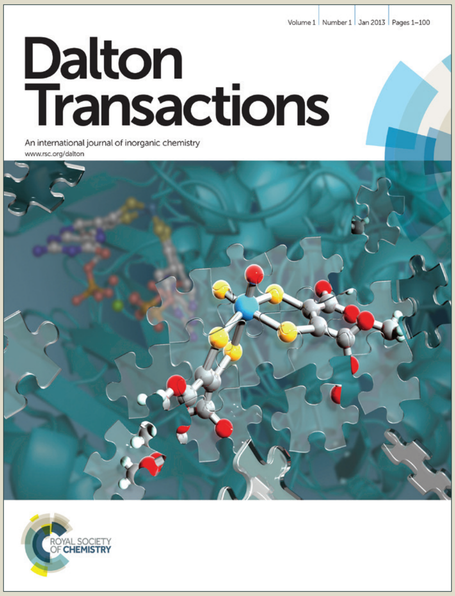

ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

# Restraining the Motion of Ligand for Modulating the Structural Phase Transition in Two Isomorphic Polar Coordination Polymers†

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***Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX***
**DOI: 10.1039/b000000x**

**A structural phase transition induced by ligand motion was found in a new polar coordination polymer: $[Cu(NCS)_2(4\text{-}APy)_2]_n$ (4-APy = 4-aminopyridine). Restraining such motion in an isomorphic compound $[Cu(NCS)_2(4\text{-}MeAPy)_2]_n$ (4-MeAPy = 4-methylaminopyridine) results distinct phase transition behaviour. These findings provide a new clue for modulating phase transition behaviour in known materials.**

Over the past decades, solid structural phase transitions have attracted considerable interest not only because of their fundamental significance on the ubiquitous critical phenomenon,[1] but also the potential technological applications in the development of switching dielectric, sensors, smart materials and tiny machines.[2] On a microscopic level, the concerted molecular motions, which accompany with large deformations and/or distortions of the lattice, usually play a significant role in triggering such structural phase transitions.[3] Therefore, the potential of rationally controlling the molecular motions are crucial for the design and construction of a material with desired structural phase transition.[3b, 4] For example, modulating the dynamical motions of protons causes distinct ferroelectric phase transition behaviours.[5] Controlling the 180° flip-flop molecular random motion of a rotator gives rise to a phase transition from disordered phase at high temperature to ordered phase at low temperature.[4] However, up to now, it remains a major challenge to manifest the molecular motions in solids.[6]

Currently, coordination polymers (CPs) have received considerable attention because of their diversity of structures and functions.[1] The designable/tuneable characteristics enable CPs as a promising platform for controlling the motions at the molecular level so as to design and synthesize new, desired phase transition materials.[7] To date, even though various types of structural phase transitions has been documented in CPs, such as order-disorder of guest,[8] displacement of some organic moieties,[9] their microscopic mechanistic details are still unclear. In this scenario, studying on molecular motions in the lattice of those CPs will increase our knowledge on the phase transition, as well as its utility for new devices.[10]

During our research on the molecular motion in specific confined environment in CPs, a structural phase transition induced by ligand motion was found in a polar chain complex: $[Cu(NCS)_2(4\text{-}APy)_2]_n$ (**1**) (4-APy = 4-aminopyridine). By restraining such motion of ligand in an isomorphic compound $[Cu(NCS)_2(4\text{-}MeAPy)_2]_n$ (**2**) (4-MeAPy = 4-methylaminopyridine), distinct phase transition behaviour was obtained.

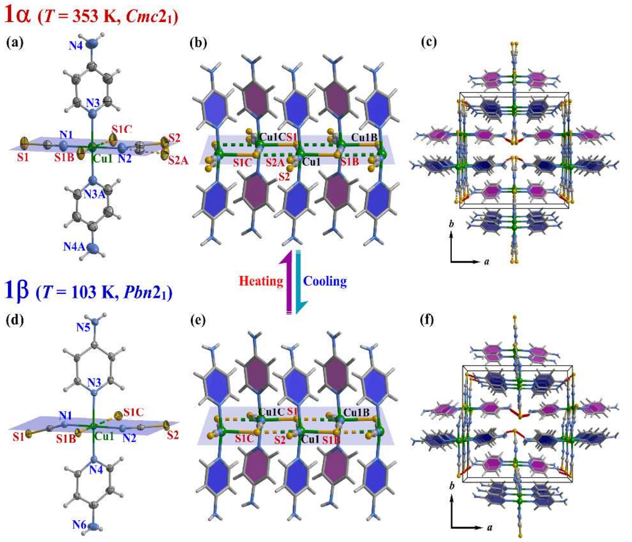

**Fig. 1** The coordination environments of Cu(II) ion in **1α** (a) and **1β** (d). The one-dimensional chain of **1α** (b) and **1β** (e). The packing structure of **1α** (c) and **1β** (f) viewed along with the *c* axis. Hydrogen bonds are represented by red dotted lines. Symmetry codes: A) 1−*x*, *y*, *z*; B) 1−*x*, 2−*y*, 0.5+*z*; C) 1−*x*, 2−*y*, −0.5+*z*.

Green block crystals of **1** were obtained by evaporation of a methanol solution containing stoichiometric $Cu(SCN)_2$ and 4-APy ligands. In-situ single-crystal X-ray analyses reveal that **1** crystallizes in the orthorhombic space group $Cmc2_1$ at 353 K (the high temperature phase, **1α**) and in the space group $Pbn2_1$ at 103 K (the low temperature phase, **1β**).[11] In **1α**, as shown in Fig. 1a, the Cu1 atom is located at a crystallographic mirror plane, and is approximately in square-pyramidal coordination geometry. Four nitrogen atoms from two 4-APy ligands and two $NCS^-$ groups form the basal plane [Cu–N 1.947(3)–2.027(3) Å], forming a $Cu(NCS)_2(4\text{-}APy)_2$ unit. A sulfur atom (S1B) from the neighbour $Cu(NCS)_2(4\text{-}APy)_2$ unit occupies the apical position of Cu1 atom [Cu1–S1B 2.879(2) Å], and thus, these Cu(II) ions are linked into one-dimensional square-wavy chains with [–Cu–NCS–] repeating unit along the *c* axis

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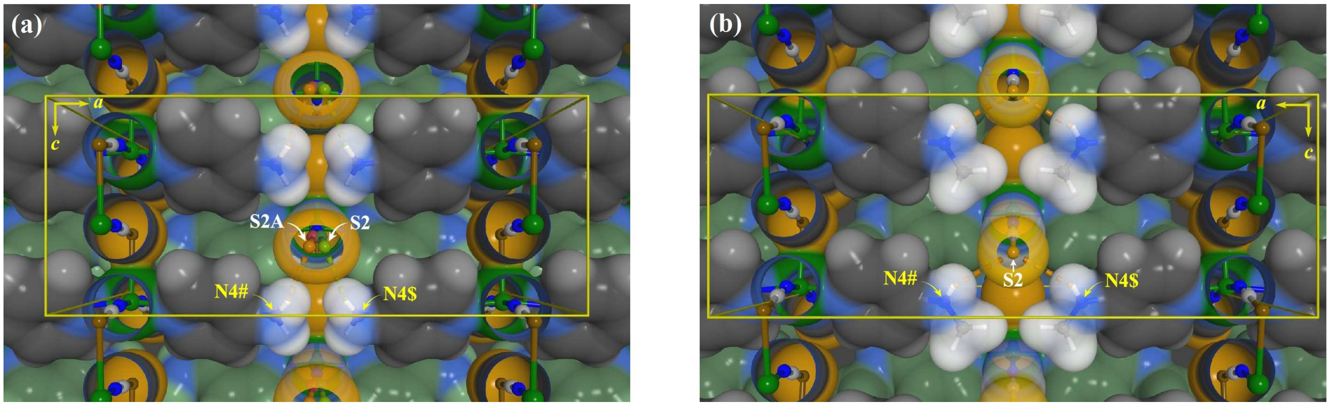

**Fig. 2** From the perspective view of the 3D packing along the *b* axis, the terminal NCS$^-$ groups are found 2-fold disordered in **1α** (a) but ordered and restrained by methyl groups from the adjacent chains in **2** (b) at 353 K. The dash lines stand for the hydrogen-bonding interactions. For clarity, the space-filling spheres of terminal NCS$^-$ groups and amino/methylamino groups are set 30% transparent, and the carbon and hydrogen atoms of pyridyl groups presented in pale green for the farther chains and gray for the closer chains, respectively. Symmetry codes: for **1α**, #) −0.5+*x*, 1.5−*y*, -0.5+*z*; $); 1.5−*x*, 1.5−*y*, −0.5+*z*; for **2**, #) 0.5+*x*, 1.5−*y*, 0.5+*z*; $) 0.5−*x*, 1.5−*y*, 0.5+*z*.

by the bridging μ$_{1,3}$-NCS$^-$ groups (Fig. 1b). Moreover, Cu1 atom is also weakly interacted with the sulfur atom from the adjacent bridging NCS$^-$ groups [Cu···S1C 3.531(2) Å]. It seems that S1 atom might coordinated to two Cu$^{2+}$ atoms with the equal Cu···S distances. However, the 4-APy ligands array along the chain in a typical herringbone fashion (Fig. S5), restricting the distance between S1-atom-interacted Cu$^{2+}$ ions [Cu1B···Cu1C 6.397(1) Å]. Thus the shorter and longer Cu···S distances are alternately present, eventually resulting in a polar [Cu(NCS)$_2$]$_n$ chain. Besides that, the terminal NCS$^-$ groups are found in 2-fold disordered about the mirror plane. By the interchain hydrogen-bonding interactions between the terminal NCS$^-$ groups and the amino groups of the two adjacent chains [3.426(6) Å for N4#–H···S2, Fig. 2a and Table S3], each chain is interacted to four neighbour chains with the same polarity, resulting in a polar three-dimensional (3D) supramolecular network (Fig. 1c). The observed Flack parameter of 0.03(2) indicates the pure polarity of the entire tested single crystal.

Compared to that of **1α**, as depicted in Fig. 1d, the asymmetric unit in **1β** doubled and all the atoms located at the general positions, due to the loss of mirror symmetry at low temperature (Fig. S7). The local coordination environment of Cu1 atom is found to be slightly changed, and the 1D polar polymeric nature of the [Cu(NCS)$_2$]$_n$ chain is retained in **1β**, though the intrachain Cu1–S1B bond length is reduced to 2.834(1) Å and the weak-coordinated Cu1···S1C distance is reduced to 3.486(1) Å (Fig. 1e). Moreover, the observed Flack parameter of 0.02(1) in **1β** indicates that the polarity is not changed during the phase transition.

Thermogravimetric (TG) analyses reveal that **1** is stable up to 393 K. Moreover, in the differential scanning calorimeter (DSC) plots, an endothermic/exothermic peak appeared at 341.8/338.7 K in the heating/cooling run (Fig. S6 and S8), confirming the reversibility of the phase transition for **1**. The lambda-shaped peaks and a small heat hysteresis (*ca.* 3 K) implied the phase transition might be a continuous one. Given that entropy change $\Delta S = R\ln N$ ($R$ is the gas constant, and $N$ is the ratio of possible configurations in the disordered system), the $\Delta S$ is 0.36 J·mol$^{-1}$·K$^{-1}$ and $N$ is close to 1.0, further supporting the second-order characteristic for this structural phase transition. In addition, the phase transition was further confirmed for **1** by the variable-temperature powder X-ray diffraction analysis (Fig. S9).

During the structural transition from **1α** to **1β**, a notable displacement of the NCS$^-$ groups from the mirror plane passing through the [Cu(NCS)$_2$]$_n$ chains was found. In **1β**, the bridging NCS$^-$ groups markedly deviated the least-squares plane of N1, Cu1, N2 and S1A atoms [0.805(1) Å for S1 and 0.343(2) Å for C1, respectively]. Moreover, the terminal NCS$^-$ groups become ordered in **1β** with deviations from this plane [0.185(1) Å for S2 and 0.053(2) Å for C2, respectively]. As a result, two different interchain hydrogen-bonding interactions are found [3.545(3) Å for N5#–H···S2 and 3.490(4) Å for N6$–H···S2, respectively, see Fig. 1f]. This fact implies that the motions of NCS$^-$ groups, especially the hydrogen-bonding involved terminal NCS$^-$ groups, may be the essential reason for the phase transition.

In order to further gain insight into the phase transition details in **1**, we modified the hydrogen donor by introducing a methylamino group, and obtained its isomorphic compound **2**, supposing that the motions of terminal NCS$^-$ groups may be suppressed by the methyl group, and thus, resulting in distinct phase transition behaviour. Indeed, for **2**, the single-crystal diffractions at 103 and 353 K revealed that it crystallizes in the space group *Cmc*2$_1$, same as that of **1α**. Similar to **1α**, at 353 K, polar [Cu(NCS)$_2$]$_n$ chains with alternately presence of weak-coordinated Cu···S interactions [3.884(2) Å] and Cu–S coordinated bond [2.774(2) Å] are found in **2** (Fig. S10). The interchain hydrogen-bond interactions and the resulted 3D supramolecular network of **2** are almost the same with those of **1α**, except that the terminal $NCS^-$ groups in **2** are found orderly located on the mirror plane at 353 K. As shown in Fig. 2b, each terminal $NCS^-$ group is attracted by two N–H groups *via* hydrogen-bonding interactions, and is repulsed by two methyl groups from the opposite side *via* the steric exclusion. As a result, the motion of each terminal $NCS^-$ group is well restrained along the *a* and *c* directions, thus the structure of **2** was found almost unchanged by lowing temperature to 103 K. The absence of phase transition in the temperature region of 200–373 K was further confirmed by the DSC measurement for **2** (Fig. S11). Though phase transition of **2** might occur at lower temperature, which was not detected in our investigated temperature range ($T$ > 103 K), the phase transition temperature of **2** was found at least 237 K lower than that of **1**. This fact clearly indicates that the microscopic origin for the phase transition of **1** should be the dynamic motions of the $NCS^-$ ligands, and more significantly, restraining such ligand motion can give rise to a distinct phase transition behaviour.

In order to manifest the molecular motions, the general approaches focused on the modification of the sizes and/or geometries of motional units. For instance, in a series of arylammonium-crown ether supramolecular assemblies,[12] modulation of the motional cation conformation resulted in different phase transition behaviours. In CPs, similar cation-dependent phase transition behaviours were found in the perovskite-type compounds $[(CH_3)_nNH_{(4-n)}][Mn(N_3)_3]$ ($n$ = 1−4)[13] and $[AmineH]^+[Mn(HCOO)_3]^-$ (AmineH = protonated amines) frameworks.[14] However, at the same time, the modulations of the sizes and/or geometries of motional units seem so strong that usually cause a dramatic change in the crystal packing, which make the mechanism of phase transition more complicated. In contrast, an alternative and moderate way that slightly modulating the specific environment around the motional units may keep the crystal packing and it was still less explored in CPs.[15] In the present case, we are interested in the microscopic and specific confined environment around the motional $NCS^-$ groups and modulated it through the steric hindrance effect. This strategy effectively restrains the motion of ligand and results in distinct phase transition behaviours of **1** and **2**. Moreover, the modification of ligands does not change the molecular packing, hence the bulky properties such as polarity retained even though the phase transition behaviour is tuned.

In conclusion, structural phase transition induced by the ligand motion is demonstrated in a 3D hydrogen-bonded polar supramolecular network consisting of one-dimensional Cu(II) chains. Moreover, restraining the motional groups *via* the steric hindrance effect resulted in the distinct phase transition behaviour in its isomorphic compound. This fact well demonstrates that a slight modulation of the specific confined environment around the motional units is a moderate way to control the motion of ligands and to tune the structural phase transition yet keep the crystal packing unchanged. The present strategy provided a new clue for the design and synthesis of new phase transition materials or tuning phase transition behaviour for known materials.

## Acknowledgements

This work was supported by the NSFC (21290173, 21121061 and 21301198), the 973 Project (2012CB821706), and NSF of Guangdong (S2012030006240). W.-X. Z. is grateful for "100 Talents Program of SYSU" initial funding.

## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and characterizations. CCDC 980360, 980361, 980362, 980363. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/b000000x/

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***Short text and illustration for table of contents:***

Structural phase transition induced by ligand motion was found in a new polar coordination polymer, and a distinct phase transition behaviour can be achived *via* modulating the specific confined environment around the motional ligand in its isomorphic compound.