# **Inorganic Chemistry**

# Transformation of One-Dimensional Achiral Structure to Three-Dimensional Chiral Structure: Mechanistic Study and Catalytic **Activities of Chiral Structure**

Purna Chandra Rao,<sup>†</sup> Sonu Pratap Chaudhary,<sup>†</sup> Denis Kuznetsov,<sup>‡</sup> and Sukhendu Mandal<sup>\*,†</sup>

<sup>†</sup>School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, Thiruvananthapuram, Kerala, India, 695016

<sup>‡</sup>National University of Science and Technology "MISIS", Department of Functional Nanosystems and High Temperature Materials, Leninsky pr.4, Moscow, Russia, 119049

# **S** Supporting Information

ABSTRACT: We have isolated two copper-based coordination polymers through solvent diffusion and solvothermal methods using copper salt, furan dicarboxylic acid (FDC), 4,4'-bipyridine (bpy) in MeOH/ethylene glycol, and water solvents. Compound 1 is adopting  $P2_1/c$  space group and adopts a one-dimensional wirelike structure with a free carboxylate anion. Compound 2 crystallizes in chiral space group P65. This is a three-dimensional structure with helical chains. This helicity might be the reason for chiral generation and symmetry breaking. We have converted compound 1 to compound 2 using grinding, followed by a solvothermal method. The circular dichroism data of 2 showed that it is an enantioenriched compound. We have shown that compound 2



is a very good catalyst for chemo- and regioselective enamination reaction and for azide-alkyne Huisgen cycloaddition, respectively.

# INTRODUCTION

The chirality is an imporant research area in biology and materials science due to their rich application and similarity to natural phenomena. The research on the targeted synthesis of homochiral materials is eminent for their applications in enantioselective separation, nonlinear optics, catalysis, and magnetism.<sup>1–16</sup> Generally, enantiopure starting reagents produce homochiral materials. The applications of these materials are hindered due to the cost effectiveness of enantiopure reagnets. Even chiral materials can be synthesized from achiral reagents where chirality can be generated either through spontaneous resolution or by chirality induction. Separation and crystallization of homochiral materials from achiral units still remains an unexplored area. Symmetry breaking can induce chirality in the final structure by affecting the nucleation or crystal growth.<sup>17-22</sup> The example of induced chirality through symmetry breaking where the final product does not contain any chiral unit is very rare. This process has an advantage compared to spontaneous resolution due to the enantiopure product formation, where as spontaneous resolution produces opposite handedness or racemic twins.<sup>23,24</sup> There are several reports on chiral symmetry breaking, but the proper mechanism or factors repsonsible for this are not very clear.<sup>25-28</sup> According to Kondepudi et al., during the stirring of the reactions mixture, secondary crystal

nuclei may rapidly clone the parent structure. This is known as chiral autocatalysis. Once the cloned structure formed, it leads to the formation of enantiopure crystals.<sup>29</sup> It is also predicted that supramolecular interactions like H-bonding or  $\pi - \pi$ stacking may induce the symmetry breaking.<sup>18,24,30,</sup>

The structural transformation of flexible metal-organic frameworks (MOFs) through dehydration/desolvation or rehydration/resolvation has gained much interest in gas adsorption due to breathing behavior.<sup>32,33</sup> This transformation does not create major changes in the structural framework. However, structural changes using external stimuli (like thermal treatment, mechanical grinding) involve breaking and reforming of bonds. Structural transformation with major structural changes using external stimuli have been studied extensively in several inorganic-organic hybrid open-framework compounds such as phosphates,<sup>34</sup> and phosphites.<sup>35</sup>

Metal-organic frameworks or coordination polymers (CPs) can be used as good heterogeneous catalysts. These inorganicorganic hybrid structures have many advantages compared to the conventional homogeneous catalysts mainly due to easy separation, recovery, and high thermal and wide ranges of chemical stability.<sup>36</sup> MOFs or CPs with a coordinately

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Figure 1. (a) The one-dimensional wire structure of 1, (b) three-dimensional structure of 2, (c, d) left-handed helices in 2, (e) topological representation of compound 2.

unsaturated metal center often act as Lewis acid catalysts. Usually, the Cu(II) ion displays dynamic Jahn–Teller distortion<sup>37</sup> and can produce open Lewis acid centers. These Lewis acidic centers are useful for various reactions such as azide–alkyne cycloaddition, enamination of  $\beta$ -ketoesters, oxidation–coupling reaction, Henry reaction, etc.<sup>36</sup>

In this work, we have identified two single crystals,  $[Cu(H_2O)_3(FDC)(bpy)] \cdot 3H_2O$ , 1, and  $[Cu(H_2O)(FDC) - Cu(H_2O)(FDC)] \cdot 3H_2O$ , 1, and  $[Cu(H_2O)(FDC) - Cu(H_2O)(FDC)] \cdot 3H_2O$ . (bpy)]·H<sub>2</sub>O, 2. Compound 1 was synthesized at room temperature through the solvent diffusion method, while compound 2 was formed at 140 °C through the solvothermal method. Compound 1 adopts a centrosymmetric space group  $(P2_1/c)$ , while 2 in a chiral space group  $(P6_5)$ . Compound 1 is a one-dimensional wirelike structure with a pendent FDC anion. Compound 2 is a three-dimensional chiral helical structure. It contains a 65 rotation axis, which contributes to the chirality. The presence of a free carboxylate group in compound 1 provoked us to explore its reactivity. To do this, we have ground compound 1 with 4,4'-bipyridine and then heated it at 120 °C in MeOH and H<sub>2</sub>O, which resulted in formation of compound 2. This is one of the rare examples where we have transformed a centrosymmetric one-dimensional structure to a chiral three-dimensional structure. Transformation reactions were analyzed in detail using time-dependent PXRD data. On the basis of PXRD data, it was understood that transformation take places through some intermediate structure. Due to the unsaturated nature of the Cu metal center in 2, it exhibits Lewis acidic behavior. We have explored this Lewis acidic behavior for chemo- and regioselective enamination of  $\beta$ -ketoester and azide-alkyne Huisgen cycloadditions, respectively.

#### EXPERIMENTAL SECTION

**Materials and Methods.** All the reagents were purchased from Sigma-Aldrich and used directly without further purification. Singlecrystal X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer with  $\lambda_{MoK\alpha} = 0.71073$  Å. Powder X-ray diffraction spectra were recorded using an X'pert PRO (PANalytics) powder diffractometer. The PXRD experiments were done in a slow and continuous scan rate mode using Cu as anode material (K $\alpha_1 = 1.540598$  Å). TLC analyses were done using precoated TLC silica gel 60 F254 (Merck) plates. The plates were visualized by using a UV lamp and dipping the plates into chromic acid staining solution, followed by heating. NMR spectra were recorded on an Avance II-500 (Bruker) NMR spectrometer. IR spectra were recorded by preparing KBr pellets, using an IR Prestige-21 (Shimadzu) spectrometer. The solid-state circular dichroism (CD) spectra were acquired from a Jasco J-650 spectrometer with KBr pellets.

Typical Synthetic Procedure for Compounds 1 and 2. Synthesis of Compound 1. Cu(NO<sub>3</sub>)<sub>2</sub>·2.5 H<sub>2</sub>O (0.5 mmol, 116.2 mg) was dissolved in 20 mL of methanol. We have taken two glass vials; in one, FDC (0.5 mmol, 78 mg) was dissolved in 10 mL of water. After that, we adjusted the pH 8-9 with 0.1 M KOH solution. In the other vial 4,4'-bipyridine was dissolved in 10 mL of water. These two ligand solutions were mixed and stirred for 1 h using a magnetic bar. In a separate vial, we have prepared the buffer solution of 5 mL of methanol and 5 mL of water. The buffer solution (2 mL) was added dropwise very carefully (avoid the fast addition) to the stirred ligand and coligand solution (4 mL). Later, the metal salt solution (4 mL) was layered on this with the same attention. This reaction mixture was kept at room temperature without any disturbance for 5 days. Light blue color crystals were formed at the bottom of the vial. The crystals were washed several times with water and methanol to remove the unreacted reagents. Then, crystals were dried at rt for further use. Analysis of 1 Calculated for  $C_{16}H_{22}N_2O_{11}Cu$  ( $M_r = 481.89$ ): C, 39.88; H, 4.60; N, 5.81. Found: C, 39.66; H, 4.54; N, 5.83. IR data (KBr, cm<sup>-1</sup>): 3376, 3251, 1608, 1579, 1357, 1220, 1076, 1018, 959, 810, 642. Yield: 50% (calculated based on the FDC ligand).

Synthesis of Compound 2. In one vial,  $Cu(OAc)_2 \cdot H_2O$  (0.5 mmol, 99 mg) was dissolved in 4 mL of water; in the other vial, 6 mL of ethylene glycol was added to the FDC (0.5 mmol, 78 mg) and 4,4'-bipyridine (0.5 mmol, 78 mg). After that, both were mixed and was sonicated for 15 min. This reaction mixture was transferred into a Teflon vial, and kept at 140 °C for 24 h. Blue colored rod-type crystals were formed at the bottom of the vial. The crystals were washed with methanol four to five times to remove the unreacted reagents. Finally, crystals were dried in an oven for further use. Analysis of 2 Calculated for  $C_{32}H_{28}N_4O_{14}Cu_2$  ( $M_r = 817.65$ ): C, 46.89; H, 3.44; N, 6.84. Found: C, 46.67; H, 3.25; N, 6.62. IR data (KBr, cm<sup>-1</sup>) 3302, 1608, 1577, 1363, 1220, 1076, 1014, 960, 810, 723, 644. Yield: 66% (calculated based on the FDC ligand).

**Experimental Procedure for the Transformation of Compound 1 to Compound 2.** The compound 1 (23 mg, 0.047 mmol) and 4,4'-bipyridine (0.06 mmol, 10 mg) were weighed in a reaction vial. After that, we transferred the compounds into a mortar and pestle and then ground the mixture for 15 min. To this, we have added 2 mL of methanol and 2 mL of water and then transferred the reaction mixture into a 10 mL vial, kept at 120  $^{\circ}$ C for 72 h. After 3 days, the resultant crystalline material was washed with methanol four to five times to remove the unreacted reagents. This material was dried in an oven for further studies. The powder XRD studies confirmed that compound 1 was transformed to the compound 2.

Single-Crystal X-ray Diffraction. The suitable crystals of compounds 1 and 2 were carefully selected under a polarizing microscope and experimented on a Bruker AXS Smart Apex CCD diffractometer at 298 K for single crystal data. The diffraction data were collected using Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation with an  $\omega$  scan with of 0.3°. The SAINTPLUS<sup>38</sup> was used for reducing the diffraction data and the SADABS program<sup>39</sup> for the correction of an empirical absorption. The crystal structural models were determined by direct methods using SHELXS2014 and the refinement was done with SHELXL2014 present in the SHELXTL V6.14 package.<sup>40</sup> All the hydrogen atoms and non-hydrogen atoms were refined during the final refinement process. The anisotropic thermal parameters were used for the refinement of non-hydrogen atoms, and isotropic thermal parameters were applied to all the hydrogen atoms. The refinement of the full-matrix least-squares structure on  $F^2$  was done by using the WINGX package of programs.<sup>41</sup> We have presented the crystallographic parameters of compounds 1 and 2 in the Supporting Information.

CCDC- 1487080–1487081 contain the crystallographic data for 1 and 2, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc. cam.ac.uk/data request/cif.

#### RESULTS AND DISCUSSION

Structure. Single-crystal studies show that compound 1 adopts a centrosymmetric space group, P21/c. The Cu-O/N bond lengths are in the range of 1.958-2.430 Å (Table S2). The Cu ion has distorted octahedral geometry with two nitrogen atoms of the 4,4'-bipyridine molecules, three coordinated water molecules, and one carboxylate oxygen atom. The  $CuO_4N_2$  octahedral units linked through 4,4'bipyridine molecules to form the one-dimensional wirelike structure (Figure 1a). This binding mode creates a carboxylate anion and hanging from the copper ion center. Compound 2 crystallizes in the chiral space group P65 with a Flack parameter of 0.03, indicating enantioenrichment of the single crystal despite the use of achiral reagents. The asymmetric unit contains one Cu ion, one FDC anion, one 4,4'-bpy ligand, one coordinated and lattice water molecule. The Cu ion adopts distorted trigonal bipyramidal geometry with two oxygen atoms from the carboxylate moiety, one from a coordinated water molecule, and two nitrogen from the 4,4'-bipyridine molecule. The Cu–O/N bond lengths are in the range of 1.951–2.386 Å (Table S4). The FDC anion links two Cu ions in monodentate fashion and the 4,4'-bipyridine molecule bonded to two Cu ions. This connectivity results in an infinite three-dimensional structure with 2-fold interpenetration (Figure 1b,e). The interconnection of neighboring Cu ions through ligands results in a left-handed  $6_5$  helical chain along the (101) axis (Figure 1c,d). The existence of  $6_5$  screw axes contributes to the chirality of the compound 2. The three-dimensional structure adopts uninodal four-connected topology qzd quartz-dual "dense" net (Figure 1e) with a short Schläfli symbol of  $\{75.9\}$  (td10 = 2079) (see the SI).42

**Characterization.** Experimental powder X-ray diffraction patterns of 1 and 2 were entirely consistent with the simulated XRD patterns, indicating crystalline phase purity for both the compounds (Figures S1 and S2). The thermogravimetric analysis shows that both the compounds were stable up to

250 °C. For both the compounds, the first weight loss after 150 °C is due to the loss of lattice and coordinated water molecules. After that, both the compounds lost the organic framework at around 250 °C (Figures S3 and S4). The IR spectra analysis exhibits the peaks corresponding to the water molecules and carboxylate moiety (Figures S5 and S6).

Chirality in Compound 2. In order to investigate the absolute configuration of 2, four crystals were randomly picked from four different batches of reaction mixture and the corresponding crystal structures were refined by the singlecrystal X-ray diffraction method with the same set of atomic coordinates. The results reveal that all of them crystallize in space group P6<sub>5</sub>, and the Flack absolute structure parameter from each refinement of four crystals is close to zero (Table S5). In order to get a better insight into the chirality of 2, UVvis DRS and solid-state circular dichroism (CD) spectra on single crystals picked from different reactors as well as bulk samples were measured. The dichroic signals in the CD spectra indicate that compound 2 is enantioenriched (Figure S7). It is interesting to find the origin of the chirality of this structure as no driving forces were employed. The structural analysis and solid-state CD spectra reveal that spontaneous chiral symmetry breaking occurred during the course of crystallization and enantiomerically enriched crystals were formed. The formation of the  $6_5$  helix might be the origin of chirality. To find out the reason for the enantiomeric excess, we have checked all starting materials and found that all are optically inactive. There is always a statistical probability that first nucleation might lead to the symmetry breaking. Based on Kondepudi and co-workers, a parent crystal should clone a number of secondary crystals with the same structural integrity.<sup>8</sup> Thus, the particular handedness of the bulk samples depends on which handedness is preferentially formed.

**Transformation of Compound 1 to Compound 2.** The presence of the uncoordinated carboxylate anion in compound 1 provoked us to convert it to a higher dimensional structure. To do this, we have ground compound 1 and 4,4'-bipyridine and then mixed with a methanol—water mixture (2:2, v:v ratio). Then, the mixture was transferred in a Teflon vial and heated at 120 °C for 72 h. The XRD patterns of the products of the reaction indicate that 1 transforms to 2 in 72 h (Figure 2). We have carried out control experiments by doing grinding,



**Figure 2.** Time-dependent powder X-ray diffraction for transformation for compounds **1** to **2** and intermediate.

grinding followed by heating, and without grinding (solvothermal) methods. The results show that in none of the cases did compound 1 convert to compound 2. This proves that grinding, followed by a solvothermal method, is essential for this conversion (Figure S8). To find out the mechanism of this transformation, we have carried out a time-dependent study (Figure 2). The PXRD patterns at different time intervals show that compound 1 starts to transform in about 30 h and the whole process was completed in 72 h. To elucidate the possible mechanism of this transformation, we carefully analyzed the structures of the both the compounds. It was observed that the Cu<sup>2+</sup> ions in 1 adopt distorted octahedral geometry. There are three coordinated water molecules. This water molecules appear to be replaced by carboxylate connectivity during heating. From Figure 2, it was understood that compound 1 transforms to compound 2 through intermediate structures. To identify the possible intermediates during the transformation, we have carried out several experiments. Unfortunately, we could not synthesize any single crystals for the intermediate products. The structural arrangement of compound 2 leads to a three-dimensional structure with a helical chain. The formation of the three-dimensional helical structure from the onedimensional wire is very complicated, and in this stage, it is quite difficult to predict the proper mechanism for this transformation.

Catalytic Behavior of Compound 2. It has been shown that MOFs as heterogeneous catalyst have many advantages due to their robust nature and chemical and thermal stabilities.43,44 MOFs or CPs with a coordinatively unsaturated metal center often show the Lewis acidic behavior. Due to this characteristic, it can exhibit associated catalytic reactions.<sup>45,46</sup> The Cu(II) centers can afford open Lewis acid sites due to the dynamic Jahn-Teller distortion. These active sites are effective for several organic transformations.<sup>37</sup>Among all of these, enamination of  $\beta$ -ketoesters has a vital role in synthesizing the biological natural products like therapeutic agents<sup>47</sup> and precursors of various important antibacterial, anti-inflammatory, and antitumor drugs.<sup>48</sup> Compound 2 is a three-dimensional structure with coordinatively unsaturated Cu sites, which provoked us to explore its catalytic activity. We have activated the compound using the thermal activation method (Figures S9 and S10). With this, we have carried out the reaction between ethyl acetoacetate and benzyl amine under solvent-free conditions at room temperature (Table 1, entry 1). We have explored the scope of different substrates for this condensation reactions under the same reaction conditions (Table 1). In these cases, the reaction with ethyl acetoacetate and different types of amines have produced the high yields of  $\beta$ enaminoesters. Also, we have observed the efficient chemoselectivity in all of these reactions.

The nucleophilic reaction was observed between amine with the ketone part of the  $\beta$ -ketoesters. As no corresponding amide product was observed, this ruled out the possibility of the reaction with the ester part. Toward the examination of the catalyst role, we have done the control experiment without catalyst, and the result showed that no product was formed. This proved that the catalyst activated the carbonyl group and produced the desired product. To prove the heterogeneity of the reaction, we have carried out by filtering the catalyst after 30 min and then stirred the filtrate for another 2 h. The result showed that no  $\beta$ -ketoester was formed after filtration, which confirms the heterogeneous mechanism of the reaction (Figure S11). We have carried out the recyclability test for this catalyst,





and it showed that the catalyst can be used up to three cycles without losing any crystallinity (Figures S12 and S13). The Lewis acidic behavior of the Cu(II) center is responsible for the possible mechanistic pathway for this enamination reaction. We have compared this result with standard catalysts (Table S6). These standard catalysts are homogeneous in nature, but the present catalyst exhibits the heterogeneous behavior.

Recently, it has been reported that various copper-based MOFs or CPs were observed as prominent catalysts for azide– alkyne Huisgen cycloaddition reactions ("click" reaction).<sup>49</sup> To do this, we have carried out the reaction between an alkyne and azide under solvent-free conditions using the compound **2** as a catalyst at room temperature (Scheme 1). The results showed that benzyl azide completely converted in 6 h and produced only one product, a 1,4-substituted triazole. Corma and co-





workers have shown that, instead of Cu (I), the active Cu (II) metal center in the MOF also followed the same pathway as proposed by Sharpless (Scheme S1 in ref 49). On the basis of this mechanism, the formation of the Cu (II) acetylide species would be the reactive intermediate for the forward reaction. We also proved this by carrying out the "click" reaction by varying the initial concentrations of phenylacetylene. The experimental results have shown that, while increasing of the phenylacetylene concentration, there is a decrease in induction period (Figure 3). We also carried out the same reaction, at the constant



**Figure 3.** Cycloaddition reactions were performed at various concentrations (1, 3, and 5 equiv) of phenylacetylene compared to the benzyl azide at different time intervals. (The catalyst used in the reaction was 5 mol % based on the concentration of benzyl azide.)

concentration of phenylacetylene by varying the concentration of azide, and the results have shown that the induction period was practically negligible (Figure S14).

These results supported the same reaction mechanism where Cu(II)-phenylacetylide is the reactive intermediate, which was proposed by Corma and co-workers.<sup>49</sup> The recyclability test showed that the catalyst was active up to the third cycle without losing any catalytic activity and crystanillity (Figures S15 and S16). We have performed a leaching test, and the result shows that no metal was present in the filtrate (Figure S17).

In conclusion, we have synthesized two copper-based coordination polymers 1 and 2, respectively, using different synthetic techniques like solvent diffusion and solvothermal method. Compound 1 crystallizes in a centrosymmetric space group and adopts a one-dimensional wirelike structure with a pendent -COO<sup>-</sup> moiety. Compound 2 has the chiral space group and adopts a three-dimensional structure. The bonding mode of the ligands and metal ion creates a  $6_5$  screw axis, which contributes toward the helicity of the structure. On the basis of CD spectra, it was proved that the compound is enantioenriched. We have carried out the structural transformation from the achiral to chiral one using solid-state grinding, followed by the solvothermal method. We have explored the catalytic behavior of 2 in regio- and chemoselective enamination reaction and azide-alkyne Huisgen cycloaddition reaction with higher yields under solvent-free conditions.

# ASSOCIATED CONTENT

# **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b01836.

Details of the catalytic reactions, NMR data for new substrates and catalytic products, crystallographic data, bond lengths, TOPOS data and figures, all the characterization data, and additional data for catalytic activities (PDF)

Crystallographic data for 1 and 2 (CIF)

# AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: sukhendu@iisertvm.ac.in.

#### ORCID <sup>©</sup>

Sukhendu Mandal: 0000-0002-4725-8418

#### Notes

The authors declare no competing financial interest.

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