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Zinc(II) and Copper(II) Complexes of 4-Styrylpyridine and 1-Adamantanecarboxylic Acid: Syntheses, Crystal Structures, and Photopolymerization

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Abstract: A combination of 4-styrylpyridine (spy) and 1-adamantanecarboxylic acid (Hadc) was employed in the assembly reactions with Zn(II) and Cu(II) nitrates. The photoreactivity of the products was compared and discussed on the basis of the structure–function relationship. Zinc(II) complex **1** is a trinuclear species of type $[Zn_3(spy)_2(ad c)_6]$ in which three zinc(II) atoms are linearly arranged, with two adjacent zinc(II) atoms linked by three bridging carboxylates. Two spy ligands occupy both terminal positions, yielding the overall structure of a six-bladed windmill. Copper(II) complex **2**, $[Cu(spy)_2(ad c)_2][Cu_2(spy)_2(ad c)_4] \cdot 2DMF$, is an inorganic cocrystal comprising a mononuclear complex with a *trans* square planar geometry and a dinuclear complex with a paddle-wheel structure. In the photoreaction experiments characterized by 1H NMR spectroscopy, the zinc(II) complex was found to be photoinert, while the copper(II) complex was photoreactive to form a cyclobutene ring via the [2+2] photodimerization between two spy ligands, resulting in the preparation of a one-dimensional chain as a coordination polymer. The separations of the C=C bond pair obtained from the crystal structures for both products also support their photoreactivity. For example, the spy ligands from two adjacent monocopper(II) complexes are aligned in a head-to-tail manner with the separation of 3.899 Å between the C=C bond pair, satisfying the so-called Schmidt criteria (<4.2 Å). However, no other products satisfy this condition.

Keywords: copper(II); zinc(II); metal complexes; olefin; photocycloaddition reaction; dimerization



Citation: Lee, D.H.; An, J.; Oh, J.; Park, I.-H. Zinc(II) and Copper(II) Complexes of 4-Styrylpyridine and 1-Adamantanecarboxylic Acid: Syntheses, Crystal Structures, and Photopolymerization. *Crystals* **2023**, *13*, 1226. <https://doi.org/10.3390/cryst13081226>

Academic Editors: Jesús Sanmartín-Matalobos, Helmut Cölfen, Shujun Zhang, Heike Lorenz and Sławomir Grabowski

Received: 17 July 2023
Revised: 1 August 2023
Accepted: 7 August 2023
Published: 9 August 2023



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1. Introduction

The [2+2] photocycloaddition reactions of organic compounds in the solid state have been studied for a long time because such a solvent-free approach has been recognized as environmental-friendly benign and green chemistry with sustainability [1–4]. Engineering the crystal packing structure to align the C=C bond pairs as an olefin, however, has been a major hurdle to overcome [4–6]. Crystal engineering has been an attractive alternative to improve such an issue and the so-called Schmidt criteria (separation between C=C bonds < 4.2 Å) provide a casual guideline in predicting or evaluating the possibility of photocycloaddition reactions [7,8]. Based on these backgrounds and the recent demands for porous functional materials, related studies not only on organic compounds but also on discrete metal complexes and metal-organic frameworks (MOFs) have been actively conducted [9–14]. The formation and deformation of the coordination polyhedral of the complexes are rarely studied in a single-crystal to single-crystal (SCSC) manner [6,15].

Practically, [2+2] cycloaddition reaction is a facile network tool performing dimensional changes of coordination polymers, mainly low to high (e.g., 1D→2D or 2D→3D) [16–21]. In this sense, metal complexes with a discrete form also can be manipulated into networks by utilizing supramolecular interactions, including photocycloaddition reactions [10–12,14,22]. In other words, the conversion of monomeric complexes to polymeric form (e.g., 1D) could

open up the possibility of amplified performance and processability [14,22]. Networking of monomeric metal complexes using external stimuli, including [2+2] cycloaddition reaction, is generally less common, probably due to their intrinsic limitations, such as shapes and non-active sites [10,12]. We have interested in the photoreactive monomeric metal complexes, which can be used for networking to construct 1D polymeric species [23,24]. From our interest in this concept, we have been considering mixed ligand systems, including a neutral olefin and an anionic ligand, rather than a single ligand system because of a wealth of structural arrangement. Especially, solid-state [2+2] photocycloaddition reactions in complexes containing the 4-styrylpyridine and carboxylate ligand combinations previously were reported [17,25,26].

In this work, as a part of our ongoing study for solid-state photocycloaddition reactions, we have employed 4-styrylpyridine (spy) and 1-adamantanecarboxylic acid (Hadc) to prepare photoreactive complexes in a discrete form (Figure 1). During the course of our investigation of the zinc(II) complex, it was found to be photoinert. When the zinc(II) was replaced by copper(II) in complexation, photoreaction readily occurred, yielding a 1D network via the confirmation of a photo-induced cyclobutene derivative, 1,3-bis(4'-pyridyl)-2,4-bis(phenyl)cyclobutene (*rcftt*-ppcb), by ^1H -NMR. We have shown that the spy ligands are aligned in a head-to-tail manner [27,28] in the copper(II) complex from the crystal structure, which meets Schmidt's criteria (*vide infra*) [7,29].

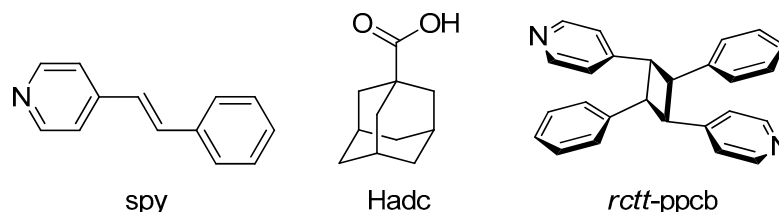


Figure 1. Chemical structures of spy, Hadc, and *rcftt*-ppcb.

2. Materials and Methods

2.1. Materials and Characterizations

All chemicals were purchased from commercial sources and used as received ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from TCI Chemicals (Tokyo, Japan); and $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ from Alfa Aesar (Haverhill, MA, USA); 1-Adamantanecarboxylic acid from Sigma-Aldrich (St. Louis, MO, USA)).

All solvents used were of reagent grade. The spy ligand was synthesized by the reported procedure [30–32]. Elemental analyses were carried out on a LECO CHNS-932 elemental analyzer. The FT-IR spectra were recorded using Varian 640-IR FT-IR Spectrometer with KBr pellets. NMR spectra were recorded using a Bruker DRX 300 spectrometer. The UV irradiation experiments were conducted using a LUZCHEM UV reactor equipped with an 8 W dark-blue phosphor lamp emitting light in the range of 300 to 400 nm, along with an Xe lamp.

2.2. Preparation of $[\text{Zn}_3(\text{spy})_2(\text{adc})_6]$ (1)

A solvothermal reaction of spy (15.2 mg, 0.084 mmol) with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (25.0 mg, 0.084 mmol) in the presence of Hadc (30.3 mg, 0.168 mmol) at 393 K in a mixture of DMF (2.0 mL) and water (1 mL) for 48 h afforded a colorless block crystalline product 1 suitable for X-ray analysis were obtained. Yield 34% (based on Hadc). Anal. Calcd $[\text{C}_{92}\text{H}_{112}\text{N}_2\text{O}_{12}\text{Zn}_3]$: C, 67.62; H, 6.91; N, 1.71. Found: C, 67.45; H, 6.97; N, 1.59. IR (KBr pellet, cm^{-1}) 2911, 2853, 2345, 1609, 1582, 1531, 1428, 1311, 1033, 827, 761, 673, 615, 552, and 487.

2.3. Preparation of $[\text{Cu}_2(\text{spy})_2(\text{adc})_4][\text{Cu}(\text{spy})_2(\text{adc})_2] \cdot 2\text{DMF}$ (2)

A solvothermal reaction of spy (15.2 mg, 0.084 mmol) with $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (15.8 mg, 0.084 mmol) in the presence of Hadc (30.3 mg, 0.168 mmol) at 393 K in a mixture of DMF (2.0 mL) and water (1 mL) for 3 days afforded a dark green block crystalline product 2 suitable for X-ray analysis. Yield 25% (based on Hadc). Anal. Calcd $[\text{C}_{121}\text{H}_{141}\text{Cu}_3\text{N}_5\text{O}_{13}]$ as $[\text{Cu}_2(\text{spy})_2(\text{adc})_4][\text{Cu}(\text{spy})_2(\text{adc})_2] \cdot \text{DMF}$ due to the DMF disorder: C, 70.41; H, 6.89; N, 3.39.

Found: C, 70.78; H, 6.72; N, 3.24. IR (KBr pellet, cm^{-1}) 2912, 2849, 2341, 1611, 1584, 1533, 1414, 1315, 1037, 822, 754, 676, 619, 556, and 489.

2.4. Preparation of $[\text{Cu}_2(\text{spy})_2(\text{adc})_4][\text{Cu}(\text{rctt-ppcb})(\text{adc})_2] \cdot 2\text{DMF}$ (**3**)

A fine powder of the **2** was packed evenly between glass slides and then irradiated under UV light for 48 h. The greenish crystals of **3** were obtained. Anal. Calcd $[\text{C}_{121}\text{H}_{141}\text{Cu}_3\text{N}_5\text{O}_{13}]$ as $[\text{Cu}_2(\text{spy})_2(\text{adc})_4][\text{Cu}(\text{spy})_2(\text{adc})_2] \cdot \text{DMF}$ due to the DMF disorder: C, 70.41; H, 6.89; N, 3.39. Found: C, 70.60; H, 6.75; N, 3.18. IR (KBr pellet, cm^{-1}) 2907, 2843, 2344, 1616, 1588, 1531, 1417, 1316, 1036, 950, 818, 753, 676, 620, 555, and 484.

2.5. X-ray Crystallographic Analysis

Crystal data for **1** and **2** at 173 K were collected on a BRUKER APEX II ULTRA diffractometer equipped with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) generated by a rotating anode. Data collection (Bruker, Billerica, US), data reduction, and absorption correction were carried out using the software package APEX2 [33]. All of the calculations for the structure determination were carried out using SHELXTL package [34]. In all cases, all nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in idealized positions and refined isotropically in a riding manner along with their respective parent atoms. Relevant crystal data collection and refinement data for the crystal structures are summarized in Table 1. In **1**, the spy ligands and carboxylate oxygen atoms of three adc ligands are disordered in two parts (spy: 87:13 and adc: 59:41; 57:43; 67:33) (Figure S1). The quality of crystal structure of **1** is poor due to the disorders but acceptable. In **2**, the adc ligands and DMF molecule are disordered in two parts (56:44 and 77:33, respectively) (Figure S2).

Table 1. Crystal and experimental data and refinement parameters of **1** and **2**.

	1	2
Formula	$\text{C}_{92}\text{H}_{112}\text{N}_2\text{O}_{12}\text{Zn}_3$	$\text{C}_{124}\text{H}_{148}\text{Cu}_3\text{N}_6\text{O}_{14}$
Formula weight	1633.94	2137.10
Temperature (K)	173(2)	173(2)
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
Z	1	1
a ($\text{\AA}$)	12.2791(3)	13.2103(11)
b ($\text{\AA}$)	12.5594(3)	13.8734(12)
c ($\text{\AA}$)	14.2650(3)	16.6325(13)
α ($^\circ$)	92.7740(10)	102.709(4)
β ($^\circ$)	115.2400(10)	111.677(4)
γ ($^\circ$)	92.8270(10)	92.990(5)
V ($\text{\AA}^3$)	1981.59(8)	2733.2(4)
D_{calc} (g/cm^3)	1.369	1.298
$2\theta_{\text{max}}$ ($^\circ$)	52.00	52.00
R_1, wR_2 [$I > 2\sigma(I)$]	0.0912, 0.2742	0.0616, 0.1499
R_1, wR_2 [all data]	0.0988, 0.2819	0.1069, 0.1716
Goodness-of-fit on F^2	1.077	1.060
No. of reflection used [$>2\sigma(I)$]	7777 [$R_{\text{int}} = 0.0347$]	10,697 [$R_{\text{int}} = 0.0850$]
Refinement	34,226	47,635

CCDC 2281724 (**1**) and 2281725 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (accessed on 17 July 2023) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

3. Results and Discussion

3.1. Preparation of Zn(II) and Cu(II) Complexes (1 and 2)

In the case of the combination of 1-adamantanecarboxylic acid with N-donor coligands, only one study of Cu(II) coordination polymers with 1-adamantanecarboxylate has been reported [35]. In the literature, a one-dimensional coordination polymer was constructed based on the endo-bidentate coordination mode of 1-adamantanecarboxylic acid with three kinds of N-donor coligands. In this study, by employing spy and Hadc, we have synthesized two complexes, and the results are summarized in Figure 2. A solvothermal reaction of spy with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the presence of Hadc at 393 K in a mixture of water and DMF solvents yielded colorless block-shaped crystals 1. When the same synthetic procedure was repeated except for employing $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ instead of the Zn(II) salt afforded a dark green single crystalline complex 2. Single-crystal X-ray (SC-XRD) analysis reveals that both 1 and 2 feature discrete type complexes, but their structures are certainly different. Moreover, they showed different photoreactivity under UV irradiation (*vide infra*).

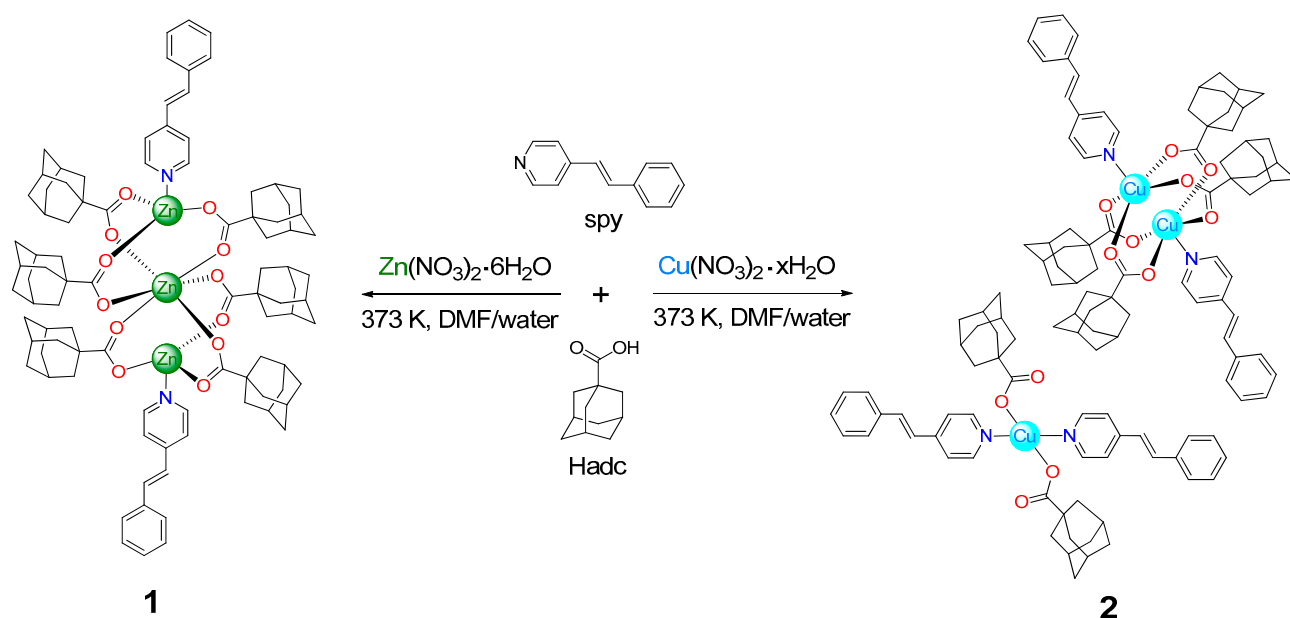


Figure 2. Solvothermal synthesis of Zn(II) (1) and Cu(II) (2) complexes.

3.2. Structural Description of the Zn(II) Complex (1)

The SC-XRD analysis reveals that the zinc(II) product 1 is a trinuclear complex of type $[\text{Zn}_3(\text{spy})_2(\text{adc})_6]$, which crystallizes in the $P-1$ space group with $Z = 1$ (Figure 3). A half formula unit is the asymmetric unit. Since 1 has a 2-fold axis, there are two crystallographically different zinc(II) atoms (Zn1 and Zn2). In 1, three zinc(II) atoms are linearly arranged, with two adjacent zinc(II) atoms (e.g., Zn1 and Zn2) linked by three bridging carboxylates from different adc ligands via Zn–O bonds [1.92(3)–2.306(7) Å] (Figure 3a). Thus, the Zn2 atom in the middle is surrounded by six oxygens adopting an octahedral geometry, while the Zn1 atom is four coordinated with one N atom from spy ligand [Zn1–N 2.099(3) Å] occupying the remaining site adopting a tetrahedral geometry (Figure 3b). The separation of Zn1...Zn2 is 3.710 Å. The three adc ligands linking Zn1 and Zn2, and the other three ads ligands linking Zn2 and Zn1A are arranged in a staggered conformation to minimize the steric hindrance between large adamantane units. Thus, the overall structure of 1 resembles a six-bladed windmill (Figure 3c). In the single molecule, two spy ligands occupy both terminal positions along the three Zn axis to form a backbone. The spy ligands and adc ligands are disordered.

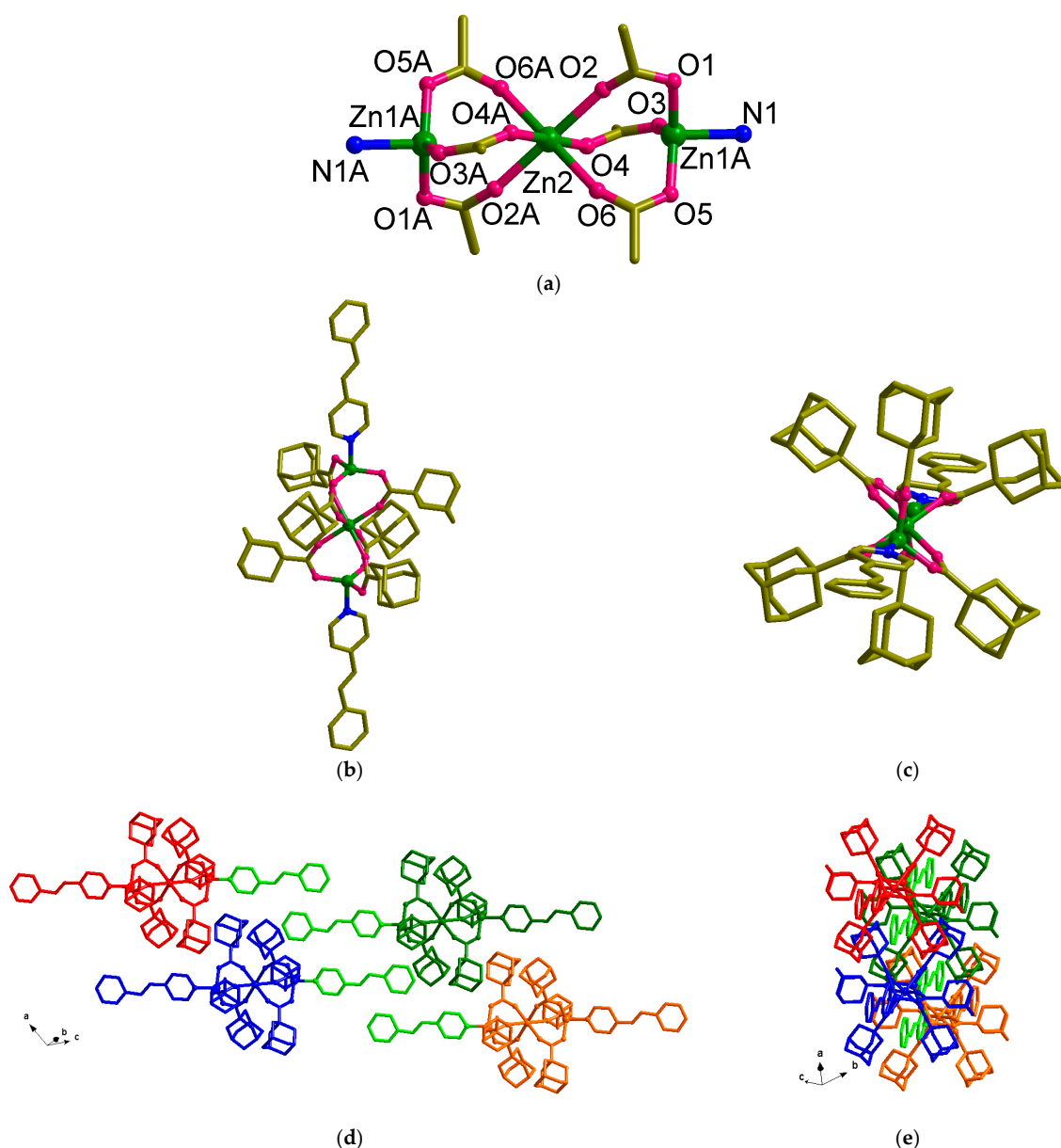


Figure 3. Structure of $[\text{Zn}_3(\text{spy})_2(\text{adC})_6]$ (**1**). (a) Core coordination unit showing a linear–trinuclear arrangement. (b) General view. (c) Top view showing a six-bladed windmill structure. (d,e) Packing structures. The hydrogen atoms are omitted.

It could be worth describing the distance between two neighboring pairs of C=C bonds. In packing, the backbones of the molecules are aligned in a parallel direction, and adamantane terminals interdigitate and interact with each other (Figure 3d,e). The separation between the C=C bond pair is 6.126 Å, which looks too far to be photoreactive. The unit cell volume of **1** calculated using PLATON is 1981.6 Å³ [36].

3.3. Structural Description of the Cu(II) Complex (**2**)

Interestingly, copper(II) complex **2** is an inorganic cocrystal that contains two neutral-charged components: a mononuclear complex and a dinuclear complex with the overall formula being $[\text{Cu}(\text{spy})_2(\text{adC})_2][\text{Cu}_2(\text{spy})_2(\text{adC})_4] \cdot 2\text{DMF}$ (Figure 4a). Complex **2** crystallizes in the *P*-1 with *Z* = 1 (Table 1). Cocrystals are single-phase crystalline structures that consist of two or more distinct ionic or molecular compounds in a specific stoichiometry [37–41]. Inorganic cocrystals are relatively rare compared to organic cocrystals which are very important in the pharmaceutical industry [42–44].

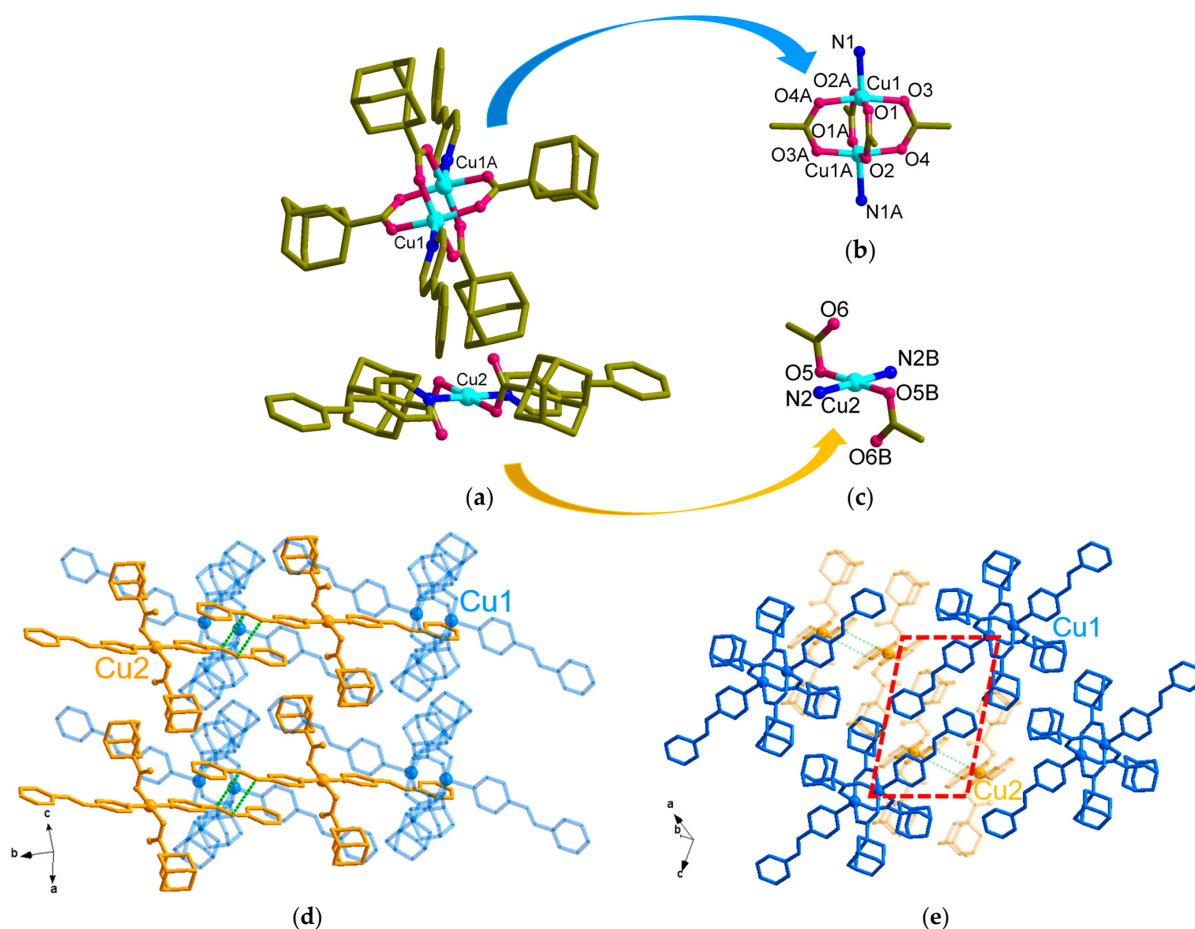


Figure 4. Structure of $[\text{Cu}_2(\text{spy})_2(\text{adC})_4][\text{Cu}(\text{spy})_2(\text{adC})_2] \cdot 2\text{DMF}$ (**2**). (a) A general view of the cocrystal showing two separated components [(top) binuclear complex and (bottom) mononuclear complex]. (b) The paddle-wheel core in the binuclear complex. (c) Core coordination unit in the mononuclear complex. (d) The local packing structure emphasizing the mononuclear complex (the distance between C=C bond pair; 3.899 Å, see green dashed lines). (e) The local packing emphasizing the binuclear complex (the distance between two neighboring pairs of C=C bond; 5.34 Å). The hydrogen atoms are omitted.

In the binuclear complex, two copper(II) atoms (Cu1 and Cu1A) are linked by four bridging carboxylates from four different spy ligands comprising a paddle-wheel core with a separation of 2.616 Å between two coppers (Figure 4b). The copper(II) center in **2** is five coordinated, being bound to four oxygen atoms via Cu–O bonds [1.961(3)–1.964(3) Å] to generate a square plane. The apical position is occupied by one spy ligand yielding a square pyramidal geometry. In the mononuclear complex, the copper(II) center is four coordinated being bound to two spy ligands and two monodentate carboxylates, resulting in a *trans* square planar geometry (Figure 4c). In packing, the mononuclear complex shows more efficiently packed probably due to its planar conformation (Figure 4d) than the binuclear complex with a spherical shape (Figure 4e). In the local packing structure for the mononuclear complexes, for example, it is found that the separation between the C=C bond pair is 3.899 Å via the intermolecular π – π interaction in a head-to-tail manner (Figure 4d). While the separation between the C=C bond pair for the binuclear complexes is much longer (5.34 Å, Figure 4e). A detailed photoreactivity based on the structure–function relationship is discussed in the following section. The spy and adC ligands are disordered. The total potential void volume of **2** checked using PLATON is 66 Å³, which corresponds to 2.4% of the total volume, and the unit cell volume is 2733.2 Å³ [36].

3.4. Photoreactivity of Complexes 1 and 2

The photoreactivity of complexes 1 and 2 was investigated in the powdered form using UV light mixing at wavelengths of 350 nm and 254 nm with the LUZCHEM setup. First, zinc(II) complex 1 was found to be photoinert. This result is undoubtedly attributed to the distance between two neighboring pairs of C=C bond (6.126 Å) in 1, which is much longer than Schmidt's criteria.

Unlike 1, Cu(II) complex 2 was found to be photoreactive via ^1H NMR spectroscopy. The solid-state crystalline 3 obtained after exposing UV irradiation for 48 h was dissolved in $\text{DMSO-}d_6$ with a small drop of nitric acid. The solubility changes of the samples seem to be associated with the photopolymerization discussed in the later part (*vide infra*). The ^1H NMR spectrum of 3 shows the decreased area of an olefin peaks at 7.55 and 8.01 ppm, and the appearance of cyclobutene peaks at 4.96 ppm, showing the 1:1 ratio between free spy and *rctt*-ppcb (Figure S4). This result indicates that half of the spy ligands in 2 underwent a structural transformation to *rctt*-ppcb.

As mentioned, complex 2, $[\text{Cu}_2(\text{spy})_2(\text{adc})_4][\text{Cu}(\text{spy})_2(\text{adc})_2] \cdot 2\text{DMF}$, consists of two components: a mononuclear complex and a binuclear complex in a 1:1 ratio (Figure 4). Notably, the spy ligands in the adjacent mononuclear complexes are aligned in a head-to-tail manner with a distance of 3.899 Å between the C=C bond pair, satisfying Schmidt's criteria (Figure 5) [7,29]. Considering the proper distance between the C=C bond pair and spy content ratio (50%) of the mononuclear complex part in 2, the ^1H NMR data indicate that the [2+2] photocycloaddition reaction for the mononuclear part occurred quantitatively. Consequently, the mononuclear complex in 2 underwent intermolecular [2+2] photocycloaddition reaction to perform a dimerization quantitatively, resulting in the preparation of 1D coordination polymer 3. In the IR data, it was difficult to find a significant difference in the vibrational modes of molecules for the cycloaddition reaction.

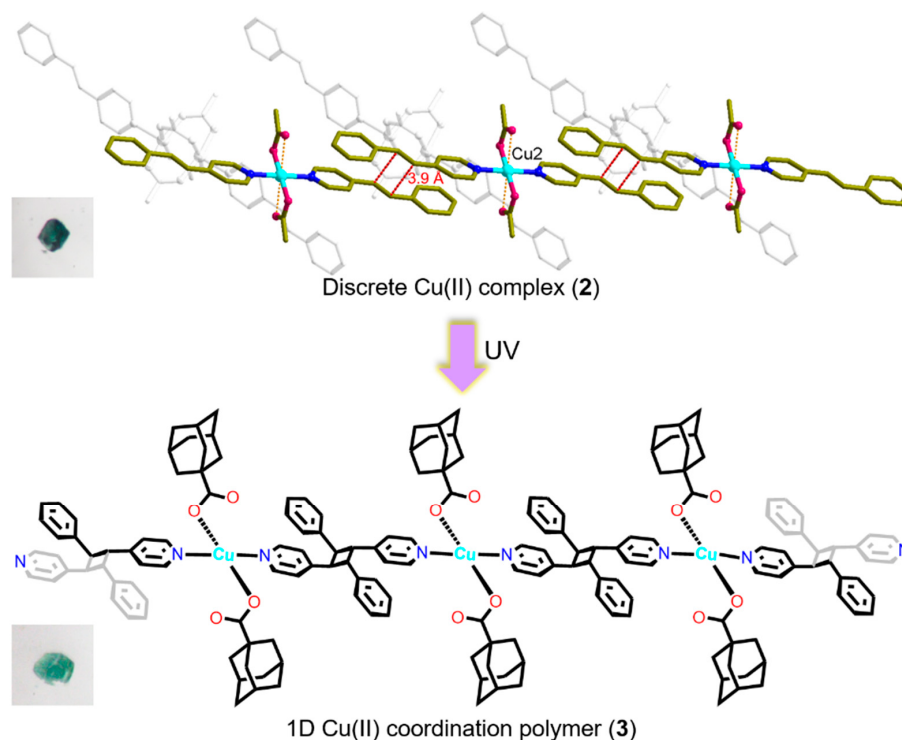


Figure 5. Structural conversion of the mononuclear complex part in 2 to one-dimensional coordination polymer 3 via the solid-state [2+2] photocycloaddition reaction (Some components are not shown for clarity).

4. Conclusions

In summary, employing a mixed ligand system including 4-styrylpyridine (spy) and 1-adamantanecarboxylic acid (Hadc) was successful to prepare Zn(II) and Cu(II) complexes in a discrete form. [2+2] photocycloaddition reactions in the solid-state metal complexes containing the 4-styrylpyridine and carboxylate ligand combinations are a good approach for crystal engineering to generate a higher-dimensionalization of coordination polymers. The selection of metal ions in the monomeric complexes shows a great effect on their photoreactivity. For example, Zn(II) complex with a paddle-wheel structure was photoinactive. In the cocrystal of Cu(II) complex **2**, a mononuclear complex was photoreactive, while a binuclear complex remained photoinert. Schmidt's rule is well applied in these results because the spy ligands from two adjacent monocopper(II) complexes are aligned in a head-to-tail fashion with a distance of 3.899 Å between two neighboring pairs of C=C, while no other photoinert products satisfy this rule. A more systematic study on the preparation of monomeric complexes and how metal species affect photoreactivity are in progress.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13081226/s1>, Figure S1. Crystal structure of $[\text{Zn}_3(\text{spy})_2(\text{adc})_6]$ (**1**). The spy ligands and oxygen atoms of adc ligands are disordered; Figure S2. Crystal structure of $[\text{Cu}_2(\text{spy})_2(\text{adc})_4][\text{Cu}(\text{spy})_2(\text{adc})_2] \cdot 2\text{DMF}$ (**2**). The adc ligands and DMF molecule are disordered; Figure S3. ^1H NMR spectrum of **1** in $\text{DMSO}-d_6$ with a small drop of HNO_3 to dissolve the crystals; Figure S4. ^1H NMR spectra of (a) **2** and (b) **3** in $\text{DMSO}-d_6$ with a small drop of HNO_3 to dissolve the crystals; Table S1. Selected bond lengths (Å) and bond Angles ($^\circ$) for **1**; Table S2. Selected bond lengths (Å) and bond Angles ($^\circ$) for **2**.

Author Contributions: Conceptualization, I.-H.P.; methodology, I.-H.P.; validation, D.H.L., J.A. and J.O.; formal analysis, D.H.L., J.A., J.O. and I.-H.P.; investigation, D.H.L., J.A. and I.-H.P.; resources, I.-H.P.; data curation, D.H.L., J.A. and I.-H.P.; writing—original draft preparation, D.H.L., J.A. and I.-H.P.; writing—review and editing, J.A., J.O. and I.-H.P.; visualization, J.A. and J.O.; supervision, I.-H.P.; project administration, I.-H.P.; funding acquisition, I.-H.P. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the NRF of Korea (2021R1C1C1006765 and 2022R1A4A1022252) and COMPA (2023-23020001-11, R&D Equipment Engineer Education Program).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

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