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Single-crystal to single-crystal photochemical structure transformation of a ladder-like coordination polymer with dinuclear Zn(II) platform

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ABSTRACT

A new coordination polymer, namely $[Zn(Hnbdc)_2(bpe)]_n$ (**1**) (H_2nbdc = 3-nitrobenzene-1,2-dicarboxylic acid and bpe = 1,2-bi(4-pyridyl)ethylene), has been hydrothermally synthesized and characterized preliminarily by elemental analysis, infrared spectroscopy, thermal analysis, and X-ray diffractions. Single crystal X-ray diffraction showed that compound **1** possesses a ladder-like topology structure featuring carboxyl-bridged dinuclear Zn(II) spaced by parallel bpe coligand pairs and has the capacity of undergoing a 100% photochemical [2 + 2] cycloaddition reaction to transform into compound $[Zn(Hnbdc)_2(rctt\text{-}tpcb)]_n$ (**2**) in a single-crystal to single-crystal form. In addition, the fluorescent property of **1** was also investigated.

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Solid-state photochemical [2 + 2] cycloaddition reaction of C═C bonds in various organic compounds and metal complexes has been well studied in the past few decades [1–5]. A number of weak interactions, for example, halogen bonds [6], hydrogen bonds [7–9], and $\pi\cdots\pi$ stacks [6,10], have been used to align the C═C bonds in crystal lattice in a congenial manner for the [2 + 2] cycloaddition reactions, which normally yield stereospecific products in solid state that may be difficult to achieve in solution. However it is still very difficult to rationally design a molecule with the preconceived arrangement for the reactions, meanwhile the average polymerization degree of photochemical product is seriously influenced by various factors such as temperature, excitation wavelength, intensity and time of radiation. As a result, photochemically reactive crystals upon exposure to exterior lighting may result in dimers, polymers, isomerization, partly polymeric products, and even no photoproducts, which are highly dependent on specific radiation conditions [11–13].

Of various organic ligands, the ditopic spacer *trans*-1,2-bi(4-pyridyl) ethene (bpe) has been one of the popular choices for studying photochemical [2 + 2] cycloaddition reactions in metal complexes and coordination polymers [12–15], wherein the bpe ligands have been found in parallel arrangements within the distance required by the geometric criteria of Schmidt (less than 4.2 Å) for photochemical [2 + 2] cycloaddition reactions. Furthermore, single crystal X-ray crystallography is one and only tool currently available to characterize unequivocally the photochemical products, whereas the reports about single-crystal to single-crystal (SCSC) transformations by [2 + 2] cycloaddition reactions are still rare [5,12,16,17], as few crystals can retain the single crystalline during photochemical structure transformations. Herein, we report a ladder-like metal coordination polymer, $[Zn(Hnbdc)_2(bpe)]_n$ (**1**) (H_2nbdc = 3-nitrobenzene-1,2-bicarboxylic acid and bpe = 1,2-bi(4-pyridyl)ethylene), which displays a photochemical activity upon UV irradiation in the solid state to result in a [2 + 2] cycloaddition product $[Zn(Hnbdc)_2(rctt\text{-}tpcb)]_n$ (**2**) with the 100% *rctt*-cyclobutane isomer in a SCSC manner.

Hydrothermal reaction of a mixture of $Zn(OAc)_2 \cdot 2H_2O$, H_2nbdc, and bpe (molar ratio 1:2:1) in water at 120 °C for 4 days afforded colorless blocks of $[Zn(Hnbdc)_2(bpe)]_n$ **1** in ~85% yield [18]. Powder X-ray diffraction (PXRD) of **1** is in good agreement with the pattern simulated from the single-crystal data, implying the good phase purity (Fig. S1). IR spectra show several characteristic bands [18]. The strong absorptions at 1560–1630 and 1300–1450 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of carboxylic groups, respectively. The presence of undeprotonated carboxylic group was supported by a sharp IR peak near 1703 cm^{-1} and a broad band in the range of 2400–3000 cm^{-1}, which corresponds to the C═O and –OH stretching vibrations respectively. Thermal gravimetric analysis (TGA) shows that the structure is stable to about 260 °C and then suffers a sharp weight loss until the heating end (Fig. S2).

Single crystal X-ray analysis reveals that compound **1** crystallizes in triclinic crystal system, space group $P-1$ [19] (Table S1) and its structure features a one-dimensional infinite coordination polymer with a

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quasi-trapezoidal shape. The asymmetric unit contains one crystallographically Zn(II) ion, two $Hnbdc^-$ anions, and one bpe molecule, as shown in Fig. 1(a). The Zn(II) center is located in a triangular bipyramid geometry with the coordination sphere defined by three carboxylate O atoms from two $Hnbdc^-$ anions in the equatorial plane, leaving two apical positions occupied by two N atoms from two bpe molecules. The Zn–O bond lengths are 1.963(4), 2.011(4) and 2.024(4) Å, and two Zn–N bond lengths are 2.176(4) and 2.177(4) Å, respectively (Table S2).

The deprotonated carboxyl groups of two $Hnbdc^-$ anions adopt a bidentate-bridging and a monodentate coordination mode, respectively. Two Zn(II) neighbors are connected by two carboxyl groups forming one $[Zn_2(OCO)_2N_4O_2]$ dinuclear unit with the Zn…Zn distance of 3.8404(18) Å, as shown in Fig. 1(b). The carboxyl-bridged dinuclears are extended along the particular direction by paired bpe coligands to produce an infinite one-dimensional coordination polymer (Fig. 1(b)) with ladder-like topology. Furthermore, the presence of undeprotonated –COOH groups leads to the formation of intrachain H-bonding interactions (O(9)–H(9)···O(3): $d = 2.662(6)$ Å, $\theta = 168.2°$; and O(4)–H(4)···O(10): $d = 2.604(6)$ Å, $\theta = 154.4°$) (Fig. S3), and no H-bond interaction is observed between the chains. The entire 3D supramolecular packing is mainly consolidated by interchain $\pi \cdots \pi$ interactions between the phenyls of $Hnbdc^-$ anions with centroid distances of 3.619 and 4.040 Å and planar angles of 2.495 and 0.000°, respectively (Fig. 1(c)).

A pair of bpe coligands is approximately parallel with face to face $\pi \cdots \pi$ interactions for adjacent pyridyl rings. The centroid distance and planar angle of two adjacent pyridyl rings are 3.833 Å and 4.361°, respectively, and the distance of two C=C bonds is 3.946 Å (less than 4.2 Å). These structural features provide an opportunity to study the photochemical structural transformation in the solid state. After UV irradiation of the single crystals of **1** for 72 h, the color of the crystals changed from colorless to light yellow, but the transparency and shape of the crystals remained intact during UV irradiation, preliminarily implying a feasibility of the SCSC transformation.

The single crystal X-ray data confirmed that the olefinic bonds of bpe pairs in **1** are photoactive, which leads to the formation of $[Zn(Hnbdc)_2(rctt\text{-}tpcb)]_n$ (**2**) [18] with the 100% *rctt*-tetrakis(4-pyridyl) cyclobutane (*rctt*-tpcb) that is one of four region isomers (*rctt*, *rtct*, *rcct* and *rccc*) [4]. The coordination environment of Zn center in **2** [19] is consistent with that in **1** (Tables S1 and S2, Fig. S4), whereas the two pyridyl rings are bent towards each other with an interplanar angle of 21.862° (Fig. 2). The Zn···Zn distance within dinuclear units increases from 3.8404 Å in **1** to 4.0406 Å in **2**, and the Zn–*rctt*-tpcb–Zn distance of 13.5507 Å in **2** is slightly shorter than Zn–bpe–Zn

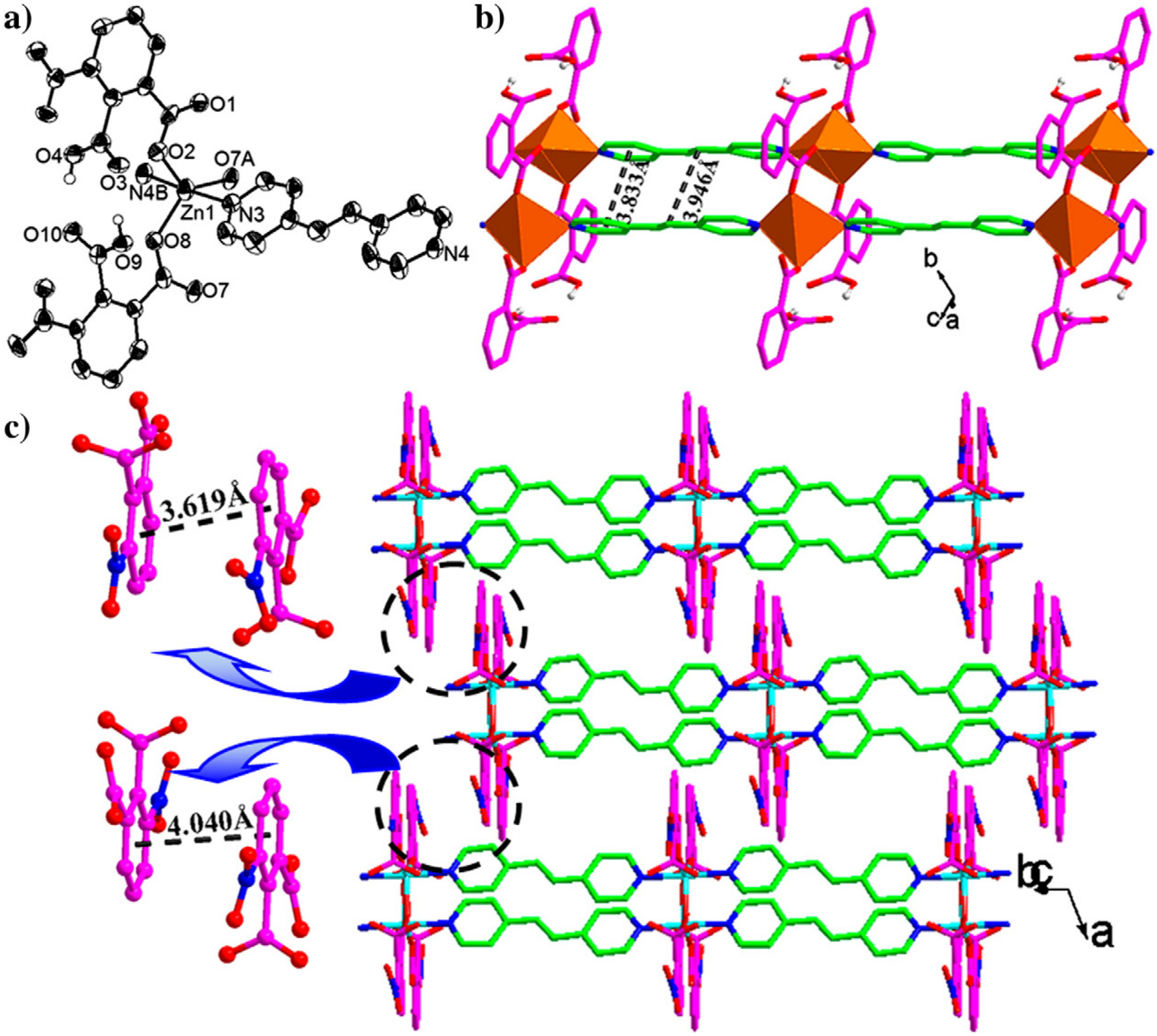

Fig. 1. (a) The ORTEP drawing of the coordination environment of the Zn center in **1**. Symmetry code: A = $-x + 1, -y + 2, -z + 1$; B = $x, y + 1, z + 1$; (b) View of the ladder-like coordination polymer with nitro groups omitted for clarity; (c) The stack of the ladders highlighting the interchain $\pi \cdots \pi$ interactions. All hydrogen atoms of carbon atoms are omitted for clarity.

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