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Two-step postsynthetic modifications of a dinuclear Zn(II) coordination compound: Investigating the stability of the coordination chromophore

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ABSTRACT

Attempted two-step postsynthetic modifications (Click reaction and recrystallization) of a dinuclear Zn(II) coordination compound $Zn_2(OOC–C_6H_4–N_3)_4(quinoline)_2$ lead to the formation of a mononuclear Zn(II) compound – $Zn(OOC–C_6H_4–C_2HN_3–COOCH_3)_2(quinoline)\cdot DMSO$. In this feasibility study, the relatively low stability of the coordination chromophore around Zn(II) in the starting material is evidenced by Hirshfeld surface analysis and results in the transformation of coordination chromophore during the postsynthetic reaction. Diffusion Ordered Spectroscopy NMR experiments confirmed that the intermediate complex $Zn(OOC–C_6H_4–C_2HN_3–COOCH_3)_2$ formed by Click reaction exists in the coordinated form in the solution phase despite the loss of the neutral ligand-quinoline. The final product $Zn(OOC–C_6H_4–C_2HN_3–COOCH_3)_2\cdot(quinoline)\cdot DMSO$ with a mononuclear crystal structure was formed by recrystallizing the intermediate with presence of quinoline.

1. Introduction

In recent years, materials scientists have explored postsynthetic modification (PSM) as a powerful approach for functionalizing coordination complexes, particularly coordination polymers, in order to enhance chemical and physical properties of these materials [1–3]. Biochemists have also used PSM as a route to facilitate chemical modifications of metal-binding proteins [4]. More interestingly, covalent reactions on coordinated forms of certain organic molecules could result in the selective introduction of substituents on the ligand, while the same reactions on free forms of ligand molecules cannot do so [5]. A number of advantages of the PSM approach as described above are often related to the stability of coordination chromophore of the starting material throughout the PSM reaction process, where the coordination chromophore is defined as the coordination environment around transition metal centers.

Our group recently reported the postsynthetic modification of a dinuclear Cu(II) coordination compound with a paddle-wheel dicopper tetracarboxylate structure and two axial ligand molecules (quinoline) [6]. In that study, the paddle–wheel dicopper(II) tetracarboxylate coordination chromophore with axial quinoline ligands remains intact throughout the Click reaction [7–9], which was evidenced by NMR and ESR results. The dicopper(II) tetracarboxylate chromophore has exhibited its robustness under diverse reaction conditions in a few newly reported cases as well [10,11]. Very recently, Stang and co-workers also reported that a class of dinuclear Pt(II) coordination complexes decorated with amine or maleimide groups can be modified via suitable postsynthesis without disrupting prismatic cores of those compounds [12]. With comparison to Cu(II) and Pt(II), some transition metals such as Zn(II), are often more "labile" due to weaker affinities between the transition metal and organic ligands [13,14]. Therefore, we were interested in investigating PSM of Zn(II) coordination systems not only for comparison purposes from our previous study and others, but also for the fact that Zn(II) containing coordination complexes include some important functional materials [15,16] and bioactive compounds [17–19] in general. In this context, $Zn_2(OOC–C_6H_4–N_3)_4(quinoline)_2$ (complex **1**) was chosen as a *proof-of-principle* compound to investigate the stability of coordination chromophores of Zn(II) coordination systems during PSM.

As a follow up to our previous work [6], current study reports on the attempted two-step PSM of $Zn_2(OOC–C_6H_4–N_3)_4(quinoline)_2$ (complex **1**) (note: complex **1** is used as the code for the starting material; **2** is the code for the intermediate compound after 1st step; **3** is the code for the final product): 1st step – formation of an intermediate compound **2** with methyl propiolate via Huisgen 1,3-dipolar cycloaddition (Click reaction); 2nd step – formation of the final product **3** by recrystallization of **2** with

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presence of quinoline. It is worth noting that several examples of Click reactions to modify metal–organic coordination complexes or organometallic species have been reported in recent years [20–23]. Single-crystal XRD, 1D, 2D NMR, and Diffusion Ordered Spectroscopy (DOSY) [24,25] NMR were used to characterize these coordination complexes in this work. In current study, DOSY and Hirshfeld Surface Analyses were particularly used to investigate the stability of coordination chromophore during PSM.

2. Experimental

2.1. Materials and methods

Zinc nitrate hexahydrate, solvents, 3-ethynylpridine and methyl propiolate were purchased from Sigma Aldrich Co. Sodium 4-ethynylbenzote was purchased from VWR international Inc, and 4-azidobenzoic acid was purchased from TCI America. Deuterated solvents were purchased from Cambridge Isotope Laboratory. All the materials were used as received, without further purification.

Single-crystal X-ray diffraction data were collected on a BRUKER SMART-APEX CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares refinement with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were generated geometrically and included in the refinement with fixed position and thermal parameters. IR spectra were recorded on an ATI Mattson Infinity series FTIR instrument. NMR experiments were recorded on either a Bruker DRX-300 with a z-gradient BBI probe or Bruker DPX-400 with a z-gradient BBO probe operating at 300.13 MHz and 400.13 MHz for ^{1}H observe respectively. DOSY spectra were acquired using the Bruker pulse program ledbpgp2s for **2**, using sinusoidal gradients with durations between 1.25 and 3.5 ms. The gradient strength was varied between 2% and 95% in 128 increments for **2**. Diffusion times of 70 to 80 ms were used for **2**. DOSY spectra were processed using the Bruker Topspin software with exponential line fitting.

Single crystal molecular graphics were generated using Accelrys MS Modeling v4.0. Hirshfeld surface graphics were generated using CRYSTALEXPLORER 2.1, (2007) University of Western Australia [34].

2.2. Synthesis of the complexes

Note: Standard personal protective equipments including safety glasses, lab coat, and gloves must be worn. Handle azide reactions behind a blast shield in the fume hood. Do not combine untreated aqueous or organic azide waste with other waste.

*$Zn_2(OOC–C_6H_4–N_3)_4(quinoline)_2$ (**1**):* 4-azidobenzoic acid (1 mmol, 163 mg) and zinc nitrate hexahydrate (0.5 mmol, 297 mg) were dissolved in 10 ml methanol, then 1 ml quinoline was added into the solution. The solution was transferred to a 20 ml glass vial which was loosely capped and allowed to stand for about a week. Colorless prismatic crystals (complex **1**) were obtained at the bottom of the vial. Crystal data: CCDC 832826, $Zn_2C_{46}O_8N_{14}H_{30}$, M = 1037.58, Triclinic, $P\bar{1}$, a = 8.3381(17) Å, b = 9.4324(19) Å, c = 15.273(3) Å, α = 80.33(3), β = 87.11(3), γ = 69.63(3). Z = 1, V = 1110.0(4) Å^3, R values: ($I > 2\sigma(I)$) R_1 = 0.0950, wR_2 = 0.2665; GOF = 0.902. Yield: 164 mg, 63.1%. IR (DMSO, 2500–1400 cm^{-1}): 2122.72, 1700.53, 1618.15, 1601.68, 1568.50, 1501.35, 1460.39 cm^{-1}. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 8.908 (d, J = 3.12 Hz), 8.37(d, J = 8.16 Hz), 8.04(s), 8.005 (d, J = 3.66 Hz), 7.96 (d, J = 8.04 Hz), 7.77 (t, J = 7.5 Hz), 7.61(t, J = 7.5 Hz), 7.54 (q, J = 4.1 Hz), 7.14 (d, J = 8.16 Hz).

*$Zn(OOC–C_6H_4–C_2HN_3–COOCH_3)_2$ (**2**):* Complex **1** (0.25 mmol, 260 mg) and 90 μl methyl propiolate (1 mmol) were suspended in 10 ml mixture solution of water and *t*-butanol (v:v = 1:1) in a round flask. Sodium ascorbate (25 mg, prepared 1 M solution in water) was added and copper (II) sulfate pentahydrate (0.1 mmol, 25 mg, prepared in water) was added sequentially while stirring. The mixture was stirred vigorously overnight. Pale yellow solid product **2** was obtained by filtration and washed with cool water and ether for several times, and then was dried under vacuum for several hours. Yield: 259 mg, 93.0%. IR (DMSO, 2500–1400 cm^{-1}) 1659.7, 1437.3, 1314.6 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.59, 8.13, 8.07, 3.9 ppm. ^{13}C NMR (DMSO-d_6, 400 MHz): δ 160.98, 140.11, 138.20, 131.45, 127.85, 120.46, 52.49 ppm.

2.2.1. Recrystallization of **2**

*$Zn(OOC–C_6H_4–C_2HN_3–COOCH_3)_2$·(quinoline)·DMSO (**3**):* 20 mg pale yellow zinc complex **2** was added in 14 ml mixture solution of methanol, quinoline and DMSO (volume ratio 9:3:2). The mixture was heated up to 90 °C until the solid was dissolved. The solution was allowed to slowly cool down to room temperature. Single crystal did not form immediately after the solution was cooled down. Pale yellow single crystals **3** were formed gradually in about one week. Crystal data: CCDC 832827, $ZnC_{33}O_9N_7SH_{29}$, M = 765.06, triclinic, $P\bar{1}$, a = 7.8535(16) Å, b = 12.429(3) Å, c = 17.564(4) Å, α = 98.68(3), β = 100.40(3), γ = 91.27(3). Z = 2, V = 1664.8(6) Å^3, R values: ($I > 2\sigma(I)$) R_1 = 0.0659, wR_2 = 0.1141; GOF = 0.928. Yield: 12 mg, 43.7 % (based on Zn).

3. Results and discussion

The postsynthetic modification of complex **1** in this work includes 2 steps: (1) the formation of an intermediate (complex **2**) via Click reaction and (2) recrystallization of complex **2** to form the final product (complex **II)** with presence of quinoline (anicllary ligand). The two-step PSM process is schematically shown in Fig. 1.

3.1. NMR characterizations of complexes **1** and **2**

The ^{1}H spectra of methyl propiolate, complex **1**, and complex **2** are displayed in Fig. 2. Methyl propiolate was successfully 'clicked' with all the 4-azidobenzoate moieties on complex **1** to form 1-(4-carboxyphenyl)-4-methoxycarbonyl-1,2,3-triazole (L) as evidenced by the disappearance of the acetylenic proton at 4.57 ppm, the persistence of the ester methyl resonance at 3.9 ppm, and the emergence of the new triazole proton at ~9.7 ppm. The ^{1}H spectrum of **2** indicates that quinoline ligands disappeared after the reaction. The loss of quinoline may be partly related to the existence of Cu in the reaction mixture. All proton and carbon assignments in Fig. 2 were based on HSQC and HMBC NMR experiments (see Supporting information).

Complex **2** in DMSO was investigated by using Diffusion Ordered Spectroscopy NMR experiments. DOSY methods are based on pulsed-field gradient spin-echo NMR experiments. DOSY is an effective tool to analyze intermediates and to discriminate different species in solution [14,26–28]. The aligned triazole proton, phenyl proton and ester methyl proton resonances shown in ^{1}H DOSY spectra of **2** (Fig. 3a) indicate all these nuclei are from a single species in solution. These two sets of aligned triazole proton, phenyl proton and ester methyl proton resonances shown in the DOSY spectra of the mixture of free 1,4-triazole ligand and **2** (Fig. 3b) correspond to free and coordinated ligands, respectively. These aligned peaks exhibiting a faster diffusion coefficient ($\mathrm{Log}D \approx -8.15$ m^2/s) correspond to free ligand (L) and the aligned peaks exhibiting a slower diffusion coefficient ($\mathrm{Log}D \approx -8.72$ m^2/s) correspond to the coordinated ligand (L). The comparison between DOSY spectra in Fig. 3a and b clearly indicates that the intermediate compound-**2** exists in the coordinated form in solution. Although the exact molecular structure of **2** cannot be derived

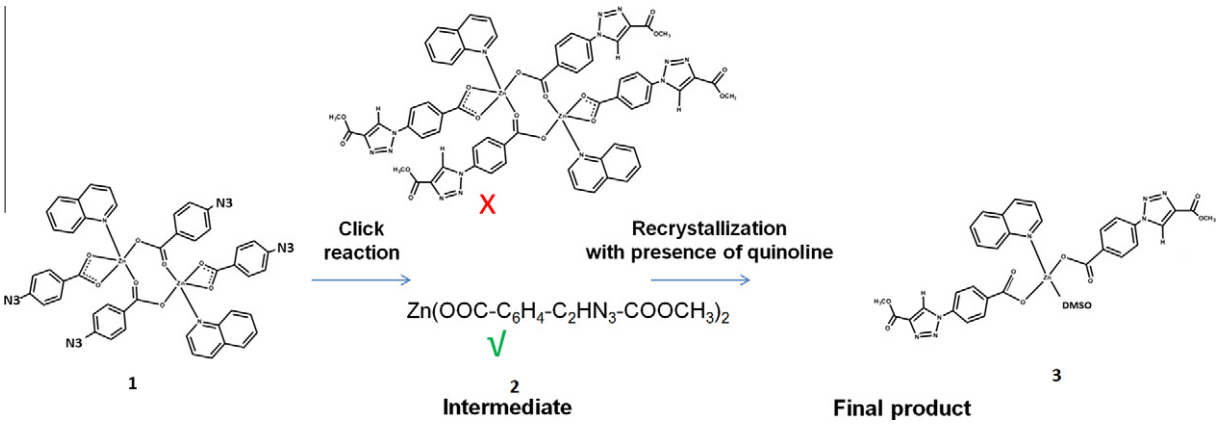

Fig. 1. Schematic illustration of the two-step PSM process.

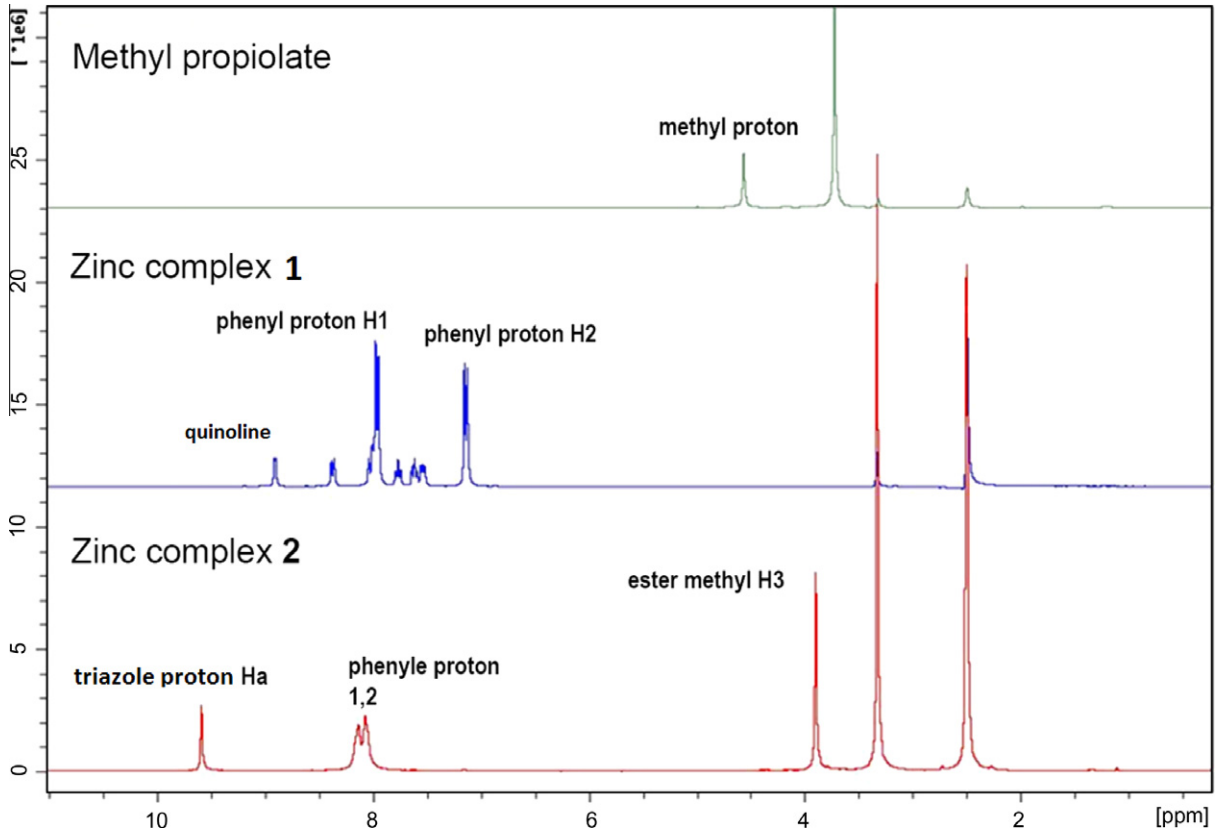

Fig. 2. ^{1}H spectra of methyl propiolate (top), complex **1** (middle), and complex **2** (bottom).

from our NMR data, it is apparent that coordination chromophore of complex **1** was disrupted with the loss of quinoline ligand over Click reaction.

3.2. Crystal structures and Hirshfeld surface analyses

The coordination geometry of zinc(II) in complex **1** is a distorted tetrahedron. Bond length results (Å) around Zn(II) in complex **1** are as follows: (two closely coordinated Zn–O bonds: Zn1–O1 1.979(6); Zn1–O3 1.938(7)); Zn–O (the carbonyl in the neighboring structure unit) bond: Zn1–O4 2.023(6); (Zn-quinoline bond) Zn1–N1 2.030(7). As shown in Fig. 4, complex **1** is a weakly bound dimer in which the carbonyl from an adjacent structure unit binds to the zinc (Zn1–O4 bond length 2.023(6) Å). The dimeric unit of complex **1** crystallises on an inversion center. The four azide groups at peripheral positions of complex **1** provide reactive sites to further decorate this coordination compound. The final product – complex **3** after Click reaction and recrystallization processes has a mononuclear crystal structure with Zn(II) surrounded by two carboxylate groups, one quinoline and one DMSO. The coordination geometry of **3** can be described as a distorted tetrahedron as well (Fig. 5). To further identify and understand the coordination chromophore around Zn(II) in the crystal, we have performed Hirshfeld surface analysis by selecting Zn(II) and its adjacent atoms in crystal structures for both the starting material (complex **1**) and the final product (complex **3**). The Hirshfeld surface [29] defines the volume of space where the promolecule electron density exceeds that from all neighboring molecules, and Hirshfeld surface analysis has

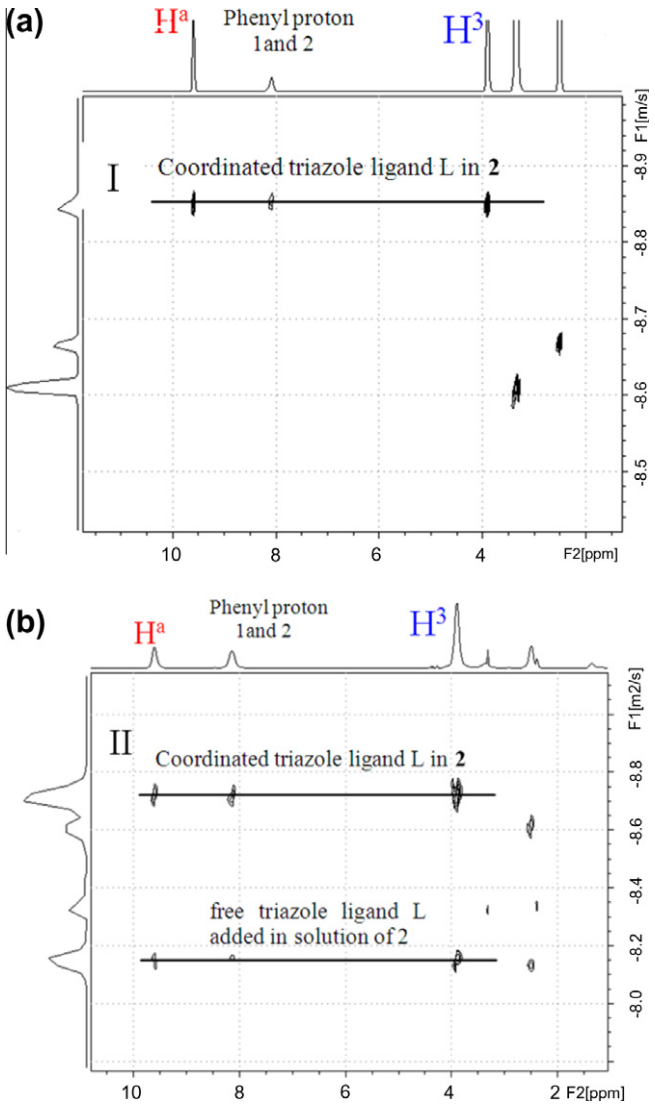

Fig. 3. (a) ^{1}H DOSY spectrum of complex **2** and (b) ^{1}H DOSY spectrum of mixture of complex **2** and free L–H.

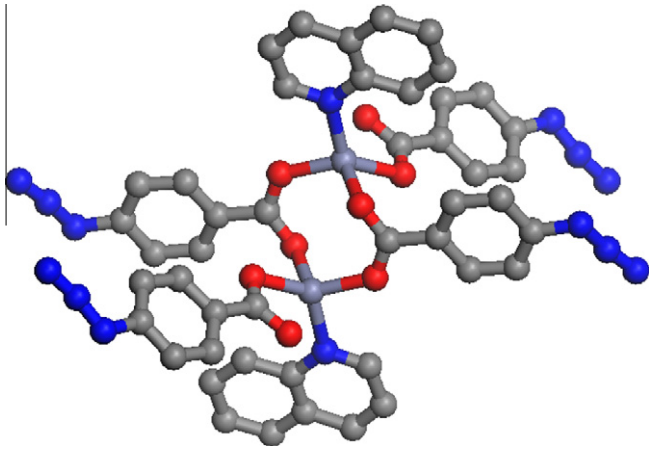

Fig. 4. The single crystal structure of complex **1** showing a dimeric structure unit.

proved to be a powerful approach to study intermolecular interactions by visualization [30–32]. It is interesting that Hirshfeld

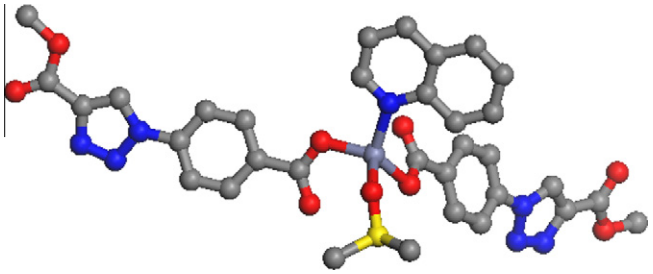

Fig. 5. The single crystal structure of complex **3** showing a mononuclear structure unit.

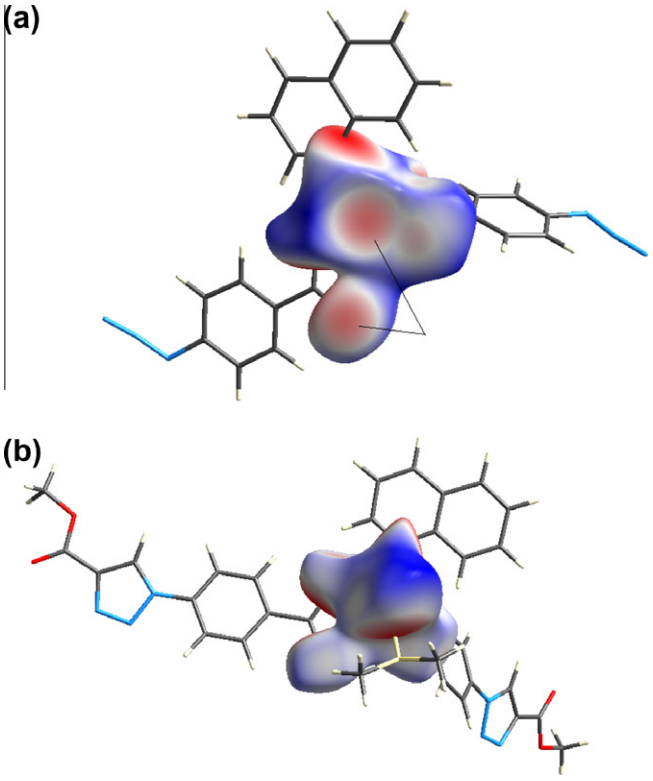

Fig. 6. (a) The Hirshfeld Surface of the coordination chromophore around Zn(II) in complex **1**; (b) The Hirshfeld Surface of the coordination chromophore around Zn(II) in complex **3**.

surface analysis can also provide insightful supporting information to evaluate the stability of coordination chromophores in this case. Hirshfeld surface of the coordination chromophore of complex **1** shows two red circles (highlighted in Fig. 6a) which correspond to close contacts between a Zn(II) center and the carbonyl in the neighboring structure unit, based on which the dimer of complex **1** is constructed. The relatively faint red color of these two circles in Fig. 6a implies the weak interaction between neighboring mononuclear Zn(II) structural units. This is also consistent with the relatively long bond length between Zn1 and O4. The Hirshfeld surface analysis of the coordination chromophore of complex **3** shows no other close contacts around Zn(II) except atoms within the mononuclear four-coordinated coordination chromophore, Fig. 6b. Therefore, it is unsurprising that the original coordination chromophore of complex **1** was not retained throughout the PSM process. The coordination environment around Zn(II) transformed from weakly bound dimeric chromophore in complex **1** to a tightly bound mononuclear chromophore in complex **3**.

Based on the single crystal structure analysis, the coordination chromophore of complex **1** involves anionic carboxylic ligands and neutral quinoline ligands around Zn(II) centers. It was determined by NMR spectra that the dinculear Zn(II) compound- complex **1** was not able to retain its coordination chromophore over Click reaction with the loss of quinoline ligand. And recrystallization of the intermediate compound **2** with presence of quinoline formed a mononuclear Zn(II) compound. Quinoline was used for recrystallization as an attempt to restore the original coordination chromophore around Zn(II) in complex **1**, because quinoline is an ancilliary ligand existing in the structure of complex **1**. Single crystal structure analysis of the recrystallized product **3** reveals that the final product possesses a different coordination chromophore from complex **1**. The Hirshfeld surface analysis of complex **1** indicates the weak interaction between a Zn(II) center and the carbonyl in the neighboring structure unit, which partly explains the disruption of coordination chromophore during the PSM process.

4. Conclusions

In summary, methyl propiolate was successfully linked to azide reactive sites in complex **1**- $Zn_2(OOC–C_6H_4–N_3)_4(quinoline)_2$ and 1,4-regioisomer was formed. With comparisons to $Cu_2(OOC–C_6H_4–N_3)_4(quinoline)_2$, complex **1** lost the axial ligand-quinoline during Click reaction. In addition, the coordination chromophore of complex **1** was disrupted during the two-step PSM by forming a mononuclear Zn(II) coordination species- complex **3**. DOSY spectra suggest that carboxylate ligands remain attached to Zn(II) in solution. Hirshfeld surface analysis of complex **1** indicates that the interaction between the paired Zn(II) coordination structure units is weak and therefore leads to the cleavage of the dimeric structure during postsynthetic modifications.

PSM, as described in the introduction, is not only an alternative approach for traditional one-pot synthesis to synthesize new coordination species, but also provides utilitarian advantages in terms of material properties and/or synthetic routes compared to free forms of ligand molecules [33]. It is also clear that PSM of coordination complexes has become a topical area in supramolecular chemistry and crystal engineering with growing attention [12,20]. Current study indicates that the coordination chromophore for a coordination compound could undergo transformation during the PSM process depending on binding strength between transition metals and ligands, namely the stability of the coordination chromophore. This work also underscores the fact that the type of transition metal, pattern of metal-ligand coordination geometry, and postsynthetic reaction conditions are all important factors which should be taken into account when designing PSM of coordination complexes.

Appendix A. Supplementary material

CCDC 832826 and 832827 contain the supplementary crystallographic data for complexes 1 and 3, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.03.031.

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