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Postsynthetic modification of a coordination compound with a paddlewheel motif via click reaction: DOSY and ESR studies

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ABSTRACT

Postsynthetic strategy based on organic coupling reactions has been explored for the synthesis of novel coordination complexes with larger dimensions. A discrete coordination species with a paddlewheel motif, dicopper(II) tetracarboxylate $Cu_2(OOC\text{-}C_6H_4\text{-}N_3)_4(quinoline)_2$ (**SBU1**), was covalently modified with methyl propiolate via "Click" reaction to generate a new coordination compound $Cu_2(OOC\text{-}C_6H_4\text{-}C_2N_3H\text{-}COOCH_3)_4\cdot(quinoline)_2$ (**1**). The combination of single-crystal X-ray diffraction, diffusion NMR and ESR has confirmed the success of covalently modifying **SBU1** and the retention of the structural integrity after the postsynthetic modification.

For decades, coordination complexes have received great attention for their utilitarian properties and interesting structures [1–9]. A variety of synthetic techniques, such as diffusion [10,11], hydro/solvo-thermal [12–14], refluxing [15,16], mechanochemistry [17,18] and direct mixing [19], have been developed to synthesize coordination complexes utilizing transition metal salts and organic ligands. Ligand-exchange reactions at the metal site have also been explored as an advanced route to construct supramolecular coordination species from relatively small coordination subunits [20–22]. Furthermore, postsynthetic modification (PSM) is an alternative approach to synthesize new coordination materials from existing coordination species while generally maintaining some structure features of starting materials such as framework topology and coordination chromophore. In the past few years, PSM of metal-organic frameworks (MOFs) has proved to be a powerful approach for functionalizing MOFs to enhance their chemical and physical properties [23–25]. Several interesting examples that concerned postsynthetic reactions of metal-organic polyhedra (MOPs) have been reported very recently as well [26,27]. PSM of discrete coordination complexes has also become a topical area in supramolecular chemistry in recent years [28–30].

PSMs of coordination complexes are usually conducted in a heterogeneous fashion due to the poor solubility of coordination complexes in conventional organic solvents [25,31]. In practice, the exploration of PSM on discrete coordination complexes often raises a number of issues: (1) the stability of coordination chromophore (including the coordination geometry of the metal site and the connection of ancillary ligands, if any) during the reaction; and (2) the structure determination of the product when it is not possible to obtain a single crystal of suitable size for data collection. In order to address such issues, we have demonstrated herein a systematic study of the covalent postsynthetic modification of a discrete Cu(II) coordination species - $Cu_2(OOCC_6H_4N_3)_4\cdot(quinoline)_2$ (**SBU1**) [note: **SBU1** is only used as the code for the starting material]. **SBU1** has a dicopper tetracarboxylate chromophore (also known as the paddlewheel motif) with 4 azide groups at the peripheral positions and 2 quinoline molecules at the axial position. We have covalently modified **SBU1** with methyl propilate to form a new coordination compound **1** via Huisgen 1, 3-dipolar cycloaddition (also known as Click reaction). Single crystal XRD, (^{1}H, ^{13}C, HSQC, HMBC and 1D DOSY) NMR, and ESR were used to characterize these coordination species [32].

Postsynthetic modification of SBU1 via Click reaction. $Cu_2(OOC\text{-}C_6H_4\text{-}N_3)_4(quinoline)_2$ (**SBU1**) [33] has a dinuclear copper(II) paddlewheel structure with 4 azide groups at the peripheral positions and 2 quinoline molecules at the axial positions (Fig. 1a, b). Two uncoordinated acetonitrile molecules exist in the crystal structure of **SBU1**$\cdot 2CH_3CN$ as guest molecules. These 4 azide groups at peripheral positions of **SBU1** provide potential for further modifying this coordination species. Coupling small organic molecules

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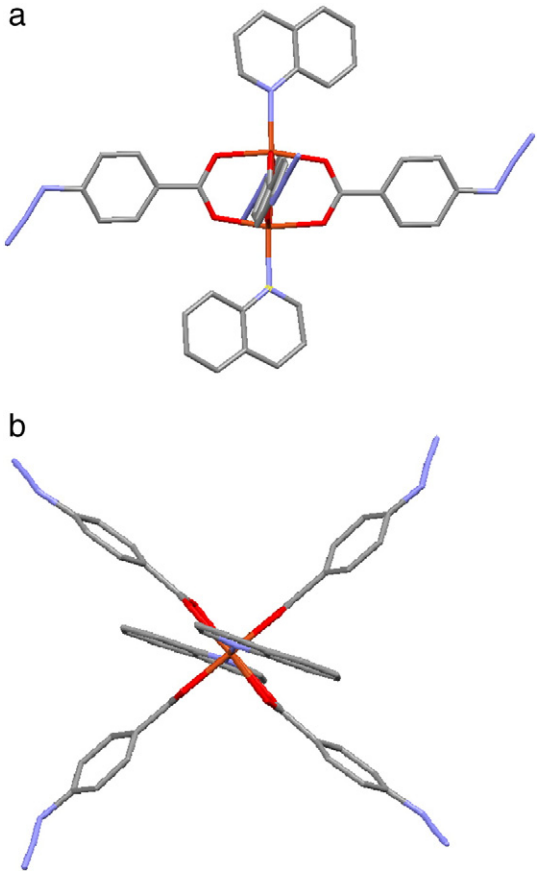


Fig. 1. (a) Molecular structure of **SBU1** derived from the single-crystal structure; (b) **SBU1** viewed along axial direction.

with discrete coordination complexes provides a simple way to modify these starting materials in terms of functionality and dimension.

In the current study, methyl propiolate was covalently linked to **SBU1** via Click reaction. Click reaction was chosen because it works at mild reaction conditions (e.g. ambient temperature) and in a variety of solvents [34,35]. It is worth noting that Click reaction has been used to modify metal-organic coordination complexes or organometallic species by a few research groups [28,36–38]. More interestingly, the formation of 1,4-regioisomer [35,39] offers a ca. 144° angle, which is critical for generating some specific geometries, such as rhombicosidodecahedron.

Green solid **1** was synthesized by coupling 4 equivalent methyl propiolate with 1 equivalent **SBU1** in THF without any catalysts [40], because certain catalyst, such as sodium ascorbate, might reduce the copper(II) in **SBU1**, thereby destroying the integrity of the paddlewheel structure. The completion of the coupling was monitored by IR spectroscopy. Disappearance of the azide peak at ca. 2122 cm^{-1} indicated the completion of the reaction.

If the coordination chromophore of **SBU1** remains intact during the Click reaction of the 4-azido-benzoate moieties with methyl propiolate, we should obtain product **1** depicted in Fig. 2. Various analytical techniques, including ^{1}H, ^{13}C, DOSY NMR, and ESR, were used to determine the structure.

NMR characterizations of SBU1 and 1. Based on the ^{1}H, COSY and HSQC NMR spectra of **SBU1** and ^{1}H spectra of free quinoline in DMSO-d6 (see Supporting Information, SI, Fig. S1-3), the 5 broadened resonances between 7 and 10 ppm observed in the ^{1}H spectrum of **SBU1** are assigned to quinoline (Fig. 3, middle). The ^{1}H NMR spectrum of **1** (Fig. 3, bottom) in DMSO-d6 confirmed that methyl propiolate was successfully Clicked on 4-azidobenzoate in **SBU1** to form 1-(4-carboxyphenyl)-4-methoxycarbonyl-1,2,3-triazole (the 1,4-triazole ligand is simplified as **L**H in this paper). Comparisons of the ^{1}H spectra of methyl propiolate (Fig. 3, top), **SBU1** and **1** clearly illustrate the disappearance of the alkyne proton at 4.57 ppm in **1**, a downfield shift

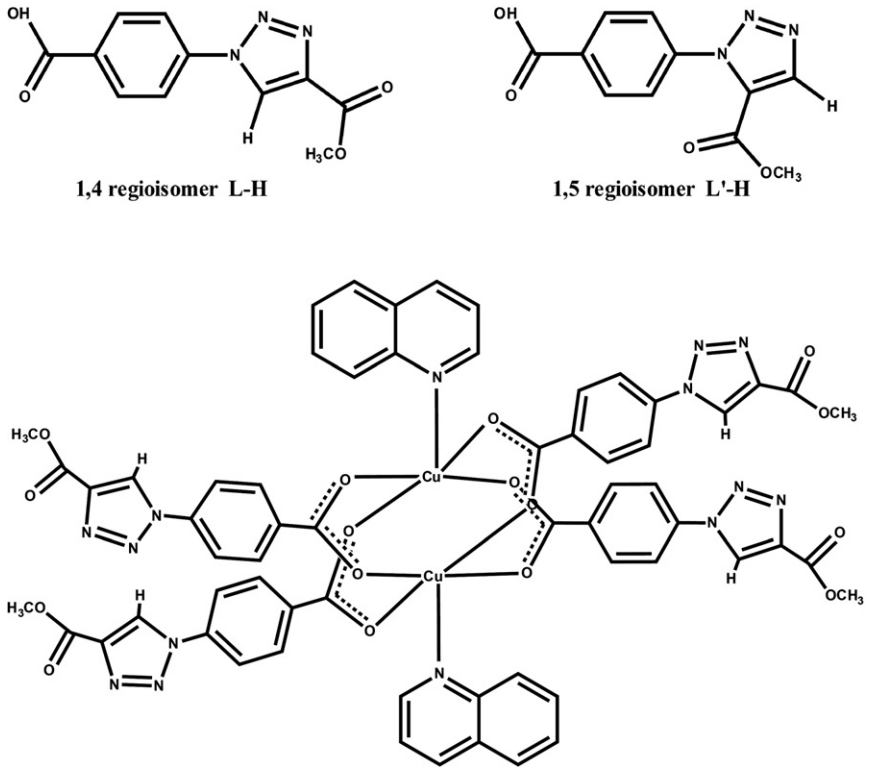
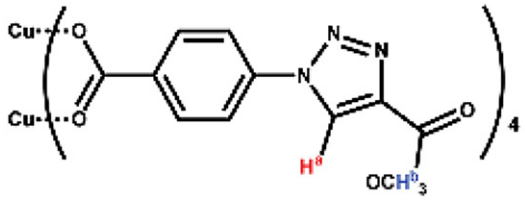


Fig. 2. Top: 1-(4-carboxyphenyl)-4-methoxycarbonyl-1,2,3-triazole (right) and 1-(4-carboxyphenyl)-5-methoxycarbonyl-1,2,3-triazole (left); Bottom: the proposed structure of **1**.
* Theoretically both 1,4-regioisomer LH and 1,5-regioisomer L'H should be present in 1. Only 1,4-regioisomer **L**H was drawn in the proposed structure for simplicity and the later on it was proved to be the real structure by experiments.



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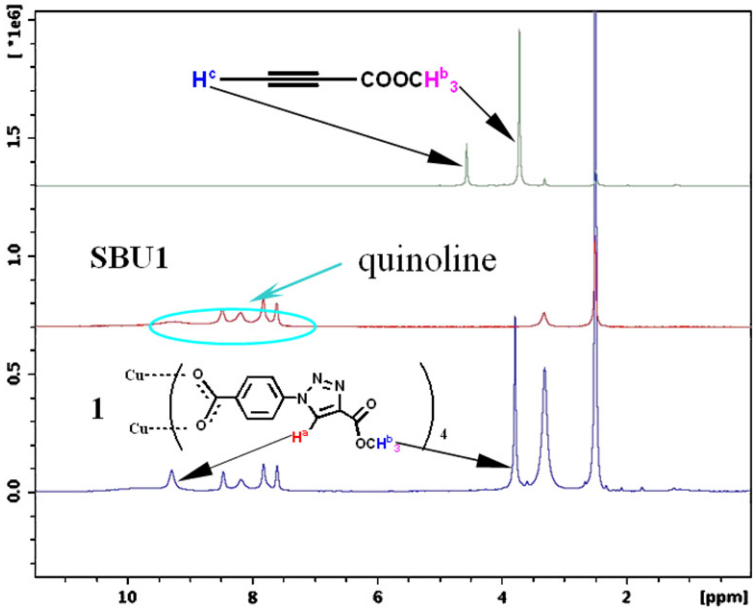

Fig. 3. ^{1}H spectra of methyl propiolate (top), **SBU1** (middle), and **1** (bottom) in DMSO-d6.

of the ester methyl protons from 3.72 ppm to 3.79 ppm, and the emergence of a new sharper peak at 9.3 ppm which lies in the expected range of triazole protons [35,41]. The integral ratio of the triazole proton peak to the ester methyl peak is 1:3, consistent with the triazole structure. The integral ratio of the new peak to the best resolved quinoline proton is 2: 1 which indicates that all 4 azide groups on **SBU1** reacted with methyl propiolate. Noteworthy in the ^{1}H spectra of **SBU1** and **1** is the absence of any resonances for the phenyl protons of the benzoate moiety. This should be attributed to the significant line broadening experienced by these protons due to fast relaxation caused by interactions of these nuclei with the unpaired electrons of paramagnetic Cu (II) center [42-45]. Resonances for the triazole/methyl ester groups could be observed, as the impact of Cu (II) diminishes with the increase of the distance from the paramagnetic center. Unexpectedly, the quinoline ligands which are closer to the paramagnetic Cu (II) center displayed sharper resonances than those of the benzoate ligands in **1**. Diffusion Ordered Spectroscopy (DOSY) [6,46–49] measurement of **1** indicated that the quinoline ligands exchanged with the solvent molecules, dimethyl sulfoxide (DMSO), because they diffused faster than the triazole resonances in the DOSY spectrum (Fig. 4a). NMR experiments conducted on free 1,4-triazole ligands synthesized by using Cu(I) catalyst, the triazole ligands extracted from **1,** and the mixture of **1** and 1,4-triazole ligands confirmed that the triazole moieties formed in **1** are 1,4 regioisomer (SI, Fig. S4–7).

In the ^{1}H DOSY spectrum of **1** in DMSO-d6 (Fig. 4a), the triazole proton H_a (9.3 ppm) and the ester methyl proton H_b (3.79 ppm) exhibit the same diffusion coefficient (LogD ≈ -8.45 m^2/s), which indicates that they are from the same species **1**. All the signals corresponding to quinoline protons were aligned and exhibited a faster diffusion coefficient (Log D ≈ -8.25 m^2/s) due to exchange with the solvent, DMSO. In this case, quinoline switches between ON and OFF state on molecule **1** and behaves more like a "free" ligand in DMSO rather than a coordinated one. Free 1,4-triazole ligand was added to the NMR sample of **1** in an effort to see both free and coordinated triazole ligands. ^{1}H DOSY spectrum (see Fig. 4b) of the mixture of free 1,4-triazole ligand and **1** shows two sets of aligned triazole ligand peaks indicating free and coordinated triazole ligands. These aligned peaks exhibiting a faster diffusion coefficient (LogD ≈ -8.32 m^2/s) correspond to free 1,4-triazole ligands, and the aligned peaks exhibiting a slower diffusion coefficient (LogD ≈ -8.45 m^2/s) correspond to coordinated 1,4-triazole ligands. The data highlight the excellent utility of diffusion ordered NMR spectroscopy for determining solution structures of coordination compounds.

ESR characterizations of SBU1 and 1. The experimental ESR spectrum of crystalline **SBU1**, as shown in Fig. 5a (blue), exhibits feature characteristic of dinuclear Cu(II) species with three peaks at 400 G (H_{z1}) ($g_1 = 16.69$), 4700 G($H_{\perp 2}$)($g_\perp = 1.41$), and 6000 G(H_{z2}) ($g_2 = 1.10$) due to the spin triplet state of the binuclear copper complex [50-54]. The spectrum can be simulated with reasonable agreement assuming large negative exchange energy (J).

In this case, the spin state energy levels may be described as a singlet ground state ($S = 0$) and an excited triplet state ($S = 1$) separated by an energy difference of 2 J [55,56]. For large J, the ESR spectrum of the triplet state can be described using an effective total spin $S = 1$ state. Fig. 5 shows the calculated spectrum (red spectrum in Fig. 5a) and the energy level diagram (Fig. 5b) for the case of large zero field spitting ($-D| > h\nu$). The parameters used to simulate the spectra are given in Table 1[57]. A small peak at 3300 G can be attributed to mononuclear Cu (II). The seven hyperfine lines evident in the z peaks at 400 G and 6000 G clearly show the interaction between two Cu(II) ($I = 3/2$) nuclei in the paddlewheel structure. The spectrum is

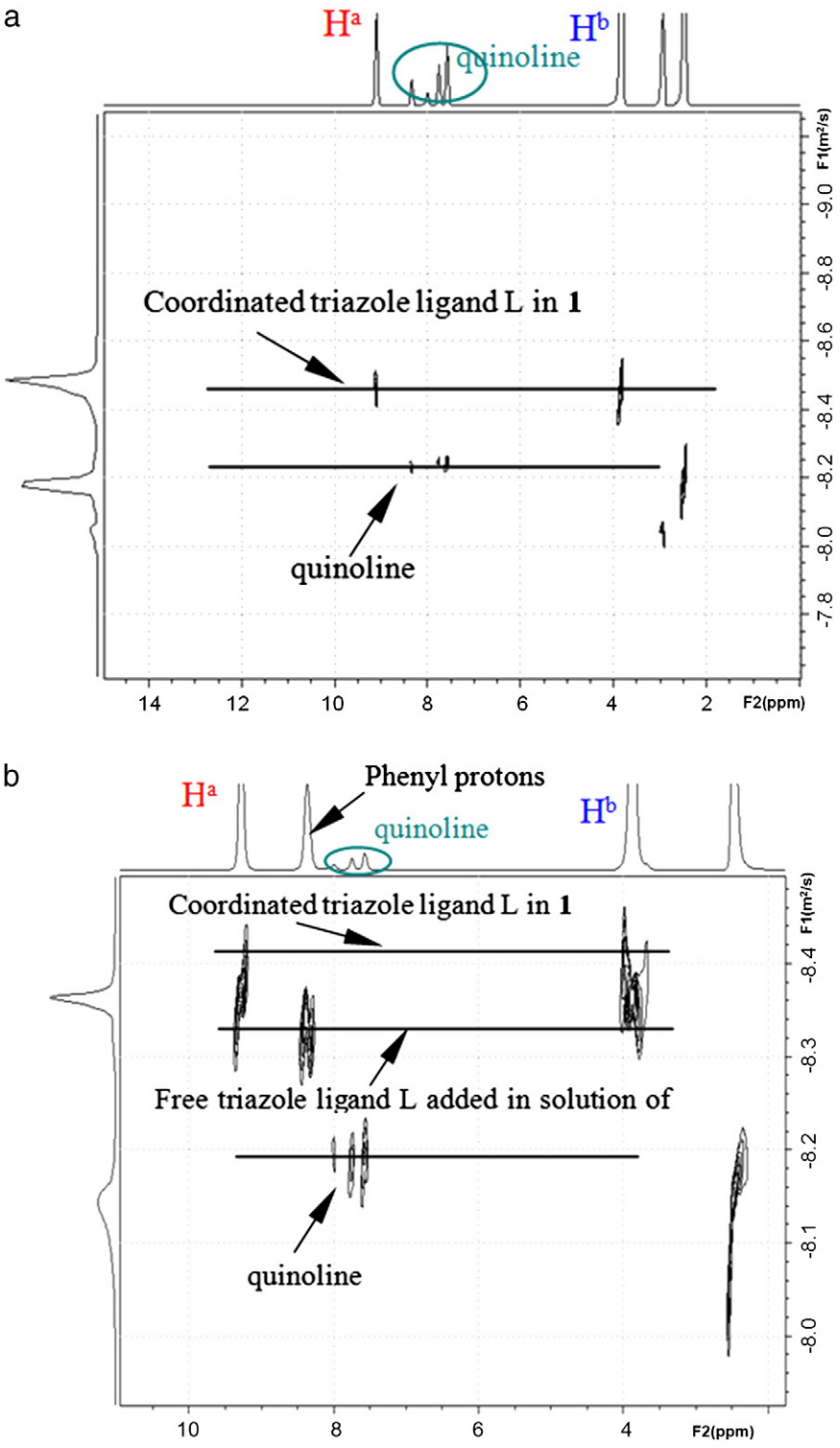

Fig. 4. (a) ^{1}H DOSY spectrum of **1** in DMSO-d6 and (b) ^{1}H DOSY spectrum of mixture of **1** and free 1,4-regioisomer LH in DMSO-d6. (X axis: ppm and Y axis: LogD).

consistent with two copper ions occupying identical sites in an axially symmetric crystal field ($E \approx 0$).

Fig. 6 compares the X-band ESR spectra of **SBU1** and **1** in frozen DMSO at two different temperatures. In addition to the peaks from the dinuclear Cu(II) noted above, the spectra exhibit a somewhat more prominent mononuclear Cu(II) peak at 3300 Gauss. The peaks in the dinuclear Cu spectra occur at nearly identical magnetic fields, indicating retention of the dinuclear paddlewheel chromophore of **SBU1** after Click reaction employed to form **1**. The relative intensity of the mononuclear and dinuclear peaks is unaffected by Click reaction; however, it is temperature dependent, with the dinuclear Cu (II) exhibiting relatively less intensity at lower temperatures. This is consistent with a large negative *J* value for the dinuclear Cu (II), so that the triplet state becomes depopulated when the temperature is reduced below 200 K. Such temperature dependence has previously been observed in similar dinuclear copper complexes [58].

Because of this inverse temperature dependence, it is difficult to quantify the relative amounts of mononuclear and dinuclear Cu from

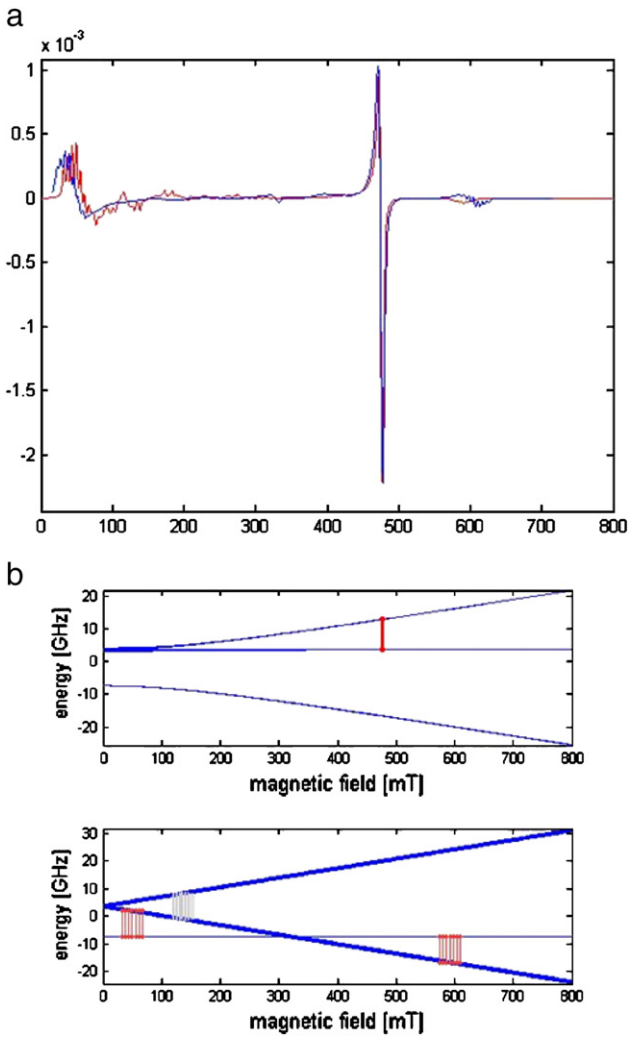

Fig. 5. (a) Crystal X-band spectrum of **SBU1** recorded at 160 K (blue) and calculated spectrum (red); (b) energy level diagram showing Δms = 1 transitions (red) and Δms = 2 transitions (gray) for the two canonical orientations B0||x,y (top) B0||z (bottom).

double integration of the spectrum. An upper limit on the amount of mononuclear present may be estimated by simulating the spectrum as a superposition of mononuclear and dinuclear spectra that have been normalized to a doubly integrated intensity of **1**. The inset of Fig. 6 shows a simulation of the spectrum assuming mononuclear to dinuclear ratio of 1:10. This simulation exhibits relative intensities of the mononuclear peak at 3300 G and dinuclear peak at 6000 G that are comparable to those of the 200 K experimental spectrum. Based on the previously observed temperature dependence of a similar dinuclear Cu complex [58], the dinuclear intensity at 200 K is still below its maximum value, which indicates an upper limit of about 10% on the relative amount of monomer present for both **SBU1** and **1** in DMSO. The results from the comparisons in Fig. 5 suggest that **SBU1** maintains its structural integrity after Click reaction and the structures of **SBU1** and **1** in DMSO are mainly dinuclear copper paddlewheel with trace amount of mononuclear impurity.

NMR and ESR analyses have confirmed the proposed structure **1** as depicted in Fig. 2. Click reaction was successfully employed to couple the 4 azide groups of SBU1 with 4 methyl propiolate molecules

Table 1
ESR parameters of calculated spectrum.

T(K)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (cm^1)	$A_{\perp}$ (cm^1)	D (cm^{-1})
160	2.06	2.45	77	15	3670

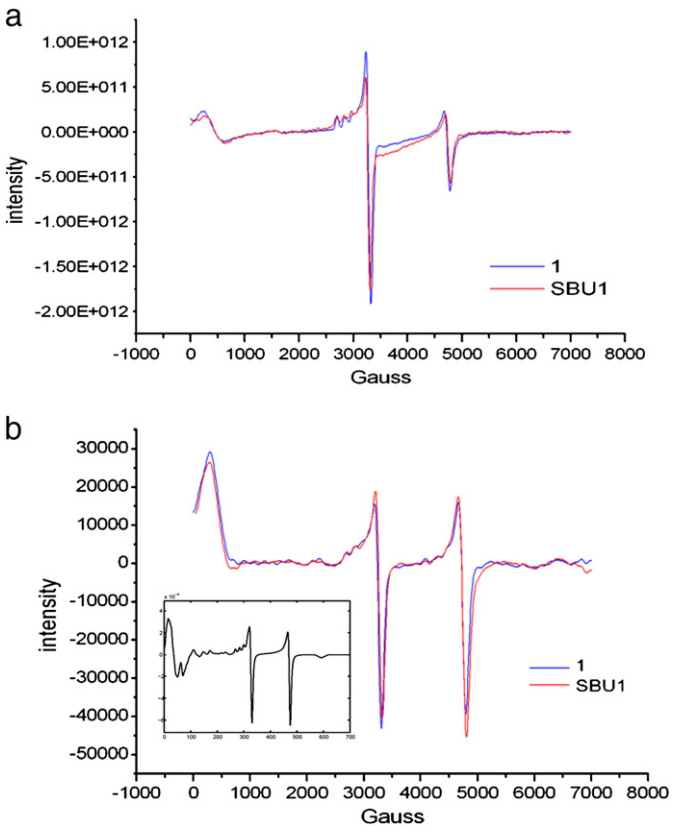

Fig. 6. X-band ESR spectra of **SBU1** and **1** in frozen DMSO at (a) 160 K and (b) 200 K. (red: **SBU1**, blue: **1**) Inset shows simulated ESR spectrum of mononuclear Cu(II) plus dinuclear Cu(II) in a 1:10 ratio.

respectively. **SBU1** was proved stable enough to survive the reaction conditions of Click reaction. Not only was the dicopper(II) tetracarboxylate coordination geometry retained throughout the Click reaction, the ancillary ligand-quinoline also remained in place in the formula of the product, which may be related to the weak coordination capacity of the used solvent-THF. Although the displacement of axial ligands can occur under certain conditions, there was no evidence of any negative effect on the integrity of **SBU1** structure.

In conclusion, we have successfully carried out the postsynthetic modification of a dicopper(II) coordination compound with a paddlewheel motif and performed structural characterizations using a variety of characterization techniques. The postsynthetic modification of coordination compound-**SBU1** with a paddle wheel structure has been successfully achieved via Click reaction. Meanwhile, the dicopper tetracarboxylate coordination chromophore of **SBU1** remains intact after Click reaction of the 4-azido-benzoate moieties with methyl propiolate. In addition, the combination of NMR and ESR techniques has proved to be powerful tools to characterize structures of non-single-crystalline coordination complexes, particularly in the solution phase. Currently, research is being focused on the synthesis of coordination polymers from discrete coordination complexes via postsynthetic modifications.

Caution: Standard personal protective equipments including safety glasses, lab coat, and gloves must be worn when conducting experiments reported in this paper. Handle azide reactions behind a blast shield in the fume hood. Do not combine untreated organic azide waste with other waste.

Appendix A. Supplementary material

Electronic Supplementary Information (ESI) available: [Synthesis of the free ligand **L**H and Figures S1-S7]. CCDC (Cambridge Crystallographic

Data Centre) reference number for **SBU1**·2CH3CN: 828956. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (Telefax: +44 1223 336408; e-mail: deposit@ccdc.cam.ac.uk).

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.09.043.

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[32] 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 1H observe respectively. DOSY spectra were acquired using the Bruker pulse programs, dstebpgp3s for 1 using sinusoidal gradients with durations between 1.25 and 3.5 ms. The gradient strength was varied between 2% and 95% in 16–32 square spaced increments for 1. Diffusion times of 14 to 20 ms were used for 1. DOSY spectra were processed using the Bruker Topspin software with exponential line fitting. X-band ESR Spectra were recorded at X-band (9.5 GHz) using a Bruker EMX ESR spectrometer equipped with a Bruker high sensitivity cylindrical resonator. Variable temperature studies were performed using a Bruker variable temperature unit (ER 4111VT) with liquid nitrogen reservoir and quartz dewar insert. ESR spectra and energy level diagrams were simulated using the EasySpin19 set of MATLAB program.
[33] Synthesis of **Cu_2(OOC-C_6H_4-N_3)$_4$(quinoline)$_2$** (**SBU1**): 4-azidobenzoic acid (10 mmol, 1.631 g) was suspended in 40 ml mixture solution of water and ethanol (volume ratio 1:1). Copper carbonate basic (2.5 mmol, 552.7 mg) was added into the suspension portion-wise. The suspension was stirred for several hours until a green precipitate formed. The green powder was obtained by filtration, and then the powder was dissolved in about 40 mL acetonitrile in presence of 5 mL quinoline and then divided into 10 small vials. Green block crystals [Cu_2(OOC-C_6H_4-N_3)$_4$(quinoline)$_2$]·2CH_3CN formed in these vials in about 3–4 days with ~80% yield. Crystallographic data for **SBU1**·2CH_3CN: $C_{50}H_{36}Cu_2N_{16}O_8$. CCDC reference number 828956. M = 1116.05, TRIGONAL, space group: *P-1*, *a = 10.852(8) Å, b = 9.292(6) Å, c = 13.409(9) Å, alpha = 77.048(13), beta = 80.273(11), gamma = 69.079(11), Z* = 1, *V* = 1224.9(15) Å [3]. R values: ($I > 2\sigma(I)$) $R_1 = 0.1368$, $wR_2 = 0.3620$; GOF = 1.085. The green crystals, **SBU1**·2CH_3CN, were collected, dried and then re-dissolved into chloroform. **SBU1** was obtained by rotovapping the chloroform solution to remove uncoordinated acetonitrile molecules in the crystal structure. IR (DMSO, 2500–1400 cm^{-1}): 2122.5 cm^{-1}, 1630.2 cm^{-1}, 1569.4 cm^{-1}, 1501.4 cm^{-1}, 1461.4 cm^{-1}. 1H NMR (DMSO-d6, 300 MHz): δ 9.31(very broad), 8.43, 8.10, 7.79, 7.69, 7.60 ppm. ^{13}C NMR (DMSO-d6): δ 135.3, 128.9, 128.09, 126.26, 39.4 ppm.
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[40] Synthesis of **Cu_2(OOC-C_6H_4-C_2HN_3-$COOCH_3$)$_4$·(quinoline)$_2$** (**1**): 0.25 mmol of **SBU1** was added into a round flask. Then 4 mL THF and 100 μl methyl propiolate (1.12 mmol) were added to the flask. Reaction mixtures were stirred at room temperature for 9 days. Green solid product **1** was obtained by filtration (washed with cool THF and hexane for several times). The product was first air dried and then dried under vacuum for ~4 – 6 hours. Yield: 82%. IR (DMSO, 2500–1400 cm^{-1}): 1738.89 cm^{-1}, 1636.35 cm^{-1}, 1609.25 cm^{-1}(sh), 1581.26 cm^{-1}, 1545.79, 1461.52 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ 9.29, 8.46, 8.18, 7.81, 7.60, 3.79 ppm. ^{13}C NMR (DMSO-d_6, 400 MHz): δ 160.17, 139.37, 138.16, 129.09, 126.93, 126.54, 51.79
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