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Synthesis, Crystal Structures, and Properties of Inorganic–Organic Hybrid Complexes Constructed from Copper(II) Macrocyclic Fragment[1]

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Abstract—Reaction of a macrocyclic copper(II) complex $[Cu(L)](ClO_4)_2 \cdot 3H_2O$ (**I**) (L = 1,3,10,12,16,19-hexaazatetracyclotetracosane) with a hexapod carboxylate ligand H_6TTHA (H_6TTHA = 1,3,5-triazine-2,4,6-triamine hexaacetic acid) and a tripod carboxylate ligand H_3TATB (H_3TATB = 4,4',4''-*S*-triazine-2,4,6-triyl-tribenzoic acid) yielded two mononuclear copper(II) complexes $[Cu(L)][H_4TTHA] \cdot 4H_2O$ (**II**) and $[Cu(L)][HTATB] \cdot 4H_2O$ (**III**). The complexes **I–III** have been structurally characterized. The crystal structures of complexes **II** and **III** show the copper(II) ion has a distorted pentacoordinate square-pyramidal geometry with two secondary and two tertiary amines from the macrocyclic complex $[Cu(L)]^{2+}$ and one oxygen atom from the carboxylate ligand group at the axial position. The UV-Vis spectra are utilized to discuss the hydrolysis of the complex **II**.

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INTRODUCTION

Supramolecular macrocyclic chemistry has been greatly advanced, and many efforts have been made to design and construct molecular solids with specific network topologies as well as with potentially interesting properties in areas, such as gas adsorption, ion exchange, magnetism, heterogeneous catalysis, luminescence [1–10]. Macrocyclic transition metal complex as an important subject, often called macrocyclic synthon, which can be used as building block to construct of macrocyclic coordination complex with bridging ligand. Overwhelming majority of interests is focused on the azide-, cyanide-, and carboxynato-bridged complexes [11–15]. Recent years, the combination of novel carboxylate bridged organic ligand and macrocyclic transition metal complex has drawn on the people of interest. Suh [16] used *tetrakis*[4-(carboxyphenyl)oxainethyl]-methane (TCM^{4-}) anion as a tetraliedral organic building block and $[Ni(Cyclam)]^{2+}$ (Cyclam = 1,4,8,11-tetraazacyclotetradecane) complex as a linear linker, resulting an eightfold interpenetrating diamondoid network. Moon [17] also used TCM^{4-} as a bridging ligand to construct of a doubly catenated rhombic grids network, which they introduced a nickel macrocyclic complex that contains two pyridyl pendant arms as a linear linker. Early days, Cao [18] utilized new ligand 2,2'-biquinoline-4,4'-dicarboxylic acid (H_2Bqdc) to construct two novel supermolecular frameworks by nickel macrocyclic complex linker. Recently, we have reported a 2D brick wail network assembled by $[Ni(Hto)]Cl_2 \cdot 2H_2O$ (Hto = 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane) and sodium azide in methanol solution [19]. The researches exhibit these macrocyclic complex synthons play an important role in predicting and controlling crystal structures. In order to investigate how the different bridging ligands affect the structures of supramolecular assembly, we focused on six-aza macrocyclic complex as a building block and multi-carboxylic acid as a bridging ligand, which can be constructed of new macrocyclic coordinated complex.

On the other hand, the copper macrocyclic complexes belong to rather unexplored class of building blocks, because of the Jahn–Teller effect of the copper ion, which induces weak binding with the ligand at the axial position [20]. Herein, we introduce the copper macrocyclic $[Cu(L)]^{2+}$ as the building block. Few papers have been published about the coordination complexes constructed from $[M(L)]^{2+}$ (M = Ni, Cu) until now [21–23]. In this paper, we obtained two mononuclear supermolecular network $[Cu(L)][H_4TTHA] \cdot 4H_2O$ (**II**) and $[Cu(L)][HTATB] \cdot 4H_2O$ (**III**) constructed by 1,3,5-triazine-2,4,6-triamine hexaacetic acid (H_6TTHA), 4,4',4''-s-triazine-2,4,6-triyl-tribeuzoic acid (H_3TATB) and copper(II) macrocyclic complex $[Cu(L)](ClO_4)_2 \cdot 3H_2O$ (**I**),

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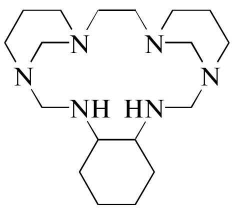
where (L = 1,3,10,12,16,19-hexaazatetracyclotetracosane).



(L)

EXPERIMENTAL

Materials and physical measurements. All the starting reagents were of analytical grade, obtained from commercial sources and used without further purification. Elemental analyses (C, H, and N) were performed using a vario EL cube CHNS/O elemental analyzer. Solution UV-Vis spectra were obtained on a Shimadzu UV1801 spectrophotometer. FT/IR spectrum was obtained on a Nicolet-Avatar 370 infrared spectroscopy in the 4000–400 cm^{-1} region, using KBr pellets. The powder X-ray diffraction measurements were performed on a Bruker D8 ADVANCE X-ray diffractometer. The H_6TTHA ligand was prepared according to the literature procedures previously reported [24]. Macrocyclic complex **I** was synthesized by a procedure similar to that of $[Ni(L)]^{2+}$ using $Cu(OAc)_2 \cdot H_2O$ in place of $Ni(OAc)_2$ [21]. The single-crystal of **I** was obtained by recrystallization of the powder in aqueous solution.

Synthesis of complex II. A aqueous solution (5 mL) of **I** (0.075 g, 0.15 mmol) was layered with a H_2O–CH_3OH (v/v = 1 : 1) solution (10 mL) of H_6TTHA (0.075 g, 0.15 mmol) at room temperature. After about 1 week, purple crystals suitable for X-ray analysis formed. The yield was 20 mg.

For $C_{33}H_{60}N_{12}O_{16}Cu$

anal. calcd., %:	C, 42.28;	H, 5.70;	N, 17.93.
Found, %:	C, 41.95;	H, 6.60;	N, 17.80.

IR (ν, cm^{-1}): 1720 (COOH), 1481 (COO^-), 1321 (COO^-).

Also large block purple crystals can be obtained by mixed the aqueous solution of **I** and H_6TTHA at room temperature in a week.

Synthesis of complex III. To a solution of **I** (0.15 g, 0.3 mmol) in 10 mL H_2O, a solution of Na_3TAHB (0.15 g, 0.3 mmol) in 10 mL aqueous solution was added with stirring, filtration and slow evaporation of the resulting solution and yielded purple crystals in one week. The yield was 60 mg.

For $C_{33}H_{57}N_9O_{10}Cu$

anal. calcd., %:	C, 55.90;	H, 5.36;	N, 13.96.
Found, %:	C, 55.45;	H, 6.23;	N, 13.86.

IR (ν, cm^{-1}): 1714 (COOH), 1514 (COO^-), 1316 (COO^-).

X–ray crystallography. The purple block crystals of complexes were chosen for room temperature 293(2) K data collection on a Bruker Smart Apex CCD diffractometer with a graphite monochromated MoK_α radiation (λ = 0.71073 Å). The structure was solved by direct method and refined by full-matrix least-squares procedure on F^2 by the SHELXL-97 program [25]. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically. The hydrogen atoms of water molecules in comples were not located.

Details of the crystal parameters, data collection, and refinement are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Crystallographic data for structures **I–III** have been deposited with the Cambridge Crystallographic Data Centre (nos. 894134 (**I**), 894135 (**II**), and 894136 (**III**); http://wvvw.ccdc.cam.ac.uk/conts/retrieving.html or deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The molecular structure of complex **I** is presented in Fig. 1a together with an atomic labeling scheme. The crystal structure of complex **I** consists of a independent $[Cu(L)]^{2+}$ unit, two ClO_4^- ions and three water molecules. X-ray crystallographic analysis shows that the structure of copper atom is coordinated by two secondary and two tertiary amines of the macrocycle ligand and two oxygen atom of the perchlorate in a distorted octahedral geometry. The Cu–N bond distances in CuN_4 plane range from 2.011 to 2.056 Å, and the average of the four distances is 2.042 Å, which is comparable to those of other square-pyramidal copper(II) complexes of tetraaza macrocyclic ligands. The NCuN angles (94.07° and 96.91°) of the six-membered chelate ring are much larger than the NCuN angles (87.37° and 85.54°) of the five-membered chelate ring, as is usual. Due to the Jahn–Teller effect, the axial Cu–O(3) and Cu–O(5) bond distances are 2.5336 and 2.9456 Å, respectively, which are longer than the Cu–N bond lengths. The axial Cu–O(12) bonds are not perfectly perpendicular to CuN_4 plane with the OCuN angles ranging from 83.7° to 98.9°.

By the reaction of copper complex **I** with H_6TTHA and H_3TATB, the complex **II** and **III** were isolated. Figure 1b shows the structure of **II** as determined by

Table 1. Crystal data and structure refinement parameters for complexes **I–III**

Parameter	Value		
	I	**II**	**III**
Formula weight	651.00	937.41	902.43
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$
a, Å	26.136(9)	10.6738(17)	20.587(11)
b, Å	11.698(4)	10.7049(17)	13.728(8)
c, Å	18.348(6)	19.391(3)	15.290(9)
α, deg	90	90.824(2)	90
β, deg	103.846(4)	104.843(2)	104.404(10)
γ, deg	90	105.416(2)	90
Volume, Å^3	5447(3)	2056.5(6)	4185(4)
Z; ρ_{calcd}, mg/m^3	8; 1.588	2; 1.514	4; 1.432
Absorption coefficient, mm^{-1}	1.064	0.617	0.592
F(000)	2728	984	1888
θ Range, deg	2.13–26.00	2.06–26.50	1.80–25.00
Reflections collected	14724	11895	20710
Independent reflections	5350	8314	7309
Data/restraints/parameters	5350/12/351	8314/6/572	7309/18/561
GOOF	1.058	1.101	0.940
Final R indices, $I > 2\sigma(I)$	$R_1 = 0.0795$	$R_1 = 0.0542$	$R_1 = 0.0767$
	$wR_2 = 0.2119$	$wR_2 = 0.1289$	$wR_2 = 0.1889$
R indices, all data	$R_1 = 0.1017$	$R_1 = 0.0794$	$R_1 = 0.1465$
	$wR_2 = 0.2336$	$wR_2 = 0.1428$	$wR_2 = 0.2191$

GOOF = $[\Sigma w(F_0^2 - F_c^2)^2/(n_{ohe} - n_{param})]^{1/2}$; $R_1 = \|F_0| - |F_c\|/\Sigma|F0|$, $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

single crystal X-ray diffraction methods. The crystal structure of **II** has a $[Cu(L)]^{2+}$ cation, one $[H_4TTHA]^{2-}$ anion, and four water molecules. In **II**, the copper ion is five-coordinate with bonds to two secondary and two tertiary amines of the macrocycle ligand and one oxygen atom of the $[H_4TTHA]^{2+}$ ligand in a distorted square-pyramidal geometry. The Cu–N distances vary from 2.023 to 2.066 Å and the Cu–O distance is 2.302 Å. The average Cu–N distance of 2.045 Å is similar to that observed in complex **I**. The Cu–O distance of 2.155(5) Å is longer than that found in Cu–O due to the Jahn–Teller effect. The axial Cu–O linkage is not perpendicular to the CuN_4 plane as the ONiN basal angles range from 92.91° to 98.21°. Due to the flexibility of H_6TTHA ligand, six of the arms show significant deviation from the central triazine ring.

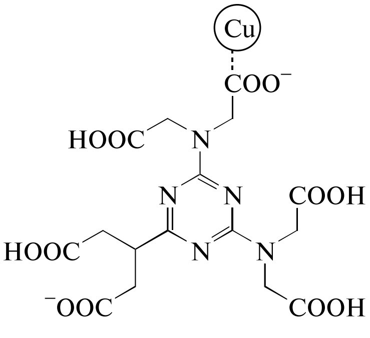
The X-ray single crystal structure reveals that complex **III** also crystallizes in mononuclear structure. The unit of complex **III** consists of one independent $[Cu(L)]^{2+}$ segment, one $[HTATB]^{2-}$ ligand, and four uncoordinated water molecules (Fig. 2a). The Cu atom in $[Cu(L)]^{2+}$ segment adopts a slightly distorted five coordinate geometry with four nitrogen atoms of the macrocycle occupying the equatorial positions, and one oxygen atoms of $[HTATB]^{2-}$ located at the

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **I**–**III**

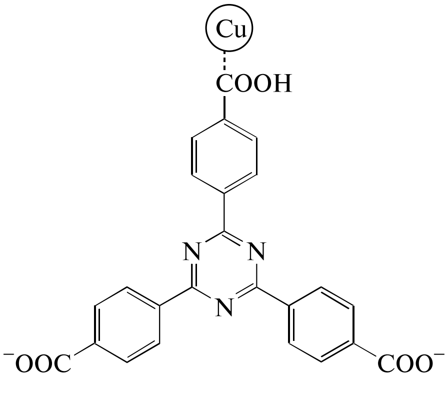
Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
I		**II**		**III**	
O(3)–Cu(1)	2.534(5)	Cu(1)–N(1)	2.023(3)	Cu(2)–N(4)	1.995(5)
O(5)–Cu(1)	2.946(11)	Cu(1)–N(4)	2.039(3)	Cu(2)–N(5)	2.018(5)
Cu(1)–N(1)	2.011(4)	Cu(1)–N(3)	2.052(3)	Cu(2)–N(7)	2.043(5)
Cu(1)–N(2)	2.025(5)	Cu(1)–N(2)	2.066(3)	Cu(2)–N(6)	2.049(5)
Cu(1)–N(4)	2.052(5)	Cu(1)–O(8)	2.302(2)	Cu(2)–O(2)	2.200(4)
Cu(1)–N(3)	2.056(5)				
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
N(1)Cu(1)N(2)	85.54(19)	N(1)Cu(1)N(4)	84.06(11)	N(4)Cu(2)N(5)	85.42(19)
N(1)Cu(1)N(4)	92.91(19)	N(1)Cu(1)N(3)	168.80(13)	N(4)Cu(2)N(7)	93.51(19)
N(2)Cu(1)N(4)	176.9(2)	N(4)Cu(1)N(3)	94.01(11)	N(5)Cu(2)N(7)	173.1(2)
N(1)Cu(1)N(3)	177.7(2)	N(1)Cu(1)N(2)	94.58(12)	N(4)Cu(2)N(6)	171.44(19)
N(2)Cu(1)N(3)	94.07(19)	N(4)Cu(1)N(2)	173.03(13)	N(5)Cu(2)N(6)	92.3(2)
N(4)Cu(1)N(3)	87.37(19)	N(3)Cu(1)N(2)	86.00(12)	N(7)Cu(2)N(6)	87.8(2)
N(1)Cu(1)O(3)	86.3(2)	N(1)Cu(1)O(8)	98.21(11)	N(4)Cu(2)O(2)	96.19(18)
N(2)Cu(1)O(3)	83.70(19)	N(4)Cu(1)O(8)	93.53(11)	N(5)Cu(2)O(2)	92.56(18)
N(4)Cu(1)O(3)	98.90(19)	N(3)Cu(1)O(8)	92.91(10)	N(7)Cu(2)O(2)	94.38(17)
N(3)Cu(1)O(3)	95.97(19)	N(2)Cu(1)O(8)	93.43(10)	N(6)Cu(2)O(2)	92.15(18)
N(1)Cu(1)O(5)	86.8(2)				
N(2)Cu(1)O(5)	86.2(2)				
N(4)Cu(1)O(5)	91.0(2)				
N(3)Cu(1)O(5)	90.9(2)				
O(3)Cu(1)O(5)	168.2(2)				

axial sites. The Cu–N average distance of 2.030 Å is similar to that observed for the complexes **I** and **II**. The Cu–O distance of 2.200 Å is comparable to the previously reported values in **II**, giving an axially elongated geometry. The axial Cu–O bond is not perpendicular to the NiN_4 plane with NCuO angles of 92.15°–96.19°. Similarly, the Cu–O bond lengths in **III** are longer than the Cu–N bond lengths due to the Jahn–Teller effect.

In those structures, the hexapod H_6TTHA ligand (a) and tripod H_3TATB ligand (b) are not completely deprotonated, only two carboxylic acid groups deprotonated for balance the charge:



(a)



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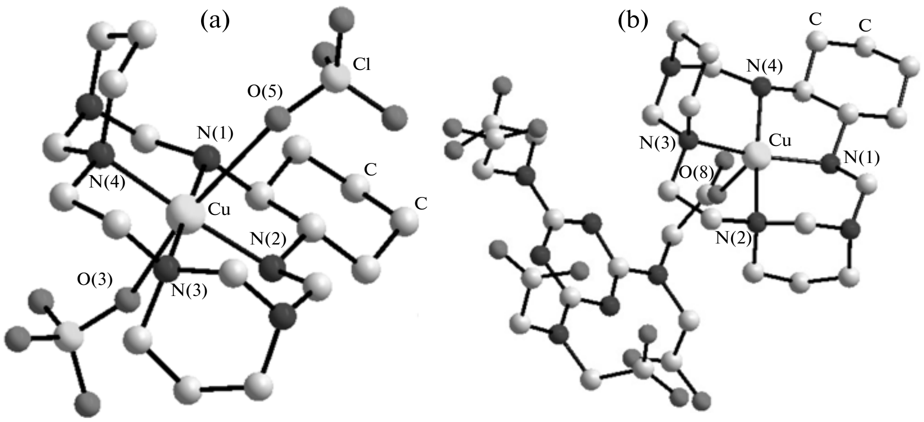

Fig. 1. An ORTEP diagram of complex **I** (a) and **II** (b) with the atomnumbering scheme. The perchlorate, water molecules, hydrogen atoms are omitted for clarity.

Hydrogen bonds displayed interesting interactions in the compound. Molecular units are linked together give rise to 3D architecture by hydrogen bonds. The hydrogen bonds produced by the deprotonation of carboxylic acid group on carboxylate ligand and secondary amines of the macrocyclic, as well as the hydrogen bonds interaction between the deprotonation carboxylic acid group and protonated carboxylic

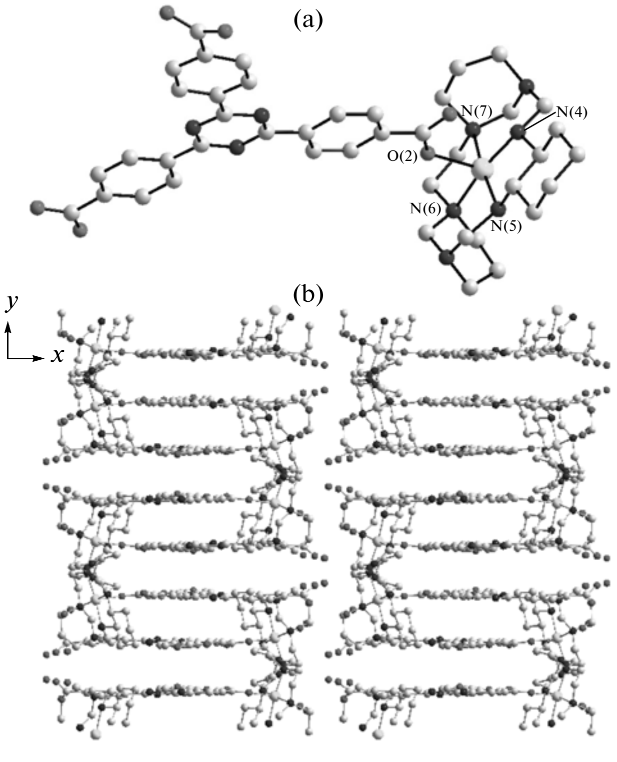

Fig. 2. An ORTEP diagram of complex **III** with the atom-numbering scheme (a); the π–π stacking interactions along the *z* axis in comples **III** (b). The water molecules, hydrogen atoms are omitted for clarity.

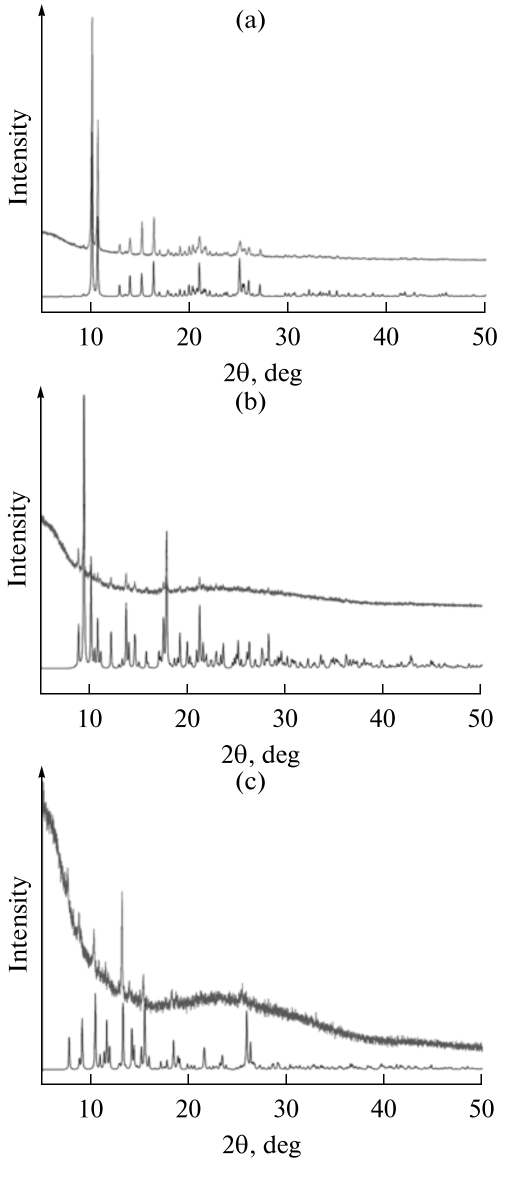

Fig. 3. The XRPD pattern of compounds: **I** (a); **II** (b); **III** (c).

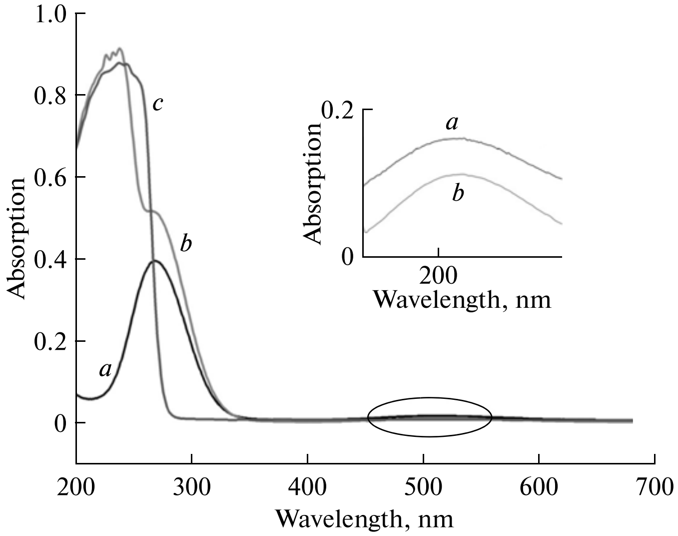

Fig. 4. UV-Vis absorption spectra of $[Cu(L)](ClO_4)_2 \cdot 3H_2O$ (*a*), $[Cu(L)][H_4TTHA] \cdot 4H_2O$ (*b*), and H_6TTHA (*c*) in distilled water solution at room temperature.

acid group. Complex **III** features the π–π stacking interactions along the *z* axis (Fig. 2b).

Powder X-ray diffraction pattern of compounds at room temperature was consistent with the simulated one based on the X-ray diffraction analysis (Fig. 3). The diffraction peaks on both patterns are corresponded well in positions, indicating the phase purity of the as-synthesized sample (Fig. 3). The IR spectra of compounds show an intense bands at 1714 and 1720 cm^{-1} due to unprotonated carboxylic acid group, which is corresponded to the crystal structure. The UV-Vis absorption spectrum of aqueous solution for complex **II** shows strong bands around 268 and 510 nm and decomposes into the building block $[Cu(L)]^{2+}$ which is consistent with $[Cu(L)][H_4TTHA] \cdot 4H_2O$ dissolves in water solution (Fig. 4). The 268 nm is assigned to the intra-ligand transitions (π–π* transitions in the C=N double bond of triazine) in the compound, the 510 nm correspond to the *d–d* bands of copper(II) ions.

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