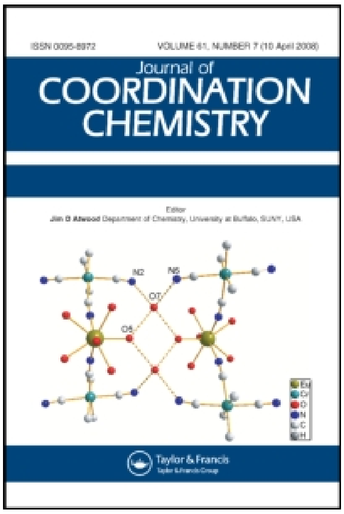

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Syntheses, crystal structures and photochemistry of two new organic-inorganic hybrid compounds based on copper-glycin complexes and paradodecatungstates

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Syntheses, crystal structures and photochemistry of two new organic–inorganic hybrid compounds based on copper–glycin complexes and paradodecatungstates

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Two organic–inorganic hybrid materials built from copper–glycin complexes and paradodecatungstates, $Na_6[\{Cu(gly)(H_2O)\}]_2[\{Cu(H_2O)\}(H_2W_{12}O_{42})] \cdot 21H_2O$ (**1**) and $Na\{Na(H_2O)_6\}\{Na(H_2O)_4\}_3[\{Cu(gly)_2\}]_2\{H_5(H_2W_{12}O_{42})\} \cdot 8.5H_2O$ (gly = glycin) (**2**), have been synthesized in aqueous solution and characterized by IR, UV, TG, elemental analysis, electrochemistry, and single-crystal X-ray analyses. In **1**, $[H_2W_{12}O_{42}]^{10-}$ building block connects two neighboring clusters with $[Cu(H_2O)]^{2+}$ groups to produce an infinite 1-D chain; then these chains are linked through $[Cu(gly)(H_2O)]^{+}$ groups to form a 2-D layer structure, which is further joined by Na^{+} to form a 3-D network. In **2**, $[H_2W_{12}O_{42}]^{10-}$ decorated by two $[Cu(gly)_2]$ moieties connects four adjacent clusters with six Na^{+} into a 2-D layer. In addition, luminescence and photocatalysis properties of these compounds have been investigated.

Keywords: Paradodecatungstates; Copper–glycin complexes; 3-D framework; Luminescent property; Photocatalysis property

1. Introduction

The rational design and the synthesis of functionalized polyoxometalates (POMs) decorated by organic molecules have received extensive attention, not only from potential applications in catalysis, biology, sorption, photochemistry, medicine, and electrical conductivity, but also from their variety of architectures and topologies [1–4]. Commonly used POM building blocks are still limited to the well-known structures, such as Keggin [5a–d], Silverton [5e], Wells-Dawson [6], Anderson [7], Lindquist [8], Waugh [9], etc. Among the various structures of POMs, one of the most interesting is the paradodecatungstate anion $[H_2W_{12}O_{42}]^{10-}$, which has some particular structural features and provides a variety of possibilities of intermolecular linkages. The relative high charge density activates the surface oxygens to facilitate formation of high-dimensional networks. Attention has been devoted to the investigation of frameworks based on building blocks of paradodecatungstates and transition metal

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complexes (TMCs). Incorporation of TMCs dramatically influences the microstructures and properties of final products, building paradodecatungstate-based metal organic frameworks with charming structures and unique properties. Some compounds constructed from $[H_2W_{12}O_{42}]^{10-}$ and TMCs have been explored in recent years. For example, Anne Dolbecq's group prepared a series of organic–inorganic hybrid materials [10] built from paradodecatungstates and Cu(II) which were synthesized by hydrothermal reactions from a mixture of sodium tungstate, copper chloride, and en (en = ethylenediamine). Two new compounds $[Cu(en)_2]_3[\{Cu(en)_2\}_2(H_2W_{12}O_{42})] \cdot 12H_2O$ and $[\{Cu(en)_2\}_4(H_4W_{12}O_{42})] \cdot 9H_2O$, formed by $[H_2W_{12}O_{42}]^{10-}$ clusters and $[Cu(en)_2]^{2+}$ complexes, have been characterized by Lin and co-workers [11, 12]. Yan *et al.* [13] synthesized 1-D chain $(enH_2)_4[\{Cu(en)_2\}H_2W_{12}O_{42}]$ and 2-D layer structures $[\{Cu(en)_2\}_4Cu(H_2O)_2H_2W_{12}O_{42}] \cdot H_2O$, which also contain $[H_2W_{12}O_{42}]^{10-}$ units linked by $[Cu(en)_2]^{2+}$. The only example of copper–glycin complexes incorporating $[H_2W_{12}O_{42}]^{10-}$ anions $Na_8[\{Cu(gly)_2\}_2]\{H_2(H_2W_{12}O_{42})\}] \cdot 24H_2O$ has been reported by Dutta and co-workers [14], where $[H_2W_{12}O_{42}]^{10-}$ clusters are interconnected through $[Cu(gly)_2]$ groups to form a 1-D chain.

The ligands in these compounds are usually en and rarely with functional groups, which possess high biological activity, important functions in medicine and more flexible coordination modes. Inspired by the aforementioned considerations and Dutta's work [14], amino acid molecules seized our attention because: (1) There are carboxyl and amino groups in the amino acid molecules so they can act as hydrogen-bonding accepters, hydrogen-bonding donors, bidentate, and tridentate ligands coordinating to various metals to give high-dimensional organic–inorganic hybrid materials [15a–e]. (2) The amino acid molecules have flexible coordination modes and important application in physiology and medicine [15f, g]. Therefore, functionalized organic–inorganic hybrid materials with high-dimensional frameworks are expected to be obtained by introducing amino acid molecules into the paradodecatungstate system.

In this article, we report the synthesis and structural characterization of two new organic–inorganic hybrid POMs mixed with glycin ligands, $Na_6[\{Cu(gly)(H_2O)\}]_2[\{Cu(H_2O)\}(H_2W_{12}O_{42})] \cdot 21H_2O$ (**1**) and $Na\{Na(H_2O)_6\}\{Na(H_2O)_4\}_3[\{Cu(gly)_2\}]_2\{H_5(H_2W_{12}O_{42})\} \cdot 8.5H_2O$ (**2**). To the best of our knowledge, no compounds based on $[H_2W_{12}O_{42}]^{10-}$ and copper–glycine complexes with 3-D structures have been reported. Luminescence and photocatalysis of these compounds have also been investigated.

2. Experimental

2.1. *Materials and methods*

All chemicals were purchased without purification. $Na_{10}[H_2W_{12}O_{42}] \cdot 20H_2O$ was prepared according to the literature method [16a]. Elemental analyses (C, H, N) were obtained with a Perkin–Elmer 2400 CHN elemental analyzer; W and Cu were analyzed on a PLASMA-SPE (I) ICP atomic emission spectrometer. IR spectra were recorded from 4000 to 400 cm^{-1} on an Alpha Centauri FT/IR spectrophotometer using KBr pellets. UV-Vis absorption spectra were recorded on a 756 CRT UV-Vis spectrophotometer. TG analyses were performed on a Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of 10°C min^{-1}. Electrochemical experiments were carried out on a BAS Epsilon Analyzer in a three-electrode cell: glassy carbon electron (GCE, diameter 3 mm) as working electrode, platinum wire as counter electrode, and Ag/AgCl/KCl (3 M) as reference electrode. Excitation and emission spectra were obtained on a SPEX FL-2T2 spectrofluorometer equipped with a 450-W xenon lamp as the excitation source.

2.2. *Synthesis of 1*

$NaWO_4 \cdot 2H_2O$ (4.00 g, 12 mmol) was first dissolved in 20 mL of distilled water with stirring and the insoluble material removed by filtration; then $CuCl_2 \cdot 2H_2O$ (0.30 g, 1.76 mmol) and gly (0.15 g, 2 mmol) were added with vigorous stirring, the mixture was adjusted to pH = 5.3 with diluted HCl (4 mol L^{-1}), refluxed 5 at 90°C, cooled to room temperature and filtered. The filtrate was kept for 2 weeks at ambient conditions and then blue block crystals of **1** were isolated in about 45% yield (based on W). Elemental analysis for $C_4H_{58}Cu_3N_2Na_6O_{70}W_{12}$ (3778.5), Calcd (%): W, 58.21; Cu, 5.05; N, 0.70; C, 1.27; H, 1.38. Found (%): W, 58.05; Cu, 5.11; N, 0.63; C, 1.21; H, 1.27. Selected IR (KBr pellet, cm^{-1}): 3430 (s), 1606 (m), 912 (m), 846 (w), 744 (s), 693 (w).

2.3. *Synthesis of 2*

$NaWO_4 \cdot 2H_2O$ (4.00 g, 12 mmol) was dissolved in 20 mL of distilled water on stirring and insoluble material removed by filtration; then $CuCl_2 \cdot 2H_2O$ (0.30 g, 1.76 mmol) and gly (0.15 g, 2 mmol) were added under vigorous stirring, the pH adjusted to 4.3 with dilute HCl (4 mol L^{-1}), refluxed 5 h at 90°C, cooled to room temperature and filtered. The filtrate was kept for 2 weeks at ambient conditions and blue block crystals of **2** were isolated in about 35% yield (based on W). Elemental analysis for $C_8H_{76}Cu_2N_4Na_5O_{76.5}W_{12}$ (3890), Calcd (%): W, 56.45; Cu, 3.26; N, 1.44; C, 2.47; H, 1.95. Found (%): W, 56.31; Cu, 3.19; N, 1.39; C, 2.52; H, 1.88. Selected IR (KBr pellet, cm^{-1}): 3430 (s), 1606 (m), 1050 (w), 913 (s), 852 (w), 744 (s), 696 (w).

2.4. *X-ray crystallography*

Measurements for **1** and **2** were performed on a Rigaku R-AXIS RAPID IP diffractometer and the data collected at 150(2) K with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full matrix least-squares on F^2 using SHELXL-97 software [16b]. Anisotropic thermal parameters were *not* used to refine all non-hydrogen atoms (Na2, O2W, O4W, O14W). The H atoms on carbon and nitrogen were included in calculated positions. The H atoms on water cannot be found from the weak residual electron peaks but were directly included in the final molecular formula. The crystal data and structure refinement for **1** and **2** are summarized in table 1. Selected bond lengths and angles for **1** and **2** are also listed in tables S1 and S2.

Table 1. Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_4H_{58}Cu_3N_2Na_6O_{70}W_{12}$	$C_8H_{76}Cu_2N_4Na_5O_{76.5}W_{12}$
Formula weight	3778.5	3890
Temperature (K)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P-1*	*P 2(1)/m*
Unit cell dimensions (Å, °)		
a	12.392(3)	12.593(3)
b	12.703(3)	23.642(5)
c	12.991(3)	14.815(3)
α	63.63(3)	90
β	88.80(3)	96.5(3)
γ	66.27(3)	90
V (Å^3)	1646.0(6)	4382.4(15)
Z	1	1
Reflections collected	12494	33041
Independent reflection	5700	7694
Data/restraints/parameters	5700/0/369	7694/30/500
Goodness-of-fit on F^2	1.094	0.988
Final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0667$, $wR_2{}^b = 0.1426$	$R_1{}^a = 0.0630$, $wR_2{}^b = 0.1211$
R indices (all data)	$R_1{}^a = 0.0827$, $wR_2{}^b = 0.1567$	$R_1{}^a = 0.1223$, $wR_2{}^b = 0.1431$

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
$^bwR^2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

2.5. *Photocatalysis experiments*

In a typical process, 30 mg of **1** was dissolved in 100 mL rhodamine B (RhB) solution ($1.8 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) at pH 2.5 (the pH of the solutions was adjusted with dilute aqueous solutions of either NaOH or $HClO_4$), then magnetically stirred in the dark for about 30 min. The solution was then exposed to UV irradiation from a 125 W Hg lamp at a distance of 4–5 cm between the liquid surface and the lamp. The solution was stirred during irradiation. At different time intervals, 3 mL samples were taken from the beaker and adjusted to pH = 9 by the addition of dilute Na_2CO_3 solution (1 mL), and subsequently analyzed by UV-Vis spectroscopy. An identical procedure was followed except **1** was replaced by **2** or $Na_{10}[H_2W_{12}O_{42}] \cdot 20H_2O$.

3. Results and discussion

3.1. *Structure description*

Compounds **1** and **2** were constructed from paradodecatungstate building blocks, very similar to those in reported structures [17–21]. The W–O bond distances in $[H_2W_{12}O_{42}]^{10-}$ can be divided into three groups: W–O (terminal) 1.706(11)–1.760(16) Å; W–O (bridging) 1.710(11)–2.268(11) Å; W–O (triply bridging) 1.877(11)–2.307(11) Å. These bond distances are in accord with reported values [18, 19, 22, 23].

The crystal structure of **1** is constructed from $[H_2W_{12}O_{42}]^{10-}$ clusters linked through $\{Cu(gly)(H_2O)\}^+$ and $\{Cu(H_2O)\}^{2+}$ groups into a 2-D layer of $[\{Cu(gly)(H_2O)_2\}_2Cu(H_2O)H_2W_{12}O_{42}]\}^{6-}$ (figure 1). In **1**, each paradodecatungstate ion is bound to six Cu(II) ions with two unique sites referred to as Cu(A) and Cu(B) (figure 2). Cu(A) is the

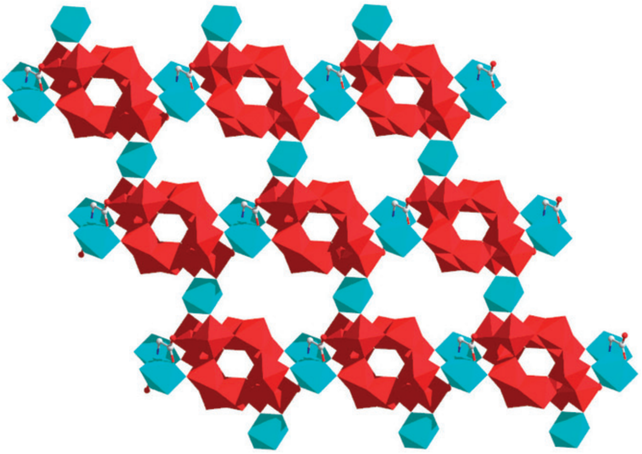

Figure 1. 2-D layer structure of **1**. Color code: W (red octahedra), Cu (sky blue octahedra), C (light gray ball), and O (red ball).

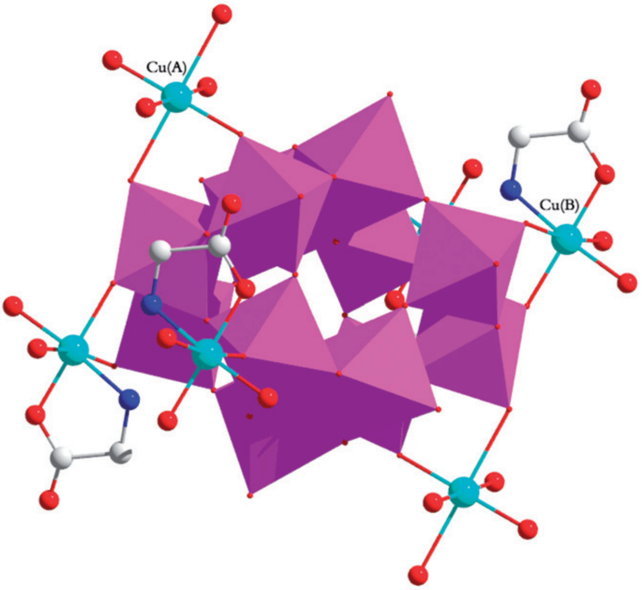

Figure 2. Two unique copper sites connected to a cluster unit in **1**. Selected bond distances (Å): Cu(A)–O: 1.954(11), 2.420(13), and 2.008(11); Cu(B)–O: 1.934(14), 1.971(20), 1.997(12), 2.488(10); Cu(B)–N: 1.977(15). Color code: W (pink octahedra), Cu (sky blue ball), N (dark blue ball), C (light gray ball), and O (red ball).

center of a distorted CuO_6 octahedron, from four terminal oxygens of two neighboring clusters and two waters. Axial Cu–O bonds are considerably longer than equatorial Cu–O bonds from Jahn–Teller distortion. This copper site connects $[H_2W_{12}O_{42}]$ clusters to form a 1-D chain (figure S1a). Cu(B) is a distorted CuO_5N octahedron from nitrogen and oxygen of glycine, two oxygens from two cluster anions, a water and as linkage between $[\{Cu(H_2O)\}H_2W_{12}O_{42}]^{8-}$ chains. In **1**, the 2-D layers of

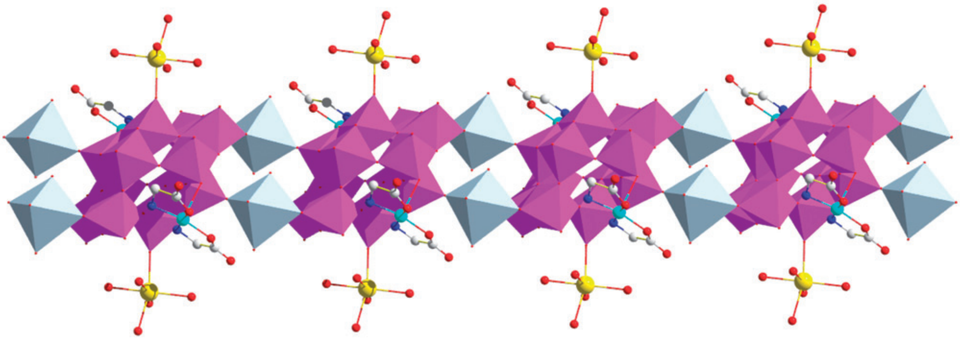

Figure 3. 1-D chain structure in **2**. Color code: W (pink octahedra), Na (light gray octahedra and yellow ball), Cu (sky blue ball), N (blue ball), C (light gray ball), and O (red ball).

$[\{Cu(gly)(H_2O)_2\}_2Cu(H_2O)H_2W_{12}O_{42}]\}^{6-}$ are further joined by Na^+ to form a 3-D network (figure S1b).

The crystal structure of **2** contains a 1-D chain of $[\{Na(H_2O)_4\}_2(H_2W_{12}O_{42})]^{8-}$ (figure 3). Each paradodecatungstate in this 1-D chain is bound to two Cu(II) ions and six $Na(I)^+$. Each glycine is a bidentate ligand utilizing its amino and carboxylate groups to chelate Cu(II). Each Cu(II) atom is coordinated by four equatorial nitrogens and oxygens from two glycine molecules and one terminal oxygen (O12) from the paratungstate clusters (figure S2a). The elongation of Cu–O (axial) distance is 2.48(0) Å and the Cu–O (equatorial) bond length is 1.96(3) Å in **2**. The $Na(I)^+$ in **2** are six-coordinate in an octahedron. These NaO_6 octahedra interlink the 1-D anionic chains to generate a 2-D layer (figure S2b).

3.2. *IR spectrum*

The IR spectrum of **1** (figure S3a) shows a broad absorption of water at $3430\,cm^{-1}$. Strong absorptions at 1606 and $1396\,cm^{-1}$ are characteristics of the carboxylate. Absorptions at 912, 846, 744, and $693\,cm^{-1}$ can be attributed to ν(W–Od), ν(W–Oa), ν(W–Ob), and ν(W–Oc) in the polyoxoanion framework. The IR spectrum of **2** (figure S3b) also exhibits the band of water at $3423\,cm^{-1}$, peaks of carboxylate at 1605 and $1378\,cm^{-1}$ and peaks located at 1050, 913, 852, 744, and $696\,cm^{-1}$ attributed to vibrations of W–O in the polyoxoanion of **2**.

3.3. *Electrochemistry*

Electrochemical properties of the two compounds at pH = 4.8 (0.5 M $CH_3COONa + CH_3COOH$) buffer at scan rate of $100\,mV\,s^{-1}$ are shown in figure S5(a) and (b). Compound **1** shows four redox peaks in the range 850 and −600 mV, and the peak potentials of $E_f = (E_{pa} + E_{pc})/2$ are 203, 155, −289, and −376 mV (*vs*. Ag/AgCl). The redox waves of 203 and 155 mV can be attributed to Cu^0 and Cu^{2+}. Peaks of −289 and −376 mV correspond to redox of the $W^{VI/V}$ in the polyoxoanion framework. Similar results have been observed in other Cu-decorated POMs [24].

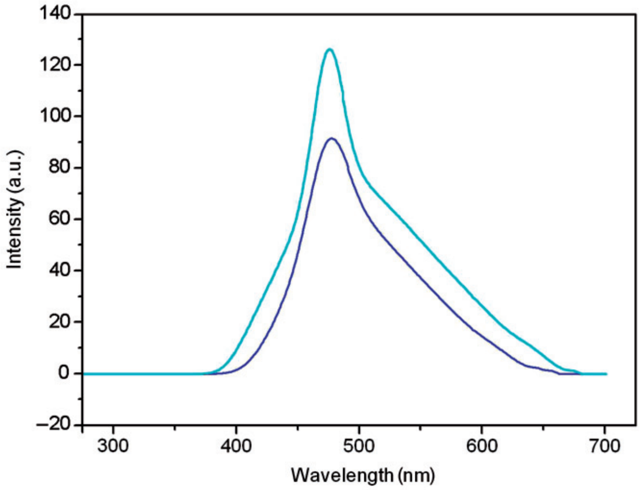

Figure 4. Solid-state emission spectra of **1** and **2** at room temperature (**1** – blue line, **2** – green line).

Compound **2** also shows four redox peaks in the range 850 and −600 mV, and the peak potential are 192, 149, −302, and −412 mV; the redox waves of 192 and 149 mV can be attributed to Cu^0 and Cu^{2+} and waves at −302 and −412 mV are attributed to $W^{VI/V}$ in **2**, as assigned for those of **1**.

3.4. *TG analyses*

In order to examine the thermal stability of **1** and **2**, TG analyses were carried out in N_2 atmosphere with a heating rate of $10°C\,min^{-1}$. The TG analyses curve of **1** (figure S6a) shows weight loss of 11.12% in the range of 70–250°C corresponding to removal of water (Calcd 11.43%). The weight loss of 3.98% at 270−430°C is in accord with decomposition of two glycine molecules (Calcd 3.92%). A small weight loss of 0.49% between 405 and 440°C is consistent with the release of one water molecule (Calcd 0.48%), according to the following decomposition reaction: $Cu_3[H_2W_{12}O_{42}] \rightarrow 3CuO \cdot 12WO_3 + O_2 + H_2O$.

The TG analyses curve of **2** (figure S6b) shows weight losses of 12.32 and 7.71% in the range of 70–270 and 280–450°C, respectively. Similarly, these observed values are in accord with the removal of water (Calcd 12.26%) and decomposition of four glycines (Calcd 7.61%). A small weight loss of 1.65% between 470 and 500°C is consistent with the release of three and a half water molecules (Calcd 1.62%), according to the following decomposition reaction: $Cu_2[H_5(H_2W_{12}O_{42})] \rightarrow 2CuO \cdot 12WO_3 + 0.25O_2 + 3.5H_2O$. The IR spectra of thermal decomposition products of **1** and **2** are shown in figure S7(a) and (b).

3.5. *Luminescence*

Compounds **1** and **2** exhibit strong luminescence in solid state at room temperature (figure 4), with maximum emissions at 473 nm ($\lambda_{ex} = 254$ nm) and 471 nm ($\lambda_{ex} = 254$ nm), respectively. There are no obvious emissions for the organic components

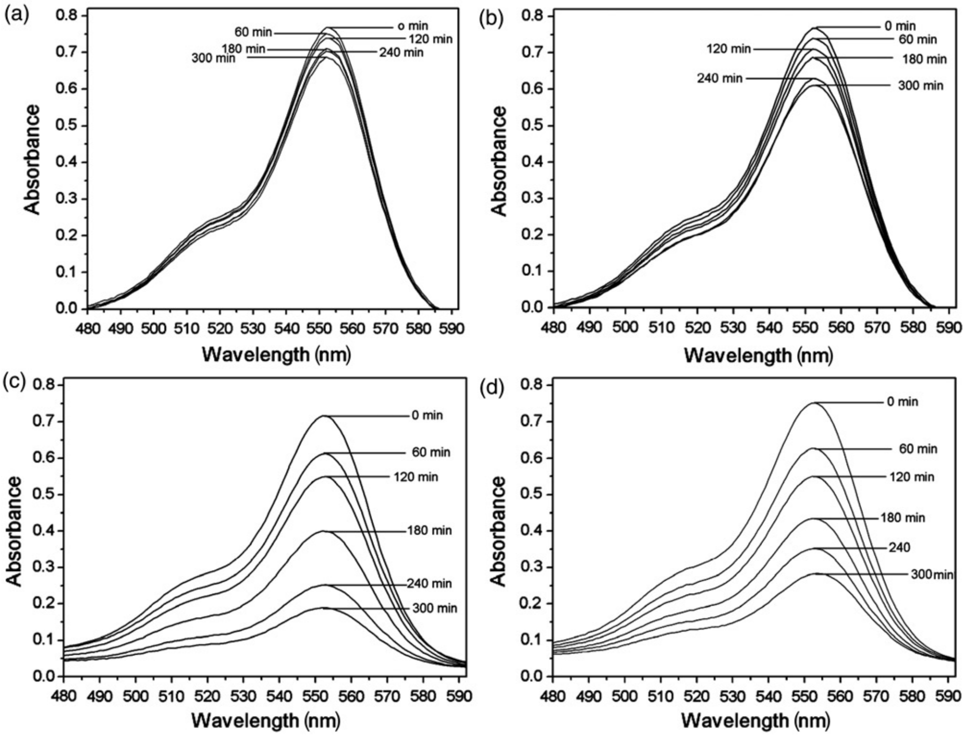

Figure 5. Changes in UV-Vis absorption spectra of RhB solutions (1.8×10^{-5} mol L^{-1}): (a) direct photocatalysis; (b) in the presence of 30 mg $Na_{10}[H_2W_{12}O_{42}] \cdot 20H_2O$; (c) in the presence of 30 mg **1**; and (d) in the presence of 30 mg **2**.

or metal ions under the same experimental conditions so luminescence may be attributable to WO_6 of the polyanion core $[H_2W_{12}O_{42}]^{10-}$ [25–28].

3.6. *Photocatalysis*

Several polyoxotungstates exhibits photocatalytic activity on degradation of organic substances under UV irradiation [29]. The photocatalytic performance of **1** and **2** were investigated with photodegradation of RhB. Under the same conditions we tested RhB with $Na_{10}[H_2W_{12}O_{42}] \cdot 20H_2O$ as photocatalyst without photocatalysis. Changes in UV-Vis absorption spectra of RhB solutions with different photocatalysts are shown in figure 5. Comparing to a and b, the absorption spectra of c and d decreased upon irradiation, indicating that **1** and **2** have good photocatalysis. Changes in C_t/C_0 plots of RhB solutions *versus* reaction time, figure 6, confirm that **1** and **2** are good photocatalysts for degradation of RhB.

4. Conclusion

Two organic–inorganic hybrid compounds based on copper–glycine and paradodecatungstates, **1** and **2**, were isolated by conventional synthetic strategies. The IR and

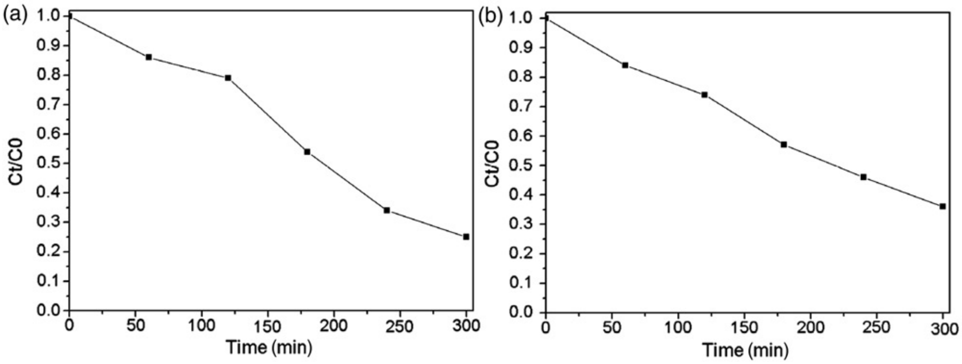

Figure 6. Changes in C_t/C_0 plot of RhB solutions (1.8×10^{-5} mol L^{-1}) *vs*. reaction time: (a) in the presence of 30 mg **1** and (b) in the presence of 30 mg **2**.

UV-Vis spectra show characteristic bands of paradodecatungstates. Luminescence properties of these compounds have also been investigated. The synthesis of **1** and **2** shows that $[H_2W_{12}O_{42}]^{10-}$ is a versatile building block which can be modified by transition metal–amino acid complexes to construct high-dimensional architectures.

Supplementary materials

The IR spectra, UV spectra, TG curves, and electrochemical property of **1** and **2** and the additional tables are available. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as deposition numbers CCDC-724761 for **1** and CCDC-724762 for **2**. The data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK via Fax (+44 1223 336033) or Email (deposit@ccdc.cam.ac.uk).

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