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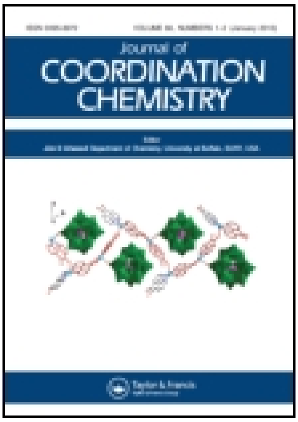

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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Accepted author version posted online: 20 Jun 2013.Published online: 24 Jul 2013.

To cite this article: Xiong Gan, Xiaoxi Hu, Zhongfeng Shi & Yanzhen Yin (2013) The synthesis of polyoxometalate-based metal-organic frameworks under ionothermal conditions, Journal of Coordination Chemistry, 66:16, 2930-2939, DOI: 10.1080/00958972.2013.817570

To link to this article: http://dx.doi.org/10.1080/00958972.2013.817570

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 16, 2930–2939, http://dx.doi.org/10.1080/00958972.2013.817570

The synthesis of polyoxometalate-based metal-organic frameworks under ionothermal conditions

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(*Received 2 January 2013; in final form 6 May 2013*)

Using ionic liquid (IL) [Bmim]Br (Bmim=1-butyl-3-methylimidazolium) as solvent has resulted in a polyoxometalate-based metal-organic framework (PMOFs), $[Cu^{I}Bbi]_4SiW_{12}O_{40}\cdot H_2O$ (**1**) [Bbi=1,1-(1,4-butanediyl)-bis(imidazole)], and was produced via an ionothermal route. Its structure was determined by single-crystal X-ray diffraction. Compound **1** is a 1-D ladder with large voids, resulting in a 3-D supermolecular structure using the classic Keggin-type anion as a second building block. This means utilizing ILs to construct 3-D PMOFs can be efficiently realized. Additionally, electrochemical, electrocatalytic, and photocatalytic properties of **1** were studied.

Keywords: Ionothermal; Polyoxometalate-based frameworks; Topology; Electrochemistry; Electrocatalysis; Photocatalysis

1. Introduction

Ionothermal synthesis uses ionic liquids (ILs) as both solvent and potential template/structure directing agent in the formation of solids [1–8]. It directly parallels hydrothermal synthesis in which the solvent is water. The particular property of ILs is their low vapor pressure (so little, if any, autogenous pressure is produced at high temperature), and the ILs have significant advantages when replacing highly volatile organic solvents [9–14]. ILs show a range of properties that make them suitable media to prepare inorganic and inorganic–organic hybrid materials [15, 16]. They are relatively polar solvents, ensuring reasonably good solubility of inorganic precursors [9–14]. The fundamental difference between ILs and solvents used in hydrothermal and solvothermal synthesis is that they are ions. The ionic nature of ILs imparts particular properties in ionothermal syntheses [17].

ILs play important roles in ionothermal syntheses. They may bring particular advantages into the syntheses, involving anion control, chiral induction effect, hydrogen-bond directing effect, and structural template agents [18–20]. Furthermore, the weak coordination ability of ILs may bring more comfortable reaction environments for self-assembly of polyoxoanions. ILs possess tunable acidity, which may offer alterable reaction environments with different pH values for synthesis of different polyoxoanions [21–26]. Finally, ILs have good solubility for inorganic precursors, can take full advantage of the good solubility to the reactant, will dissolve reactant under room temperature and stirring, and will improve the reactivity of the system. [Bmim]Br, as a room temperature IL, is

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*Corresponding author. Email: gan_xiong@tom.com air/moisture stable, neutral, non-volatile and has reasonably good solubility, pH adjustable, and weak coordinating ability. Taking advantage of [Bmim]Br with reasonably good solubility and adjustable pH, we attempt to synthesize some polyoxometalate-based metal-organic framework (PMOFs) in ionothermal reaction system.

Only a few extended PMOFs have been synthesized in ILs under ionothermal conditions [27–31], but they do not include Keggin-type PMOFs. In this paper, we report our strategy and rationale in ionothermal synthesis of Keggin-type PMOFs using classic ILs 1-butyl-3-methyl imidazolium bromide as solvent, and **1** was prepared ionothermally from a Cu(II) salt and Bbi. Herein, we obtain a 3-D supermolecular Keggin-type PMOFs with large 1-D voids. Furthermore, we carefully investigated their photocatalytic and electrocatalytic properties.

2. Experimental

2.1. *Materials and methods*

All reagents were purchased commercially and used without purification. Elemental analyses of W, Si, C, N, P, and Cu were performed by a Leaman inductively coupled plasma spectrometer. C, H, and N analyses were performed on a PerkinElmer 2400 CHN elemental analyzer. IR spectra were recorded from 400 to 4000 cm^{-1} on an Alpha Centaurt FTIR spectrophotometer with pressed KBr pellets. Cyclic voltammograms were obtained by a CHI 660 electrochemical workstation at room temperature. Platinum gauze was used as counter electrode and a Ag/AgCl electrode as reference electrode. Chemically bulk-modified carbon paste electrodes (CPEs) were used as working electrodes. Excitation and emission spectra were obtained on a SPEX FL-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source. UV–vis absorption spectra were recorded on a 756 CRT UV–vis spectrophotometer.

2.2. *Synthesis of compound*

A mixture of [Bmim]Br (2 g, 4.6 mM), $Na_2WO_4 \cdot 2H_2O$ (0.6 g, 1.8 mM), $CuCl_2 \cdot 2H_2O$ (0.18 g, 1 mM), $Na_2SiO_3 \cdot 2H_2O$ (0.1 g), and Bbi (0.06 g, 0.3 mM) was stirred for about half an hour at room temperature. The mixture was then transferred to a Teflon-lined autoclave (23 mL) and kept at 180 °C for 5 days. After the autoclave was slowly cooled to room temperature at 10 °C h^{-1}, it was maintained for one day without opening, and then, black crystals of **1** were filtered off, washed with acetone, and dried in a desiccator at room temperature (yield 79% based on W). Anal. for $[Cu^{I}Bbi]_4SiW_{12}O_{40} \cdot H_2O$ (**1**) found (%): C, 3.99; H, 0.70; Cu, 1.82; N, 1.88; Si, 0.95; W, 65.69. Calcd: C, 3.96; H, 0.73; Cu, 1.84; N, 1.85; Si, 0.93; W, 66.75.

2.3. *X-ray crystallography*

Diffraction quality single crystals were mounted on a glass fiber and crystallographic data of **1** were collected at 150 K on a Rigaku R-axis Rapid IP diffractometer using graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) and IP technique. The structure of **1** was solved by direct methods and refined by full-matrix least squares on F^2 using the

SHELXTL-97 crystallographic software package [32]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogens on carbons were included in calculated positions. Hydrogens on water cannot be found from the weak residual electron peaks but directly included in the final molecular formula. The detailed crystal data and structure refinement for **1** are summarized in table 1. Crystallographic data have been

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

Empirical formula	$H_{56}C_{40}N_{16}O_{41}Cu_4SiW_{12}$
M	3905.46
λ/Å	0.71073
T/K	150(2)
Crystal size/mm	0.50 × 0.30 × 0.20
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.475(3)
b/Å	13.731(3)
c/Å	14.309(3)
α/°	62.98(3)
β/°	65.69(3)
γ/°	78.00(3)
V/Å^3	1989.3(7)
Z	1
D_c/Mg m^{-3}	3.260
μ/mm^{-1}	18.417
F (000)	1754
θ Range/°	2.99 to 24.71
Data/restraints/parameters	6654/8/280
R_{int}	0.1197
$R_1(I > 2\sigma(I))$[a]	0.0959
wR_2 (all data)[b]	0.2177
Goodness of fit on F^2	1.075

[a]$R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b]$wR_2 = \Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]^{1/2}$.

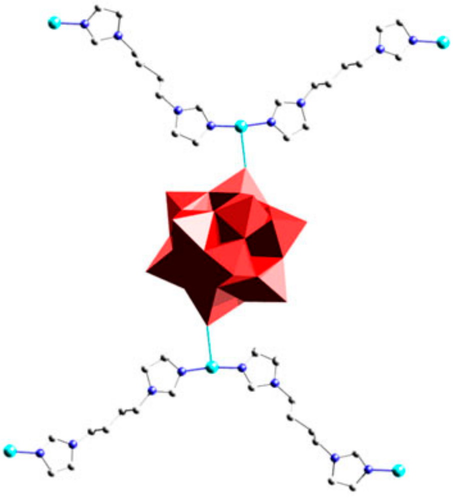

Figure 1. The polyhedral and ball-and-stick representations of **1**.

deposited with the Cambridge Crystallographic Data Center (CCDC) as deposition number (CCDC No. 784715) for **1**. The data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK via Fax: (+44 1223 336033) or E-mail: (deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Structure*

Single-crystal X-ray diffraction analysis reveals that **1** contains a classic [α-$SiW_{12}O_{40}$] Keggin structure, four crystallographically independent Cu(I) ions and one water (figure 1). Here, four crystallographically independent Cu(I) ions can be divided into two groups (Cu1

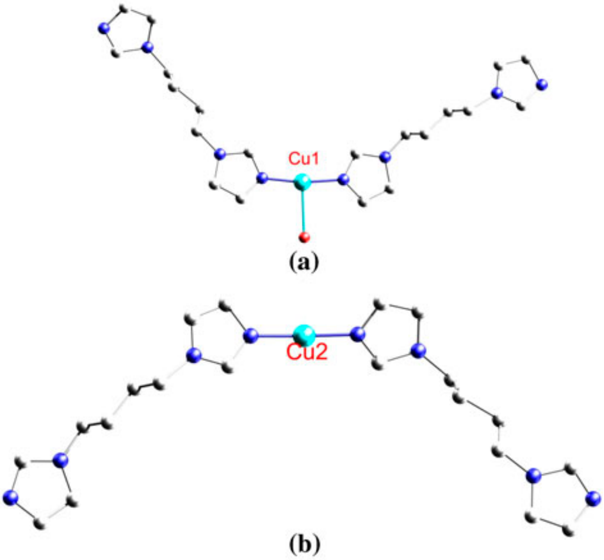

Figure 2. The coordination environment of copper ions in **1** (a) Cu1; (b) Cu2.

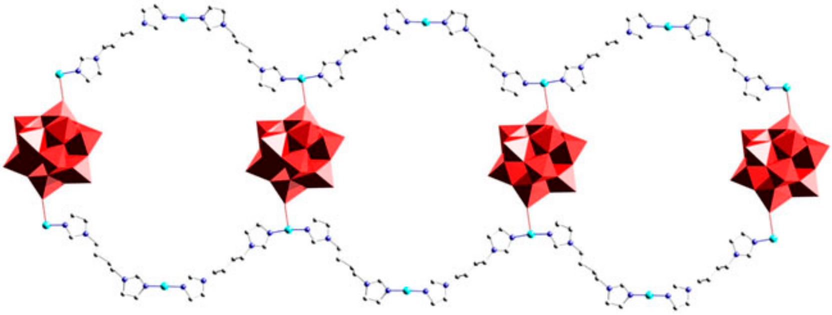

Figure 3. The polyhedral and ball-and-stick representation of 1-D ladder structure in **1**.

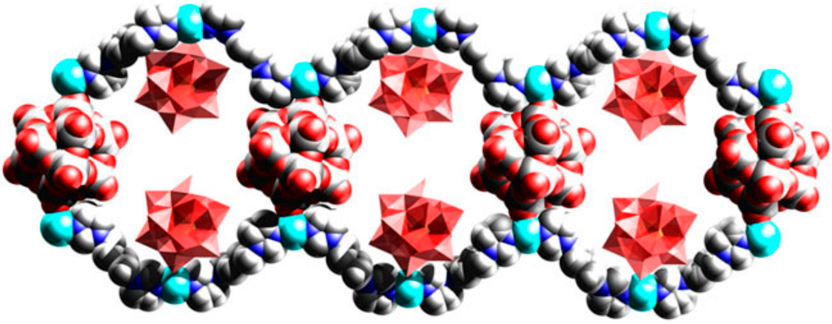

Figure 4. The polyhedral and space-filling diagram of the 1-D ladder-shape structure with two Keggin-type anions residing in the voids in **1**.

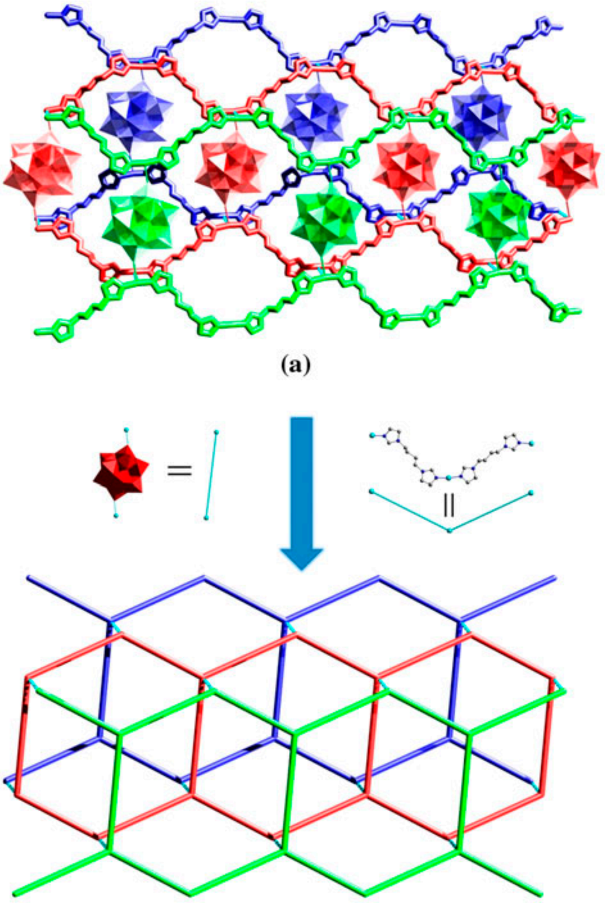

Figure 5. (a) The topological representation of 3-D supermolecule in **1** (the blue nodes symbolize the Cu(I) center, the pink sticks symbolize Keggin clusters, and the other color sticks symbolize Bbi ligands). (b) The light blue stick represents weak Cu–Cu interaction. The green, red, and deep blue 1-D ladder-shape structure representation of the different ones (see http://dx.doi.org/http://dx.doi.org/10.1080/00958972.2013.817570 for color version).

and Cu2). Each Cu1 has a three-coordinate T-type geometry which is defined by two nitrogens from two different Bbi ligands and one terminal oxygen from $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$ (figure 2(a)). However, each Cu2 shows nearly linear geometry which is completed by two nitrogens from two Bbi (figure 2(b)). In **1**, Cu1 connects with Cu2 through Bbi ligands to generate a 1-D chain and Cu1 in adjacent 1-D chains coordinate to $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$ via two terminal oxygens to obtain a ladder-shaped structure (figure 3) with grid sizes of 2.6655(1) nm in which two other Keggin structures reside (figure 4). Two Keggin structures are connected through their terminal oxygens to a different set of two Bbi-Cu chains and the other two ladder-like structures run perpendicular to the first one, resulting in a new topology (figure 5). The 1-D ladder-shaped chains stack into a 3-D supermolecular structure with a 1-D channel (figure 6).

3.2. *Electrochemistry study*

To investigate the electrochemical behavior of **1**, the compound has been used to fabricate a chemically modified carbon paste electrode (**1**-cpe) due to its high thermal stability and low solubility in water and common organic solvents.

The cyclic voltammetric behavior of **1**-cpe in 0.1 M H_2SO_4 aqueous solution at different scan rates was recorded, exhibiting three pairs of redox peaks from +500 to −500 mV. The two redox processes at negative potentials correspond to redox of the W^{VI} center in **1** and are similar to other tungsten-containing polyoxometalates. The oxidation peak at +170 mV is attributed to the redox of the Cu^{I} center for **1** (figure 7).

1-cpe possesses high stability; when the potential range is maintained between +500 and −500 mV, the peak currents remain almost unchanged over 200 cycles at a scan rate of 50 mVs^{-1}. After **1**-cpe was stored at room temperature for one month, the peak current decreased only 7% and could be renewed by squeezing a little carbon paste out of the tube. The high stability of **1**-cpe could be ascribed to the neutral inorganic–organic hybrid material of **1** which stabilizes the polyoxoanions in the compound. Further, **1** is insoluble in the acidic aqueous medium of this experiment, avoiding the loss of the modifier during measurements. Thus, **1**-cpe could be an ideal electrode material to investigate electrocatalytic properties.

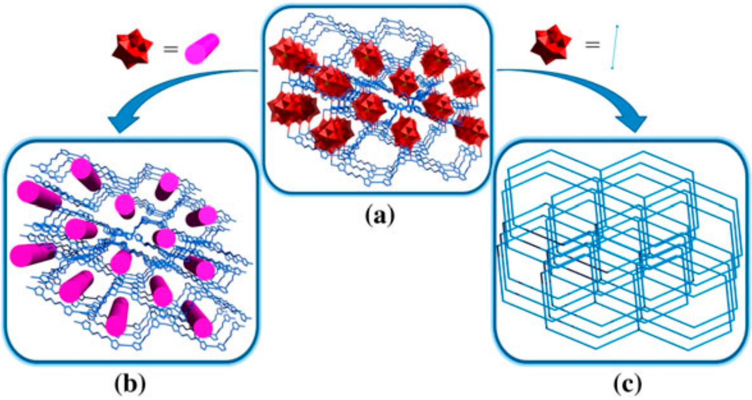

Figure 6. 3-D supermolecular and topological structure of **1**.

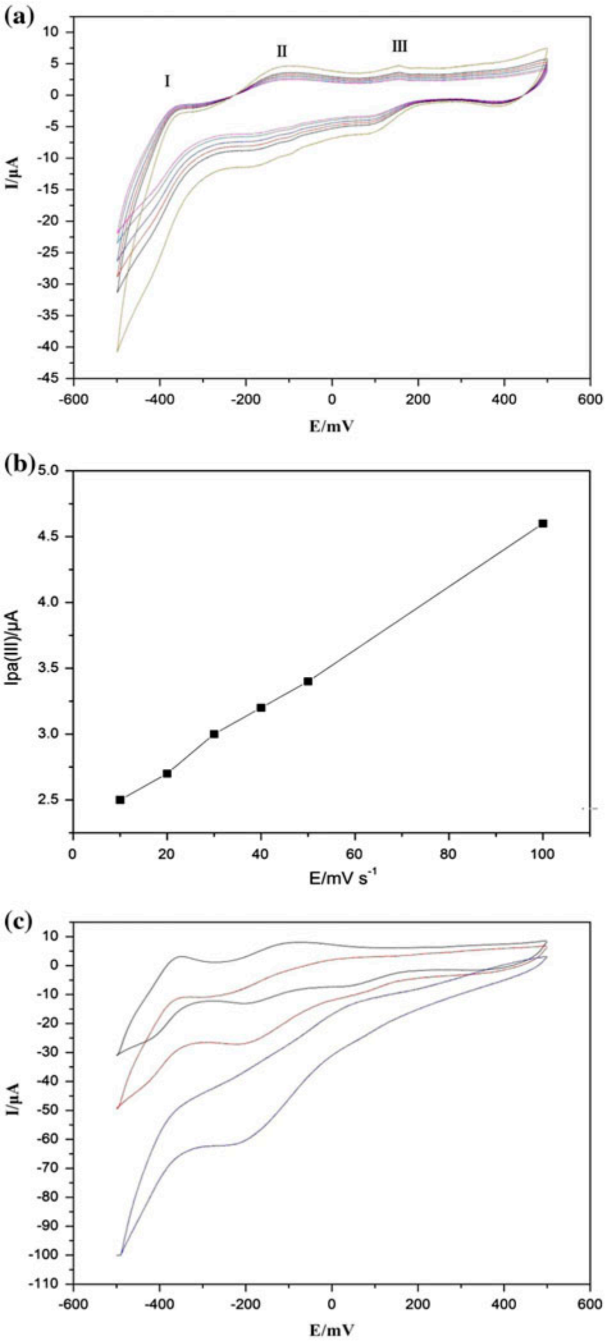

Figure 7. (a) The cyclic voltammetric behavior at different scan rates (10/20/30/40/50/1008 m Vs^{-1} from inside to outside). (b) The dependence of anodic peak III current on scan rates. (c) The electrocatalytic activity to reduce nitrite for **1**.

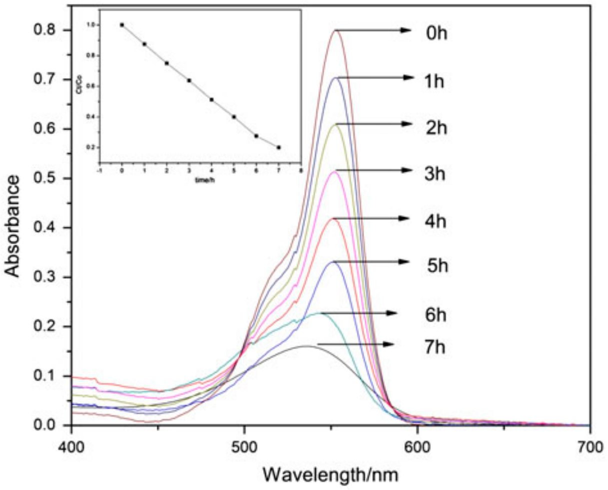

Figure 8. The photocatalysis behavior of **1** to reduce RhB in solution.

1-cpe displays good electrocatalytic activity to reduce nitrite (figure 7). For **1**-cpe, with the addition of nitrite, all reduction peak currents of W^{VI} on polyoxometalates increased while the corresponding oxidation peak currents dramatically decreased, suggesting that nitrite was reduced by polyoxoanion species [33–36]. The catalytic activities were enhanced with increasing extent of polyoxoanion reduction. In contrast, the reduction in nitrite at a bare electrode generally requires a large overpotential and no obvious response was observed at a bare cpe.

3.3. *Photocatalytic experiments*

In a typical process, 15 mg of **1** was dissolved in 100 mL rhodamineB (RhB) solution (1.8×10^{-5} ML^{-1}) at pH = 2.5 (the pH of the solution was adjusted with dilute aqueous solutions of either NaOH or $HClO_4$) and then magnetically stirred in the dark for 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 time 0 and after each hour, up to 7 h, 3-mL sample was taken out of the beaker and adjusted to pH 9 by addition of dilute Na_2CO_3 solution (1 mL) and subsequently analyzed by UV–visible spectroscopy (figure 8). In the presence of **1**, RhB degrades from 100 to 15.4% during 7 h. The degradation rate curve of **1** is nearly linear, and the degradation rate is about 12% per hour. The result indicates that **1** possesses good photocatalytic properties.

4. Conclusions

We developed a convenient method to synthesize a 1-D ladder-shape structure with large grids in which two Keggin-type anions reside and achieved a 3-D supermolecular Keggin-type PMOFs under ionothermal conditions, different from the ones obtained under hydrothermal conditions [37–41]. It may be a convenient method to obtain porous PMOFs. The electrochemical, electrocatalytic, and photocatalytic properties of **1** were studied.

Supplementary material

IR spectrum and X-ray crystallographic information file (CIF) are available for **1**. Further crystallographic data have been deposited with the Cambridge Crystallography Data Center (CCDC) as deposition number CCDC 784715 for **1**. The data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, via Fax: (+44 1223 336033) or E-mail: (deposit@ccdc.cam.ac.uk).

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (51203082) and Guangxi Natural Science Foundation (0832280).

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